Effects of thermal maturation on steroid hydrocarbons as determined by hydrous pyrolysis of Phosphoria Retort Shale

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Abstract—Hydrous pyrolysis experiments on the Phosphoria Retort Shale generate bitumen extracts and expelled oils that have steroid hydrocarbons with m/z 217-, 231-, and 253-mass chromatographic distributions that are similar to those of bitumens and crude oils in the natural system. These experiments agree with the natural observations that diasteroid hydrocarbons increase relative to their regular counterparts with increasing thermal stress, while their C_{27} through C_{29} proportionality shows a slight enrichment in C_{27}. Relative concentrations of 20S to 20R configurations of 24-ethyl-14α,17α-cholestane show the expected increase with increasing thermal stress into the early part of the primary oil generation stage, but thereafter decrease with increasing thermal stress. If this reversal is found in high maturity sections of the natural system, the utility of this transformation as a maturity index will be limited. Triaromatic- to monoaromatic-steroid hydrocarbon concentrations increase with increasing thermal stress as observed in the natural system. Preferred migration of monoaromatic steroid hydrocarbons from bitumen extracts to expelled oils places considerable doubt on currently employed kinetic models for this aromatization reaction. As in the natural system, the experiments show relative concentrations of low-molecular weight- to high-molecular weight-triaromatic steroid hydrocarbons to increase with increasing thermal stress. Assuming a first-order reaction rate, the apparent activation energy and pre-exponential factor for this apparent side-chain cleavage reaction are 175.59 kJ mol^{-1} and 2.82 × 10^{13} hr^{-1}, respectively. These kinetic parameters are geologically reasonable and are similar to those for the overall generation of expelled oil.

INTRODUCTION

REACTIONS INVOLVING isomerization, aromatization, and side-chain cleavage of steroid hydrocarbons in bitumen extracts from sedimentary rocks have been considered as thermal maturity indices (SEIFERT and MOLDOWAN, 1981; MACKENZIE and MAXWELL, 1981). Ideally, these reactions are considered to be specific molecular transformations in which their reaction coordinate is equated with the amount of thermal stress experienced by the host rock. Studies on bitumens extracted from rocks at different levels of thermal maturity have monitored these molecular transformations and have used them to evaluate the thermal history of sedimentary basins (MACKENZIE and MCKENZIE, 1983; SUZUKI, 1984; BEAUMONT et al., 1985). Some of these same molecular transformations may also be used to evaluate the thermal maturity of crude oils (SEIFERT and MOLDOWAN, 1978; SHI JI-YANG et al., 1982). Evaluation of these reactions in crude oils is difficult in the natural system because obtaining crude oils that have been expelled from the same source rock at different levels of thermal maturity is impractical. Furthermore, the transient character of crude oil poses the possibility that crude oil from the same source rock may be entrapped in several reservoirs with different thermal histories. This inability in the natural system to make a direct correlation of molecular transformations in crude oils with their source rocks may be alleviated in part by laboratory pyrolysis experiments.

Salient insights into the effects of thermal maturation on kerogens and bitumens of potential source rocks have been provided in the past by numerous laboratory pyrolysis studies (e.g., TISSOT et al., 1974; GALLEGOS, 1975; LEVENTHAL, 1976; HARWOOD, 1977; PETERS et al., 1981; LARTER and DOUGLAS, 1982). Unfortunately, the lack of an expelled pyrolysate or the unnatural conditions employed to induce an expelled pyrolysate (e.g., vacuum cryogenic trapping, carrier gas flushing, or solvent refluxing) in these experiments, renders their assessment of thermal maturation effects on crude oils questionable. A laboratory pyrolysis technique that expels a pyrolysate oil from potential source rocks in a more natural manner is referred to as hydrous pyrolysis (LEWAN et al., 1979; LEWAN, 1983; WINTERS et al., 1983). This technique involves heating unextracted rock chips of potential source rocks in the presence of liquid water at subcritical temperatures (<374°C) in an oxygen-free atmosphere. Pyrolysate oil is expelled from the rock into the encompassing water phase and collected off the water surface after the experiment. Although high temperatures (260–365°C) must be employed in these experiments to offset the long time requirements (10^6 to 10^8 years) of the natural system, the pyrolysate oils expelled from the rocks are compositionally and physically similar to natural crude oils (LEWAN et al., 1979; WINTERS et al., 1983; HOERING, 1984). An attribute of hydrous pyrolysis that is frequently neglected is its ability to provide a free-flowing liquid pyrolysate that is physically similar to natural crude oils, as opposed to tarry viscous pyrolysates provided by other pyrolysis techniques. It has also been shown that this technique pro-

vides insights on stages, kinetics, and maturation indices of petroleum generation that are applicable in the natural system (LEWAN, 1983, 1985). The objective of this study is to use hydrous pyrolysis to document the thermal maturation effects on the steroid hydrocarbons and their molecular transformations in expelled oil and retained bitumen of a sample from the Retort Shale Member of the Phosphoria Formation (Permian).

MATERIALS AND METHODS

Sample description

The sample of Phosphoria Formation used in this study is from the Retort Shale Member which is exposed on the west side of Retort Mountain (NW1/4, SW1/4, Sec. 23, T9S, R9W), in Beaverhead County, Montana. Collection of a homogeneous sample was insured by confining the sampling to a 12-cm thick interval that occurs approximately 10 m below a massive sandstone at the top of the exposure. Weathered portions of the outcrop were avoided during sampling by employing the field criteria proposed by LEWAN (1980) for collecting unweathered samples. The sample is a very fine-grained rock and may be classified as an argillaceous claystone (LEWAN, 1978). Major minerals include quartz, kaolinite, and illite, with minor amounts of pyrite. The organic carbon content of the sample is 23.6 wt% and the organic matter is in the pre-oil generation stage. Amorphous Type-II kerogen accounts for more than 90 vol% of the kerogen, with the remaining kerogen consisting of structured Type-III kerogen. The sample was crushed into chips ranging in size from 0.5 to 2.0 cm and thoroughly mixed.

