

THE OPTICAL ACTIVITY OF SHALE OIL, AN IMPORTANT PHYSICAL PROPERTY

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ABSTRACT

Optical activity is observed in oil derived from either the bitumen portion or the kerogen portion of the shale. For Green River shale, the two contribute about equally to the observed activity of the oil derived from the shale. A large percentage of the observed activity results from the presence of chiral alkanes in the shale oil. These include diterpanes, triterpanes (especially steranes) and beta-carotane. Since the chemical processes which these substances will undergo cannot be substantially different from those undergone by nonchiral alkanes, optical activity measurement can be used as a method for following the mechanisms and the kinetics of the retorting process.

INTRODUCTION

The most surprising aspect of the optical activity of shale oil is that it is, in fact, optically active. The thermal history of its production would lead to a prediction, based on conventional organic chemistry, that all carbon chiral centers had been racemized. Rather, we find that there is considerable optical activity in the oil as it is normally produced. Further, this activity is similar to but, nevertheless, significantly different from that observed for petroleum (Rosenfeld, 1967). Since optical activity holds the potential of reflecting the chemical history of the oil, the study of the characteristics of that activity is a worthwhile pursuit. This paper undertakes to define a number of these characteristics such as the variability of rotation, some chemical sources of that rotation, the effect of retorting conditions on the rotation and possible methods of interpretation of rotational data.

EXPERIMENTAL

Optical rotations were determined using a Jasco J-20 spectropolarimeter run in the ORD mode. Quartz cells of light path lengths 0.1, 1, 2, and 10 cm were used on different oils, the usual criterion for

selection being the opacity of the sample. It is possible to use the instrument to either take a rotational reading at a single, chosen wavelength or to measure rotation as a function of wavelength. The latter is called an optical rotatory dispersion (ORD) spectrum.

The wavelength range of the instrument is 200 nm to 700 nm. ORD spectra on shale oils were run between 450 and 700 nm ORD spectra and saturate fractions and pure compounds were run between 300 and 700 nm. Spectra were subjected to data reduction analysis by least squares fitting to a one-term Drude equation of the form:

$$[\alpha] = \frac{a_0 \lambda_0^2}{\lambda^2 - \lambda_0^2} \quad (1)$$

where $[\alpha]$ is the specific rotation, λ is the wavelength of observation and a_0 and λ_0 are characteristic constants of the equation (Moffitt et al., 1959).

Shales were retorted in the laboratory in a 1 x 10 cm quartz tube with a support platform incorporated 4 cm from one end. The tube was surrounded by a coil consisting of 62 cm of standard 0.122 cm diam. nichrome wire through which a current was passed by means of a variable AC autotransformer. Nitrogen was passed through the tube while retorting was in progress. Oil was collected by means of a two-step process consisting of a water-cooled condenser and a glass wool demister.

Yield studies were carried out using a Colorado-Green River Formation medium yield oil shale for which the reported yield from large scale retorting was ca 104 l/metric ton (ca 25 gal/ton). Shales from the post-burn coring of the Rock Springs, site 9 in situ retorting experiment were also retorted. The mapping of these cores has been described in detail elsewhere (Lawlor et al., 1979). Core samples (100 mesh) were exhaustively extracted with benzene-methanol azeotropic mixture and the dried extracted shale subjected to retorting as described above. In the remainder of this paper, the oil recovered by solvent extraction is designated bitumen and that

obtained from the retorting of solvent extracted shale is called kerogen oil.

Saturate fractions were obtained from oil samples by chromatography on silica. 0.500 g of oil was placed on a 2-1/2 x 90 cm column and eluted with 240 ml of n-hexane. The collected eluate was evaporated to remove solvent and volatile hydrocarbons, and diluted appropriately in cyclohexane for measurement of rotation.

ORD spectra were also obtained for pure (or nearly pure) compounds known to be chiral, saturated hydrocarbons found in oil shale. Steranes were obtained from commercial sources and were pure to the experimental limit of optical rotation criteria. Phytane, pristane gammacerane and perhydro-beta carotane were isolated from shale oils and, based on chromatographic analysis, were at least 95 percent pure.

Specific rotations at a given, single wavelength were calculated according to the formula

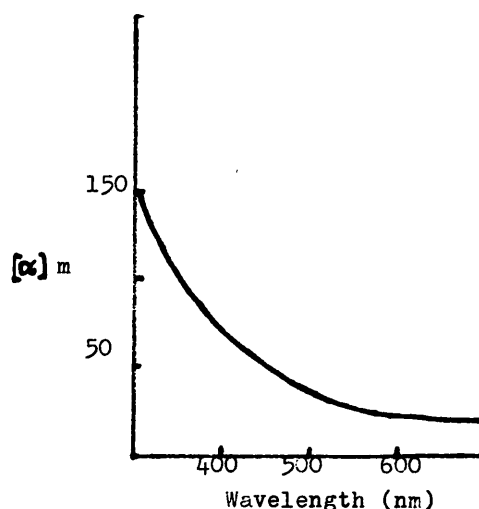
$$[\alpha] = \frac{\alpha}{c \times l} \quad (2)$$

where $[\alpha]$ is the specific rotation, α is the observed rotation, c is the sample concentration in g/ml and l is the light path length in dm. (Jirgensons, 1973).

RESULTS

The parameters of optical rotation for some pure chiral alkanes are shown in Table 1. The ORD spectrum for 5-alpha-cholestane is shown in Figure 1. The spectrum is between 300 and 700 nm. The wavelength range of the instrument is 200 to 700 nm. Measurement of rotation below 450 nm on shale oil is usually not practical because of opacity. Rotation measurements of colorless fractions below 300 nm is precluded by light-scattering from colloidal suspensions. It will be noted that the ORD spectrum generated is generally featureless; that is, no obvious maxima or minima occur within the range of observation. To a first approximation, such peaks can be elicited from the observed spectrum by application of a one-term Drude equation (equation 1). This equation predicts the position of a symmetrical Cotton effect (Moffitt, et al., 1959). The constants a_0 and λ_0 of the equation represent the height of the maximum and the position of the cross-over on the wavelength scale, respectively. Therefore, a_0 represents the rotor strength of the effect and λ_0 its

Figure 1. ORD spectrum of 5-alpha-cholestane, calculated specific rotations from actual observed rotations over the instrumental range. The general form of this curve is that observed for nearly all of the shale oils and their fractions.



position in the spectrum. It will be seen in Table 1 that for certain pure compounds (cf. gammacerane, phytane and pristane), the equation predicts Cotton effects within the wavelength range of the instrument and yet these are not observed in the actual spectra. Nevertheless, these imaginary parameters show a good fit of data points to the predicted curve, as evidenced by a high correlation coefficient (>0.9), and are independent of concentration. Hence, they can be used to reflect a large body of data (the spectrum) in a set of two repeatable, characteristic parameters.

The Drude equation cannot be applied to complex mixtures of chiral compounds. When it is applied to such mixtures the coefficient of correlation is typically less than 0.1. For this reason, in subsequent data, we have limited the observation to the specific rotation at 450 nm; designated $[\alpha]_{450}$. The ORD spectra for the oil samples subsequently reported in this paper have been recorded but, as of this writing, no systematic, meaningful method for the reduction of this data has been identified; hence the reporting of the simple $[\alpha]_{450}$ values.