Experimental procedure

One-liter general-purpose reactors (Parr Instrument Co., T316SS, No. 4653) were loaded with 400 grams of crushed rock (0.5–2.0 cm) and 260 ml of deionized water (ASTM type-III). The remaining volume was purged with helium and then filled with 240 kPa of helium. Aliquots of the sample were matured through different stages of petroleum generation by heating them isothermally for 72 hours at temperatures ranging from 260 to 360°C. In order to achieve an advanced stage of post-oil generation at subcritical water conditions, two aliquots were run at 360°C for 240 and 600 hours. An electrical heater (Parr Instrument Co., No. 4962) and a time-proportioning controller with a type-J thermocouple maintained the desired reactor temperatures within ±0.5°C. The temperature was monitored by an additional type-J thermocouple connected to a digital thermometer (Omega Engineering, Inc., Model 199).

Collection of phases

The three organic phases collected from the reactor include expelled oil, bitumen, and kerogen. Expelled oil occurs in the reactor as a floating liquid pyrolysate layer on the water surface and as a sorbed liquid pyrolysate film on the rock chips. The floating pyrolysate was collected with a Pasteur pipet and transferred to a tared vial. Water in the reactor was decanted into a separatory funnel where minor amounts of the remaining liquid pyrolysate were concentrated and collected. Benzene was used to rinse off and collect the sorbed pyrolysate film on the rock chips, reactor walls, collection pipet, and separatory funnel. The resulting solution was filtered through a 0.45 µm Fluoropore filter and the sorbed pyrolysate was concentrated by rotary vacuum evaporation of the benzene. Both floating and sorbed pyrolysates are compositionally similar and collectively referred to as expelled oil. Data on steroid hydrocarbons of the expelled oil are from analyses on the floating pyrolysate which usually comprises more than 75 wt% of the expelled oil.

The rock chips were removed from the reactor and dried in a vacuum oven at 50°C for 24 hours. Bitumen was extracted from pulverized rock chips in a Soxhlet apparatus for 72 hours with a mixture of benzene and methanol (60:40 wt%). The refluxed solvent was filtered through a 0.45 µm Fluoropore filter and the bitumen was concentrated by rotary vacuum evaporation.

Kerogen was isolated from pulverized rock chips by a series of acid treatments, which included an 18 wt% solution of HCl for 2 hours, a 52 wt% solution of HF for 18 hours, and a hot (100°C) concentrated solution of HCl for 1 hour. This was followed by a density separation with a 2.1 g/cm³ solution of zinc bromide. The floating residue was collected and considered kerogen after it had been extracted in a Soxhlet apparatus for 72 hours with a mixture of benzene and methanol (60:40 wt%).

Liquid column chromatography

Saturate and aromatic fractions were separated from the bitumens and expelled oils on a 40-cm alumina (MCB Alcoa F-20) column. The saturate fraction was eluted with 275 ml of n-heptane and the aromatic fraction was eluted with 275 ml of benzene. Eluting solvents were removed by rotary vacuum evaporation. Saturate fractions were used to examine isomerization of steranes in the m/z 217 ion chromatograms, and aromatic fractions were used to examine side-chain cleavage of triaromatic steroid hydrocarbons in the m/z 231 ion chromatograms. Unfractionated expelled oils and bitumens were used to examine aromatization of monoaromatic- to triaromatic-steroid hydrocarbons in the m/z 253 and 231 ion chromatograms, respectively.

Gas Chromatography/Mass Spectrometry (GC/MS)

Expelled oils, bitumens and their eluted fractions were analyzed on a Hewlett-Packard 5996A GC/MS instrument in the electron impact mode at 70 eV. Both the source and analyzer temperatures were held at 250°C with the transfer line set at 320°C. The chromatographic column was a Quadrex 007 bonded-phase methyl-silicone fused silica, with an ID of 0.25 mm, a length of 25 m, and a film thickness of 0.5 µm. A heating rate of 5°C/min between 30° and 330°C was programmed into the instrument, with a final hold time of 20 minutes. Samples were injected in the split mode at 330°C with helium as the carrier gas. The mass spectrometer was run in the selected-ion-monitoring mode (SIM), with 20 ions being monitored at a dwell time of 30 msec for each ion. Compounds were identified in their diagnostic ion chromatograms on the basis of relative retention times and comparisons with published data (e.g., SEIFERT, 1978; SEIFERT and MOLDOWAN, 1978; SEIFERT et al., 1983).

RESULTS AND DISCUSSION

Stages of petroleum generation

Based on results from hydrous pyrolysis experiments, LEWAN (1983, 1985) defined petroleum generation in terms of four stages, 1) pre-oil generation, 2) incipient-oil generation, 3) primary-oil generation, and 4) post-oil generation. Figure 1 shows the variations in kerogen, bitumen, and expelled oil from the different pyrolyzed aliquots of Phosphoria Retort Shale and their prescribed relationship with the stages of petroleum generation. Incipient-oil generation is characterized by the thermal decomposition of kerogen into bitumen with generation of only minor amounts of expelled oil. This is followed by primary-oil generation which is characterized by the thermal decomposition of bitumen
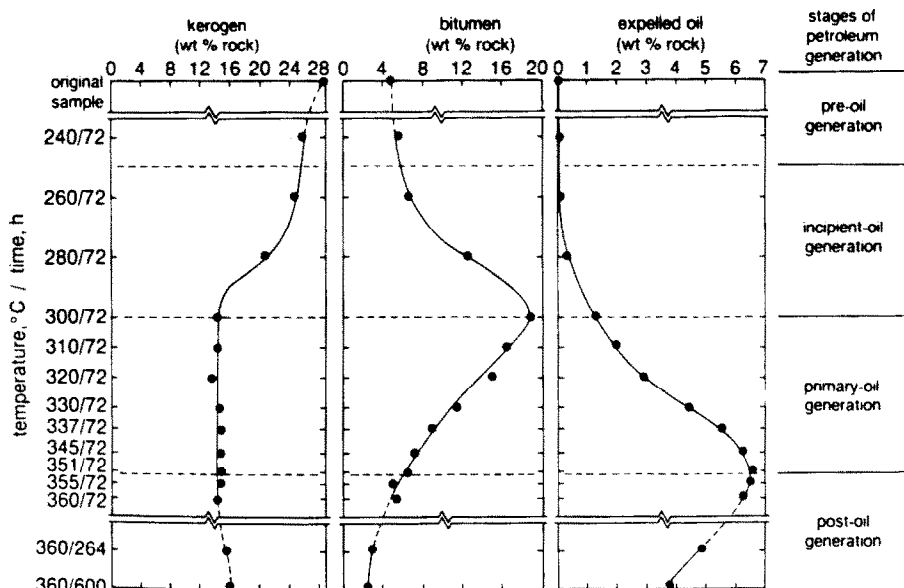
FIG. 1. The amounts of kerogen, bitumen, and expelled oil from aliquots of Phosphoria Retort Shale pyrolyzed at different temperatures and times (from LEWAN, 1985).