Figure 3 shows the effect of retorting temperature on the optical rotation of the oil obtained

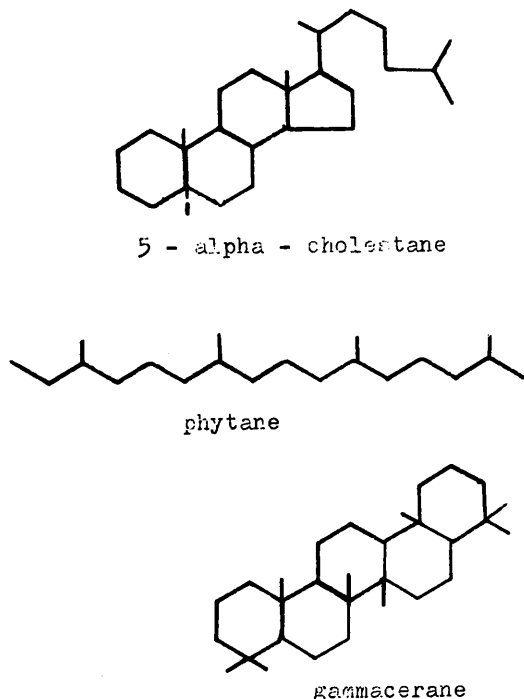
Table 1. Optical rotation parameters derived from observed ORD spectra for chiral alkanes known to be present in shale oil. Values for a_0 and λ_0 were obtained according to equation (1), in text. Values for $[\alpha]_{450}$, according to equation (2), in text.

<u>Compound</u> ¹	<u>a_0 (degrees)</u>	<u>λ_0 (nm)</u>	<u>coefficient of correlation</u> ²	<u>$[\alpha]_{450}$</u>
steranes				
5-alpha-cholestane	888	183.3	.99	48.5
5-beta-cholestane	1391	153.9	.99	49.6
5-alpha-pregnane	355	189.7	.99	26.0
5-beta-androstane	2.85	339.5	.97	1.2
triterpane				
gammacerane	45	502.9	.92	43.4
acyclic isoprane				
phytane	0.108	421.8	.96	0.37
pristane	0.075	462.0	.97	0.39
perhydro-beta-carotane	0.18	605.0	.91	-0.11

1. for representative structural formulae, see Figure 2.

2. test of goodness of fit

Figure 2. Representative structural formulae for chiral alkanes found in shale oil.



together with the effect of temperature on yield. It will be noted that rotation reaches a maximum at 450° C and then drops off. Yield approaches a maximum as the temperature is increased and is relatively constant at higher temperatures. Tables 2-4 show the optical rotations of the bitumen and kerogen oil for core section taken from the Rock Springs, site 9, *in situ* project. These are intended to demonstrate the inherent variability of rotation and the effect of retorting on rotation. Bracketed values in these tables show where there was visual evidence that retorting has occurred within those segments of the core.

Table 5 shows the effect of distillation upon the optical activity of the saturates in the resultant fraction. It is intended to demonstrate the distribution of chiral alkanes in the various fractions.

DISCUSSION

The context of the following discussion requires an explanation as to why such extensive use of saturate fractions has been made for purposes of obtaining data on optical rotation. Part of this is that saturate fractions are more optically transparent than are other readily available fractions and are, therefore, more susceptible of measurement. However, it is also our feeling that the chiral saturates represent the largest group of optically active compounds to be found in shale oil. This is based on the nature of the observed ORD spectrum of shale oils. Although there are recorded only from 700 to 450 nm, their overall shape is nonetheless very much like those observed in the saturate fraction. Eleven oils which showed a good fit to a one-term Drude equation over the spectral range had a mean $[\alpha]_{450}$ of 29.07. For twenty-two saturate fraction, this value was 43.49. If overriding amounts of chiral olefins had been present, it would be predicted to have a negative value (Asplund, et al., 1978). The overall form of the ORD spectra of shale oils corresponds to the spectrum for 5-alpha-cholestane (Figure 1) and is, therefore, regarded as indicative of an alkane ORD spectrum.

The relationship of retorting temperatures to optical activity and to yield is most simply explained by assuming that at low temperatures there is little thermal racemization but that limited

Figure 3. Standard optical rotation (Jirgensons, 1973) and shale oil yield from a Colorado-Green River medium shale retorted at various temperatures. Rotation values are reported for the intact oil rather than for the saturate fraction as is done in other parts of this paper.