into expelled oil and no significant change in the amount of kerogen. Post-oil generation is characterized by the thermal decomposition of expelled oil into gas and pyrobitumen. The insolubility of pyrobitumen makes it difficult to isolate from the kerogen and, as a result, the amount of kerogen shows a slight increase during this stage. An important observation that should be noted in Fig. 1 is that maximum bitumen generation does not coincide with maximum oil generation as is sometimes assumed in the natural system.

Steranes

Distribution of C_{27} through C_{29} steranes in the m/z 217 ion chromatograms for bitumens and expelled oils at different levels of thermal maturity are shown in Figs. 2 and 3, respectively. The identified peaks are listed in Table 1 and their distributions are comparable with those of bitumens and crude oils observed in the natural system. Anhydrous pyrolysis experiments by SEIFERT (1978) and MACKENZIE et al. (1981) generated pyrolysates deficient in diasteranes. Conversely, supercritical (>374°C) hydrous pyrolysis experiments by RULLKÖTTER et al. (1984) generated pyrolysates enriched in diasteranes. The bitumen of the original sample in this study contains only minor amounts of diasteranes, but their concentration relative to the regular steranes changes with increasing thermal stress. This change is monitored in Fig. 4 by the decimal fraction of 20R- and 20S-$\beta\alpha$ C_{28} diasteranes over 20R- and 20S-$\alpha\alpha$ and $\beta\beta$ C_{29} regular steranes. This expression for the bitumen shows a slight decrease in the pre-oil generation stage, followed by an increase in the incipient and primary oil generation stages. Both the expelled oil and bitumen show this increase, which has also been reported in the natural system (SEIFERT

and MOLDOWAN, 1978; ENSMINGER et al., 1978; MACKENZIE et al., 1980). Unfortunately, interpreting and modeling this expression as a thermal maturity
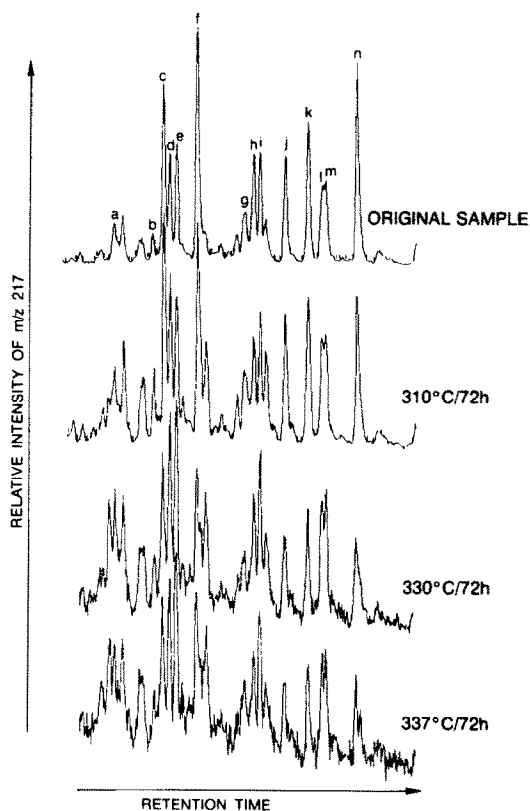

FIG. 2. The m/z 217 ion chromatograms of the saturate fraction of bitumen extracted from the original sample and aliquots pyrolyzed at 310, 330, and 337°C for 72-hour durations. The labeled steranes are listed in Table 1.
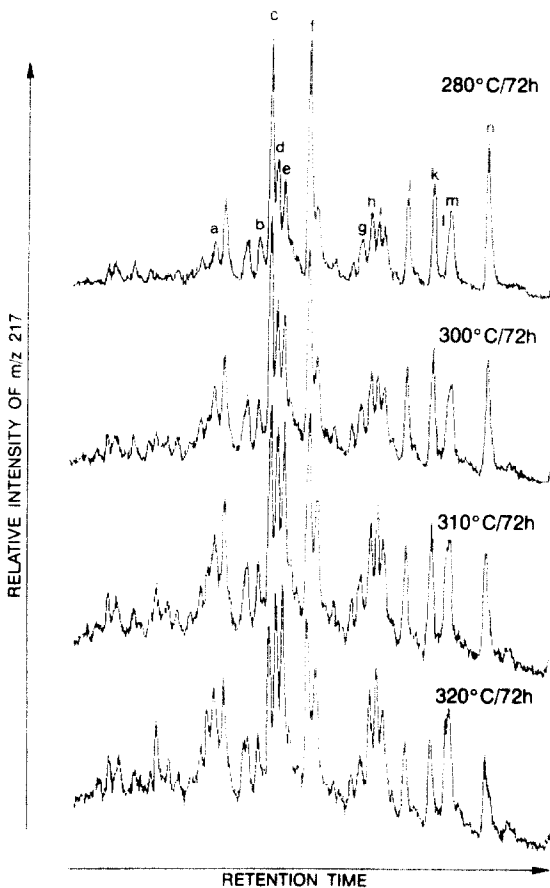
FIG. 3. The m/z 217 ion chromatograms of the saturate fraction of expelled oils from pyrolyzed aliquots at 280, 300, 310, and 320°C for 72-hour durations. The labeled steranes are listed in Table 1.