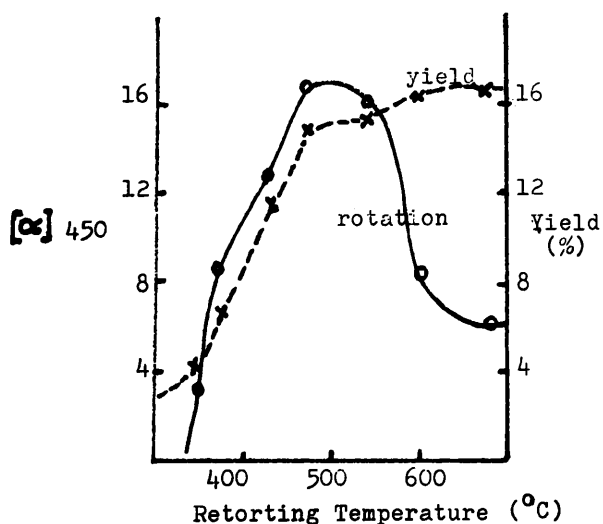


Table 2. Rotational and yield characteristics of oils obtained from core #1, Site 9 in situ project (Lawlor, et. al., 1979). This core was selected as representing one in which interspersed zones of retorting and undisturbed shale could be visually observed. Treatment of shale and division into bitumen and kerogen oil fractions are described in the text.

	Core Footage	Yield(%)	Bitumen Saturates ¹	$[\alpha]_{450}$	Yield(%)	Kerogen Oil Saturates ¹	$[\alpha]_{450}$
	138	1.18	17.96	25.5	1.93	5.97	4.72
retorted zone	139	0.75	24.30	38.0	3.33	7.58	0.32
	140	2.56	3.94	13.4	5.25	6.46	25.39
	141	2.60	4.23	20.7	6.15	9.08	9.71
	142	2.60	25.86	18.3	6.94	1.46	-35.10
	144	2.49	35.29	18.8	5.99	9.29	2.20
	145	1.42	38.66	13.8	8.59	0.90	2.67
retorted zone	146	0.56	45.72	7.6	4.38	0.64	55.00
	147	1.30	45.56	10.3	3.13	6.37	4.39
	148	1.53	27.88	10.0	3.01	9.12	0.18
	149	1.75	19.92	11.8	5.37	14.61	4.38
	150	1.39	16.00	8.8	3.68	7.07	0.90
	151	1.56	20.01	8.0	2.49	10.41	3.09
	152	0.72	13.60	13.4	4.07	2.38	3.32
	153	0.02	16.23	20.0	5.01	0.50	83.20
	154	1.08	17.29	13.6	3.29	5.89	5.24
	155	1.14	13.43	16.8	9.97	6.99	3.77
	156	1.55	17.58	10.9	3.33	5.82	5.50
	157	1.63	13.60	15.2	3.20	4.90	9.64
retorted zone	158	1.15	17.73	12.8	5.30	0.98	23.67
	159	1.43	17.46	19.4	5.14	5.11	15.69
	163	1.65	14.08	11.8	3.88	6.06	9.27
	167	1.36	16.83	13.2	6.60	5.66	7.14
	173	1.14	15.53	12.6	3.34	6.88	7.06
	174	2.44	15.03	7.26	2.91	10.58	2.27
	avg.	1.48	20.55	14.88	4.65	6.03	10.14
	std. dev.	0.66	10.77	6.62	1.93	3.51	21.02

1. as percent of oil

Table 3. Rotational and yield characteristics of oils obtained from core #5, Site 9 in situ project (Lawlor, et. al., 1979). This core was selected as representing one in which most of the observed core has been subjected to retorting as evidenced by examination. Treatment of shale and division into bitumen and kerogen oil fractions are described in the text.