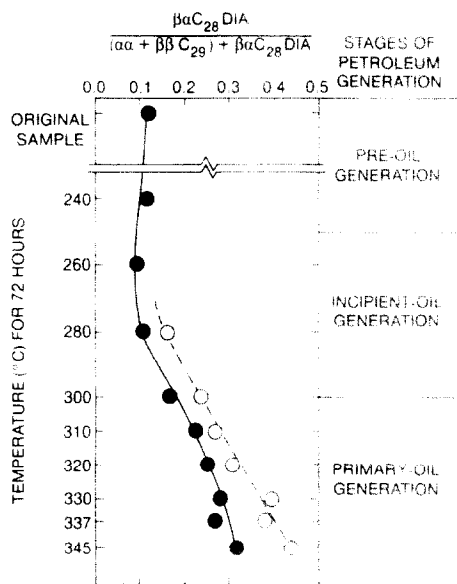
FIG. 4. Changes in concentration of diasteranes (20R + 20S$\beta\alpha C_{28}$DIA) relative to that of regular steranes (20R + 20S$\alpha\alpha C_{29}$ and 20R + 20S $\beta\beta$ C_{29}) in bitumen extracts (●) and expelled oils (○) from aliquots of pyrolyzed Phosphoria Retort Shale.

indicator is hampered by its initial decrease at low maturity levels in the bitumen and the variability of depositional factors that control its initial value (SIESKIND et al., 1979). SEIFERT and MOLDOWAN (1978) present data that suggest diasteranes are enriched relative to regular steranes in crude oils with increasing migration

distance. This is supported in part by the enrichment of diasteranes in the expelled oil relative to the bitumen during incipient and primary oil generation. It should be emphasized that only primary migration effects may be noted in hydrous pyrolysis experiments, and these are limited to short migration distances governed by the small dimensions of the pyrolyzed rock chips (0.5–2.0 cm).

Proportionality of C_{27} through C_{29} regular steranes is shown in a ternary diagram in Fig. 5. The bitumens
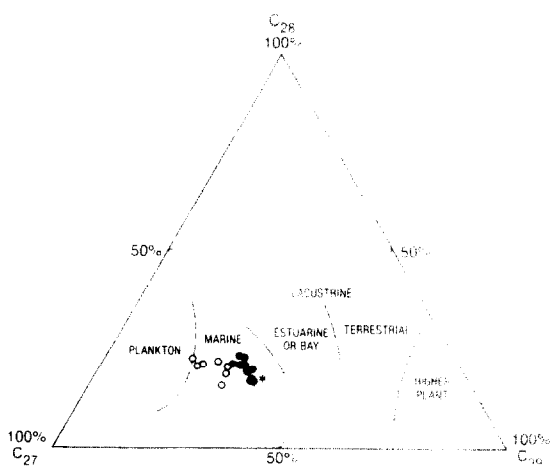
TABLE 1. LIST OF STERANES IDENTIFIED IN THE m/z 217 ION CHROMATOGRAMS IN FIGURES 2 AND 3

Peak	Compound	Abbreviation
a	24–Methyl–13β, 17α-Diacholestane (20S)	$\beta\alpha C_{28}$ DIA(20S)
b	24–Methyl–13β, 17α-Diacholestane (20R)	$\beta\alpha C_{28}$ DIA(20R)
c	14α,17α-Cholestane (20S)*	$\alpha\alpha C_{27}$ (20S)
d	14β,17β-Cholestane (20R)*	$\beta\beta C_{27}$ (20R)
e	14β,17β-Cholestane (20S)*	$\beta\beta C_{27}$ (20S)
f	14α,17α-Cholestane (20R)	$\alpha\alpha C_{27}$ (20R)
g	24–Methyl–14α, 17α-Cholestane (20S)	$\alpha\alpha C_{28}$ (20S)
h	24–Methyl–14β, 17β-Cholestane (20R)**	$\beta\beta C_{28}$ (20R)
i	24–Methyl–14β, 17β-Cholestane (20S)	$\beta\beta C_{28}$ (20S)
j	24–Methyl–14α, 17α-Cholestane (20R)	$\alpha\alpha C_{28}$ (20R)
k	24–Ethyl–14α, 17α-Cholestane (20S)	$\alpha\alpha C_{29}$ (20S)
l	24–Ethyl–14β, 17β-Cholestane (20R)	$\beta\beta C_{29}$ (20R)
m	24–Ethyl–14β, 17β-Cholestane (20S)	$\beta\beta C_{29}$ (20S)
n	24–Ethyl–14α, 17α-Cholestane (20R)	$\alpha\alpha C_{29}$ (20R)

* Peak may also contain a 24–methyl-diacholestane.

** Peak may also contain a 24–ethyl–13α,17β– diacholestane (20R).

FIG. 5. Ternary diagram of the sum of 20R- and 20S-5α(H), 14α(H), 17α(H) steranes (C_{27}, C_{28}, and C_{29}) in the expelled oil (○) and bitumen extract (●) from pyrolyzed aliquots of Phosphoria Retort Shale, and bitumen extract from the original sample (*). Dashed boundaries of ecosystems are based on C_{27}, C_{28}, and C_{29} sterols as reported by HUANG and MEINSCHEIN (1979).

show a close grouping with only a slight enrichment in C_{27} and C_{28} relative to the original bitumen. The expelled oils are slightly more enriched in C_{27} and show more scatter than the bitumens. Co-elution of diasteranes appears to be the cause of this C_{27} enrichment. Figure 4 shows that expelled oils are enriched in diasteranes relative to the bitumens, and this enrichment increases at higher levels of thermal maturity. The three expelled oils with the most diasteranes at the higher levels of thermal maturity correspond with those that have the most C_{27} enrichment in Fig. 5. In spite of some scatter, the expelled oils and bitumens plot within the marine ecosystem on the basis of sterol distributions in recent sediments (HUANG and MEINSCHEIN, 1979). This is in good agreement with geological interpretations of a marine origin for the Phosphoria Formation (SHELDON, 1957; MCKELVEY et al., 1959) in which the Retort Shale Member occurs.