Core Footage	Yield(%)	Bitumen		Kerogen Oil		
		Saturates ¹	$[\alpha]_{450}$	Yield(%)	Saturates ¹	$[\alpha]_{450}$
138	1.35	19.17	14.4	4.65	12.23	2.26
139	4.17	17.43	10.1	5.88	10.06	12.45
retorted zone	141	2.60	4.23	6.15	9.08	9.71
	142	2.60	25.86	6.94	1.46	-35.10
	144	2.33	---	4.61	4.93	2.20
	146	0.56	45.72	4.38	0.64	55.00
	150	1.40	13.37	2.28	2.06	-67.35
	151	0.79	11.99	6.84	3.10	-16.99
	152	0.67	17.94	4.77	2.44	4.17
	153	0.93	10.16	3.99	1.27	7.50
	154	1.96	3.88	3.69	1.70	- 2.35
	155	3.30	10.56	2.69	2.38	1.06
	156	2.61	10.16	2.07	2.79	- 2.03
157	1.64	14.26	5.99	2.16	16.15	
158	2.06	7.93	4.51	2.99	22.45	
159	2.90	14.01	5.74	3.03	5.92	
avg.	1.99	15.11	8.7	4.70	3.89	0.94
std. dev.	1.02	10.22	3.5	1.51	3.44	26.09

1. as percent of oil

Table 4. Rotational and yield characteristics of oils obtained from core #5, Site 9 in situ project (Lawlor, et. al., 1979). This core was selected as representing one in which no visible zone of retorting was present in the analyzed core segment. Treatment of shale and division into bitumen and kerogen oil fractions are described in the text.

<u>Core Footage</u>	<u>Bitumen</u>			<u>Kerogen Oil</u>		
	<u>Yield(%)</u>	<u>Saturates</u> ¹	<u>[α]₄₅₀</u>	<u>Yield(%)</u>	<u>Saturates</u> ¹	<u>[α]₄₅₀</u>
158	1.19	6.68	7.42	4.21	3.07	15.95
160	0.75	14.67	7.74	5.49	2.09	9.52
163	0.64	11.60	21.3	4.65	1.06	52.50
164	0.66	10.69	8.2	8.39	5.85	18.71
166	1.21	7.14	4.6	6.65	7.39	2.05
167	0.86	10.48	9.8	3.84	9.96	8.61
169	0.67	13.19	10.4	4.24	4.89	4.75
170	4.22	13.91	6.2	3.58	12.03	2.48
171	1.03	8.39	7.8	3.16	10.91	5.02
avg.	1.25	10.75	9.3	4.91	6.42	13.29
std. dev.	1.13	2.90	4.8	1.68	3.89	15.79
for 166 - 171						
avg.	1.59	10.62	7.8	4.29	9.03	4.58
std. dev.	1.48	2.94	2.4	1.37	2.88	2.61

Table 5. Standard rotation of saturate fractions of distillate cuts of randomly chosen shale oils. Shows relative amounts of optical activity in fractions at differing boiling temperatures.

Mean and Standard Deviation of 5 Randomly Chosen Cuts

<u>Cuts</u>	<u>mean</u>	<u>std. dev.</u>
naphta	-0.40	1.12
light distillate	0.30	0.08
heavy distillate	1.92	0.88
residue	0.50	1.21

amounts of chiral compounds are released from the shale. As the temperature increases, more chiral compounds are released and the total optical activity rises until temperatures are attained at which more extensive racemization is caused and then optical activity begins to drop. The selective release of chiral compounds from the shale is suggested by the presence of a shoulder appearing in the curve at 500°C (Figure 3). Of course, other explanations are possible but the one given covers the observed results.

The possibility exists that the chiral compounds obtained from shale are to be found exclusively, or largely, in the solvent extractable (bitumen) portion of the shale. To test this, we have extracted shale samples with solvent, collected the oil thus generated and examined the optical activity of the saturate fraction. Then, we have retorted the extracted shale and obtained an oil (kerogen oil) and examined the optical activity of its saturate fraction. A calculation for a typical shale sample will illustrate the approximate distribution of optical activity between the two. A randomly chosen typical value for a shale is: for bitumen, specific rotation 8.63, yield 1.21%; for kerogen oil, specific rotation 2.05, yield, 6.65%. Since rotations are additive, if the retorting process is not altered by extraction, the saturate fraction of the oil from whole shale would be predicted to have a rotation of 3.06--43.3% of this from bitumen and 56.7% from kerogen oil. Hence, bitumen and kerogen are approximately equal sources of the chiral compounds found in shale oil.

Oil extraction and subsequent ORD measurement of core segments was done for the purpose of determining the variability of rotation in the geological strata and, further, to obtain an idea of the effect of retorting conditions on rotation. Presumably, in zones of retorting the decomposed kerogen has become organic-soluble oil. Any of it remaining in the rock should show up as bitumen and be reflected in the measurement of that portion of the shale. One would expect, then, that zones adjacent to retorted zones should have larger yields of bitumen than do zones some distance from the retorting. Table 2, zones 140-144, seems to illustrate this: these zones show a bitumen content which is approximately double that of the mean bitumen content for the entire core. In a part of this segment, zones 140-

141, the percent saturates in bitumen is more like that of kerogen oil than like that of usual bitumen.

The effect of in situ retorting upon rotation of kerogen oil is striking, if inconsistent. First, the subsequent yield of oil does not appear to have been greatly, if at all, reduced as a result of retorting. However, in certain zones, the optical rotation has changed greatly, either to high positive or to negative values. This change has been accompanied by a drop in the percent saturates found in the oil. Examples of this are seen in Table 2, zones 140, 142, 146 and 153, and in Table 3, zones 142, 146 and 150. On the other hand, certain areas in the retorted zone appear to have yield and rotation values like those of unretorted areas; see Table 2, zones 151 and 152, and Table 3, zones 152 and 153. Where changes are evident, they are of such magnitude that one can have little doubt that extensive thermochemical changes have taken place. This illuminates one of the important potential uses of optical rotation of shale oil. It can be seen that the changes are not reflected in oil yields, but are reflected in measurement of standard rotation. Therefore, the latter would be the better criterion for the study of these thermal changes. Since an understanding of this might lead to an explanation for why so little kerogen was released from the shale by in situ retorting, the measurement of optical rotation would be called into use.

The appearance of apparently normal zones within retorted areas can be explained in terms of layering effects. That is, as retorting proceeds, the products tend to collect in a layered manner rather than diffusely through the neighboring zones. Again among the criteria here presented, optical rotation of the kerogen best reflects these layers; that is, the presence of layers can be most readily seen by observing the rotational data. We have attempted to test this observation through application. In Table 4, we have recorded data from a core segment in which there was no visible evidence of in situ retorting. Based on the standard rotation of the kerogen oil together with percent saturates in the kerogen oil, we conclude that zones 158-164 have, in fact, been subjected to retorting, even in the absence of visual evidence. This is of interest because it was originally believed that core #5 was well out of the retorting zone, but this, and also

other evidence (Lawlor et al., 1979) suggest that retorting had occurred in this core and, hence, the retorting area for Site 9 was larger than anticipated.

The data presented in Table 5 show that the larger part of the positive rotation is found in the heavy distillate fraction, which is where most of the chiral alkanes would be expected to accumulate. However, the most striking result of these observations is the sharp drop in standard rotations which is found. This is apparently caused by thermal racemization during distillation. The distillation temperatures are much lower than retorting temperatures yet the distillation causes considerable racemization where the retorting process, apparently, does not. This demonstration of the thermal sensitivity of oil during distillation compared to that found during retorting highlights the central mystery of the optical activity of shale oil, which is "How are chiral compounds protected when they are contained in the shale?"

SUMMARY AND CONCLUSIONS

1. Shale oil is optically active.
2. The general shape of the observable ORD spectrum of shale oil approximates that observed for chiral alkanes known to be in shale oil.
3. Optical activity is released by thermal treatment of shale in a manner such that it reaches a maximum in the oil at 500°C.
4. In retorting, the optical activity seems to be protected in some manner which is not observed on simple thermal treatment of the oil.
5. Residual optical activity of kerogen remaining in shale subjected to retorting temperatures undergoes extensive changes. The same changes are not observed in the residual bitumen.

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