Numerous isomerization reactions involving steranes are likely during thermal maturation, but the applicability of most of them as maturity indicators is restricted by co-elution problems or variability in initial values. These restrictions appear to be minimized for the 20R to 20S isomerization of the $\alpha\alpha C_{29}$-sterane, which has been used as a maturity indicator of crude oils (SEIFERT and MOLDOWAN, 1981) and bitumen extracts (MACKENZIE et al., 1980). An expression of this reaction is given by the decimal fraction of 20S divided by 20R + 20S. Figure 6 shows the change in this expression through the series of hydrous pyrolysis experiments. Initially, in the pre-oil generation stage the expression decreases in the bitumen and then increases as expected in the incipient and primary oil generation stage to a maximum, which is followed by a decrease. The maximum value of 0.56 obtained in these experiments is in good agreement with natural observations
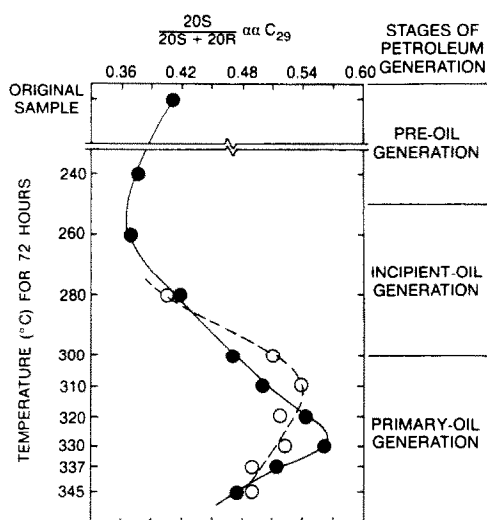

FIG. 6. Changes in concentration of the $20S\alpha\alpha C_{29}$ sterane relative to that of its 20R configuration in bitumen extract (●) and expelled oil (○) from aliquots of pyrolyzed Phosphoria Retort Shale.

(MACKENZIE and MAXWELL, 1981) and theoretical considerations (VAN GRAAS et al., 1982), but reversal of the expression beyond this maximum has not been reported in the literature. This may be an artifact of the pyrolysis technique or a lack of natural data at depths great enough to show the reversal. Both the expelled oil and bitumen extract show this reversal and if it does occur in the natural system, the utility of this parameter as a maturity index will be hampered. In addition, the initial decrease in this expression during pre-oil generation suggests that the prescribed reaction may be more complex than originally thought. If this is verified in the natural system, a simple first-order rate model for a reversible equilibrium reaction will not be applicable.

Aromatic steroid hydrocarbons

The distribution of C_{27} through C_{29} C-ring monoaromatic steroid hydrocarbons in the m/z 253 ion chromatograms for bitumens and expelled oils at different thermal maturity levels is shown in Figs. 7 and 8, respectively. The prominent peak in the bitumens and in some of the expelled oils has been identified as perylene on the basis of retention time and mass spectrum of a 99% perylene standard. Perylene is not ubiquitous in the natural system but it has been detected in a variety of sediments (e.g., ORR and GRADY, 1967; BROWN et al., 1972; PEAKE et al., 1974; WAKEHAM et al., 1979, 1980) and in some crude oils (SCHNURMAN et al., 1953; CARRUTHERS and COOK, 1954; TEPLITSKA and MANDEV, 1968; PANCIROV et al., 1980). It may be associated with algal- or vascular plant-derived organic matter in anoxic environments, and its precursor may be related to pigments endemic to some fungi (LOUDA and BAKER, 1984). Figure 7 shows that perylene occurs in the original bitumen, suggesting that it is not an artifact of hydrous pyrolysis. As shown in Fig. 8, perylene is not detected in the first expelled oil recovered at 260°C after 72 hours, but it becomes more apparent in the expelled oils generated at higher levels of thermal maturity. GIMPLEVICH (1960) found perylene in Tertiary shales of the Maikop area of Russia, but did not detect it in the crude oils from reservoirs associated with these shales. The hydrous pyrolysis data suggest these crude oils are either not sourced from the perylene-bearing shales or represent early expelled products from only partially matured perylene-bearing shales.

The C-ring monoaromatic steroid hydrocarbons in the bitumens and expelled oils generated by hydrous pyrolysis have ion chromatograms that are similar to those found in the natural system. Their intensities decrease relative to the perylene peak with increasing maturity and become undiscernible from the background in experiments exceeding 330°C for 72-hour durations. C_{27} through C_{29} proportionality is shown on the ternary diagram in Fig. 9. Compared to the steranes, this class of compounds clusters more tightly and has a higher C_{28} component. The expelled oils
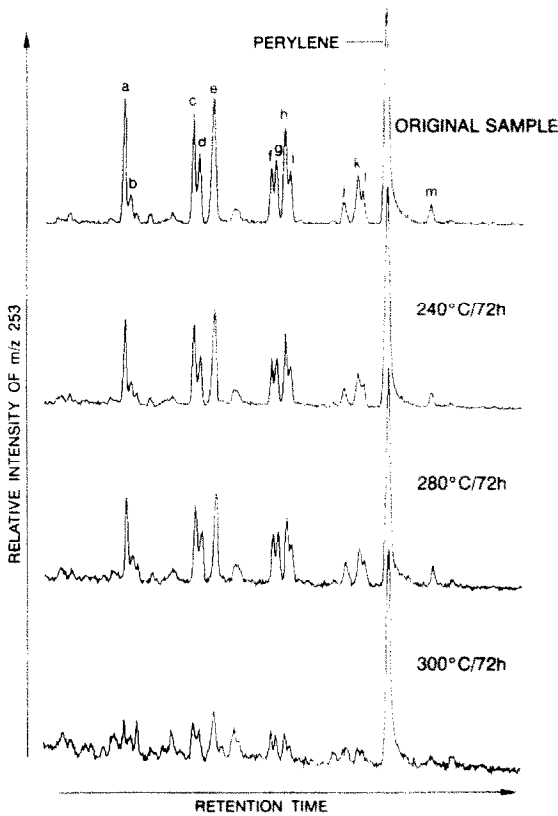
FIG. 7. The m/z 253 ion chromatograms of the whole bitumen extracted from the original sample and pyrolyzed aliquots at 240, 280, and 300°C for 72-hour durations. The labeled C-ring monoaromatic steroid hydrocarbons are described in Table 2.
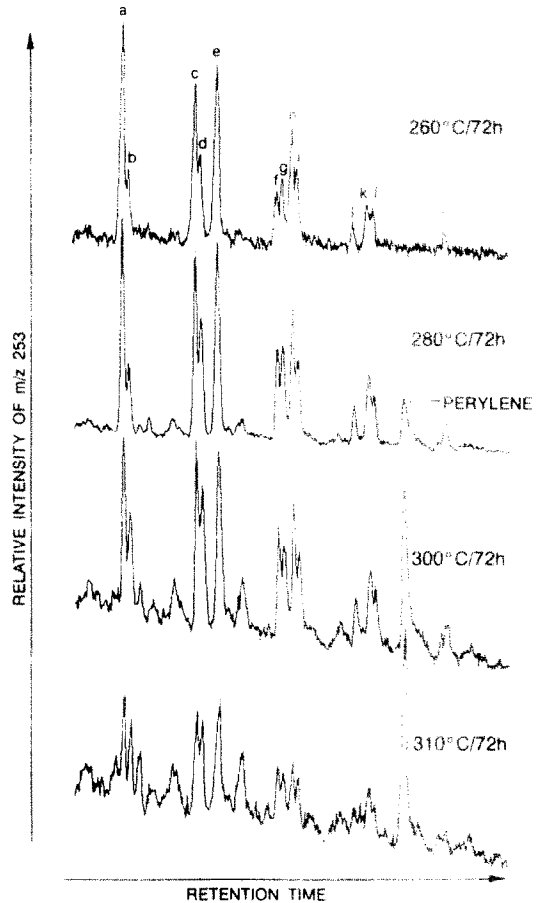

FIG. 8. The m/z 253 ion chromatograms of the whole oil expelled from pyrolyzed aliquots at 260, 280, 300, and 310°C for 72-hour durations. The labeled C-ring monoaromatic steroid hydrocarbons are described in Table 2.

TABLE 2. DESCRIPTION OF C-RING MONOAROMATIC STEROID HYDROCARBONS THAT HAVE BEEN TENTATIVELY IDENTIFIED IN THE m/z 253 ION CHROMATOGRAMS IN FIGURES 7 AND 8.

| | Substituents * | | | | Abbreviation |
Peak	R_1	R_2	R_3	R_4	of Compound
a	β(H)	CH_3	$S(CH_3)$	H	$\beta SC_{27} MA$
b	CH_3	H	$S(CH_3)$	H	$SC_{27} DMA$
c	β(H)	CH_3	$R(CH_3)$	H	$\beta RC_{27} MA$
c	CH_3	H	$R(CH_3)$	H	$RC_{27} DMA$
d	α(H)	CH_3	$S(CH_3)$	H	$\alpha SC_{27} MA$
e	β(H)	CH_3	$S(CH_3)$	CH_3	$\beta SC_{28} MA$
e	CH_3	H	$S(CH_3)$	CH_3	$SC_{28} DMA$
f	α(H)	CH_3	$R(CH_3)$	H	$\alpha RC_{27} MA$
g	α(H)	CH_3	$S(CH_3)$	CH_3	$\alpha SC_{28} MA$
h	β(H)	CH_3	$R(CH_3)$	CH_3	$\beta RC_{28} MA$
h	CH_3	H	$R(CH_3)$	CH_3	$RC_{28} DMA$
i	β(H)	CH_3	$S(CH_3)$	C_2H_5	$\beta SC_{29} MA$
i	CH_3	H	$S(CH_3)$	C_2H_5	$SC_{29} DMA$
j	α(H)	CH_3	$S(CH_3)$	C_2H_5	$\alpha SC_{29} MA$
k	α(H)	CH_3	$R(CH_3)$	CH_3	$\alpha RC_{28} MA$
l	β(H)	CH_3	$R(CH_3)$	C_2H_5	$\beta RC_{29} MA$
l	CH_3	H	$R(CH_3)$	C_2H_5	$RC_{29} DMA$
m	α(H)	CH_3	$R(CH_3)$	C_2H_5	$\alpha RC_{29} MA$

* Location on Structure:
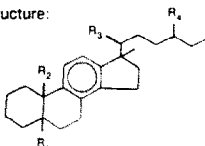
have a higher C_{27} component than the bitumen extracts, which is similar to that observed for the steranes.

The relative concentration of dia- to regular-C-ring monoaromatic steroid hydrocarbons may be expressed by a decimal fraction of the $20SC_{27}$ diamonoaromatic divided by the sum of itself plus the $5\beta 20SC_{27}$ regular-monoaromatic. As shown in Fig. 10, this expression increases with increasing thermal stress in the expelled oils and bitumen extracts of the hydrous pyrolysis experiments. The increase in this expression with thermal maturity has been reported for crude oils in the natural system, but its utility as a maturity index is hindered by variations in the amount of dia-C-ring monoaromatic steroid hydrocarbons formed during early diagenesis (MOLDOWAN and FAGO, 1986).

Aromatization of C-ring monoaromatic- to ABC-ring triaromatic-steroid hydrocarbons has been used as a maturity index to evaluate the thermal history of basins (e.g., MACKENZIE and McKENZIE, 1983; BEAUMONT et al., 1985). MOLDOWAN and FAGO (1986) have suggested that the kinetic models used in these studies may be complicated by the coelution of dia-C-ring monoaromatics with the regular-C-ring monoaromatics. Results from the hydrous pyrolysis experiments on
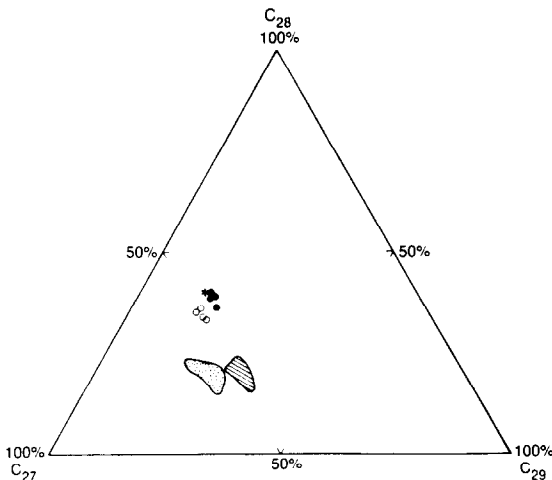
FIG. 9. Ternary diagram of the C-ring monoaromatic steroid hydrocarbons in the bitumen extracts (●) and expelled oils (○) from pyrolyzed Phosphoria Retort Shale and bitumen extract from the original sample (*). The proportionality of steranes from Fig. 5 are shown for comparison (hatched area = bitumen extracts and stippled area = expelled oil).

this transformation are shown in Fig. 11 using 5α and 5β 20R-C_{29} monoaromatics to 20R-C_{28} triaromatic as an index. The bitumen extract shows the expected increase to unity with increasing stress. The expelled oil also shows an increase, but it is consistently lower than the bitumen extract by approximately 0.25 units. This difference may be the result of either a lower rate of aromatization in the expelled oil due to its lack of contact with rock surfaces, or the monoaromatics migrating out of the rock more readily than the triaromatics during expulsion of the oil.
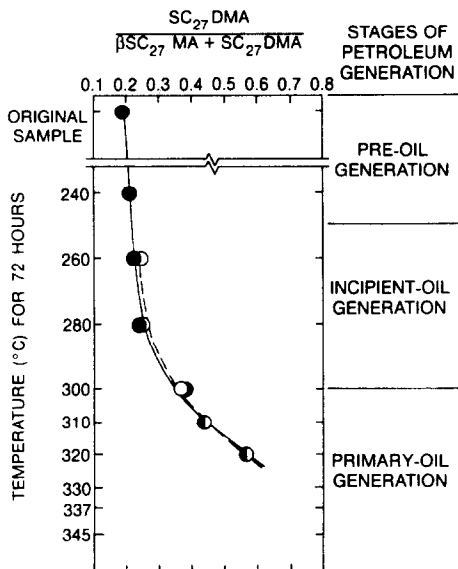

FIG. 10. Changes in the concentration of a dia-monoaromatic steroid hydrocarbon ($SC_{27}DMA$) relative to that of a regular monoaromatic steroid hydrocarbon ($\beta SC_{27}MA$) in bitumen extracts (●) and expelled oils (○) from aliquots of pyrolyzed Phosphoria Retort Shale.
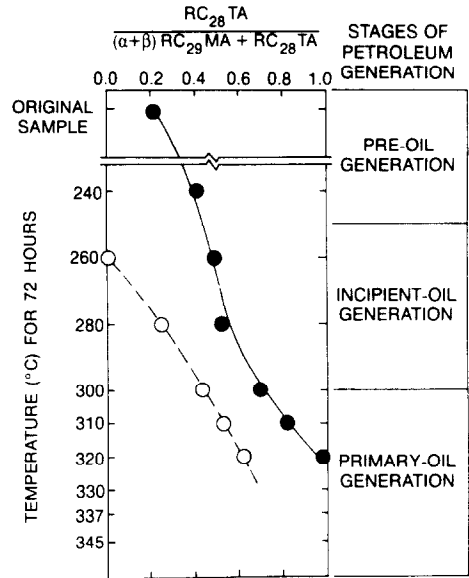

FIG. 11. Changes in the concentration of a triaromatic steroid hydrocarbon ($RC_{28}TA$) relative to that of monoaromatic steroid hydrocarbons ($\alpha RC_{29}MA$ and $\beta RC_{29}MA$) in bitumen extracts (●) and expelled oils (○) from aliquots of pyrolyzed Phosphoria Retort Shale.

Using first-order rates as established by ABBOTT et al. (1984) for this reaction, an Arrhenius plot may be constructed for aromatization in the bitumen extract from the data in Fig. 11. A linear relationship on this plot would suggest that aromatization in the bitumen was not significantly influenced by the expulsion of oil and its ensuing aromatization. As shown in Fig. 12, the Arrhenius plot is not linear and instead may be interpreted in terms of at least two different linear expressions. This interpretation suggests oil expulsion
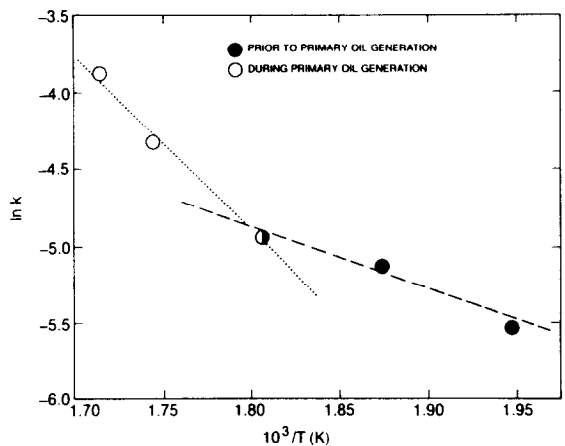

FIG. 12. Arrhenius plot for mono- to triaromatic conversion of steroid hydrocarbons in bitumen extracts from pyrolyzed aliquots of Phosphoria Retort Shale (Fig. 11). Rate constants (k) are calculated on the basis of first-order reaction rates: $k = [\ln(1 - R_0) - \ln(1 - R)]/t$; where t is the duration of the experiment and R_0 and R are the $RC_{28}TA/(RC_{29}MA + RC_{28}TA)$ decimal fractions of the original bitumen and the bitumen after isothermal heating, respectively.

does influence the aromatization parameter and, therefore, preferred migration of monoaromatics relative to triaromatics may be a plausible explanation for the data in Fig. 11. Preferred migration of monoaromatics in the natural system has been suggested as an explanation for variations in the mono- to triaromatic steroid hydrocarbon proportionality of Mahakam Delta crude oils (HOFFMANN et al., 1984). The influence of primary and secondary migration on the aromatization parameter makes its use as a maturity index questionable, and may be responsible for the large amount of scatter in its Arrhenius plot as reported by MACKENZIE and MCKENZIE (1983).

Another maturity index based on aromatic steroid hydrocarbons is the *apparent* cleavage of their side chain (SEIFERT and MOLDOWAN, 1978; MACKENZIE et al., 1981). It has been shown in bitumen extracts from the natural system that C_{20} and C_{21} triaromatics increase relative to the C_{26} through C_{28} triaromatics with increasing thermal maturity (MACKENZIE et al., 1981; SHI JI-YANG et al., 1982; SCHOU et al., 1984). A similar change occurs in the bitumen extracts (Fig. 13) and expelled oils (Fig. 14) from the series of hydrous

FIG. 14. The m/z 231 ion chromatograms of the aromatic fraction of expelled oils from pyrolyzed aliquots at 280, 310, 320, and 330°C for 72-hour durations. The labeled ABC-ring triaromatic steroid hydrocarbons are described in Table 3
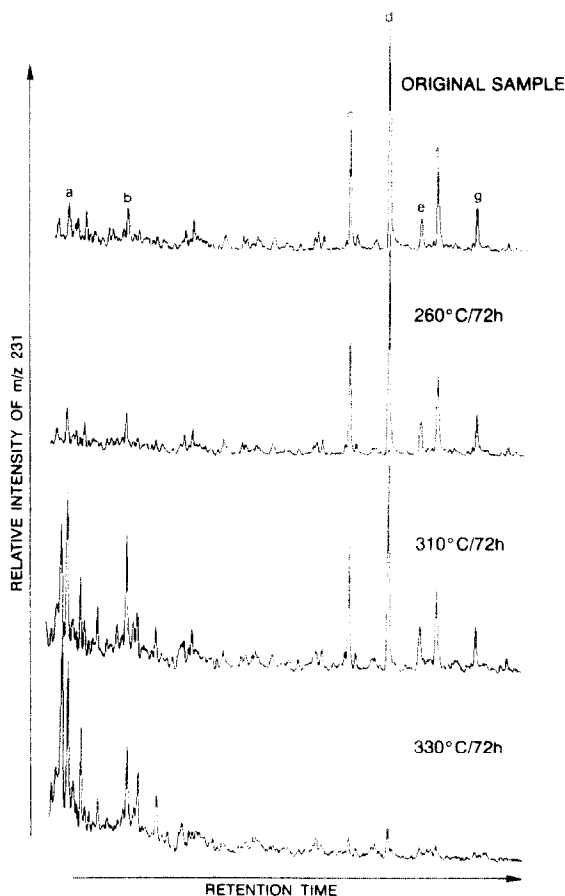
FIG. 13. The m/z 231 ion chromatograms of the aromatic fraction of bitumen extracted from the original sample and aliquots pyrolyzed at 260, 310, and 330°C for 72-hour durations. The labeled ABC-rig triaromatic steroid hydrocarbons are described in Table 3.
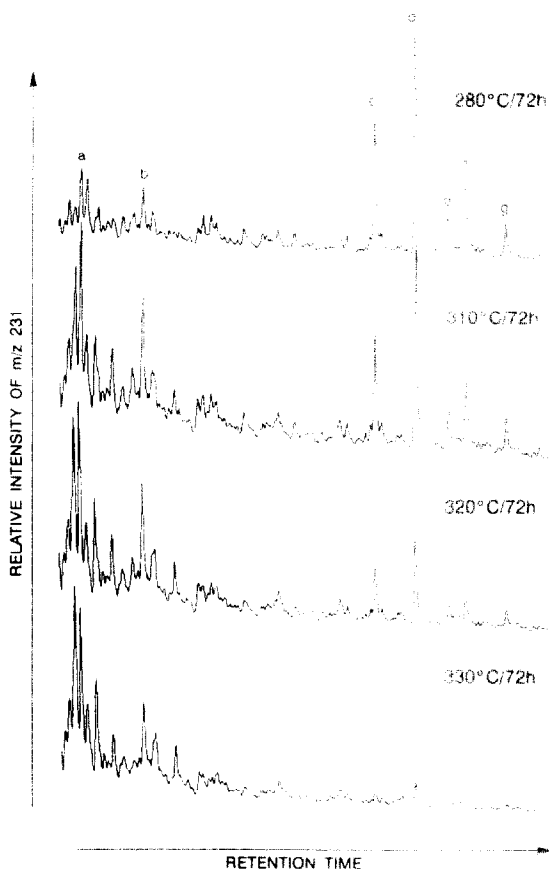
pyrolysis experiments. As shown in Fig. 15, the change in this parameter is the same for both the expelled oil and bitumen extract. An Arrhenius plot of these data (Fig. 16), assuming first-order rates, shows a good linear fit with an apparent activation energy of 175.59 kJ mol^{-1} and a pre-exponential factor of 2.82×10^{13} hr^{-1} These kinetic parameters are geologically reasonable and are essentially the same as those calculated by LEWAN (1985) for the overall generation of expelled oil from the same rock (i.e., activation energy 178.69 kJ mol^{-1} and pre-exponential factor 4.92 × 10^{13} hr^{-1}). This similarity may be fortuitous or it may be suggesting that the change in the triaromatic distribution is governed by mechanisms similar to those governing the overall generation of expelled oil.

CONCLUSIONS

A study has been made of the utility of hydrous pyrolysis in developing an understanding of thermal maturation effects on steroid hydrocarbons in the bitumen and expelled oil of an organic shale. Although the following conclusions specifically refer to organic matter in the Phosphoria Retort Shale, they provide some basic observations and concepts that may not be derived from studying only the natural system
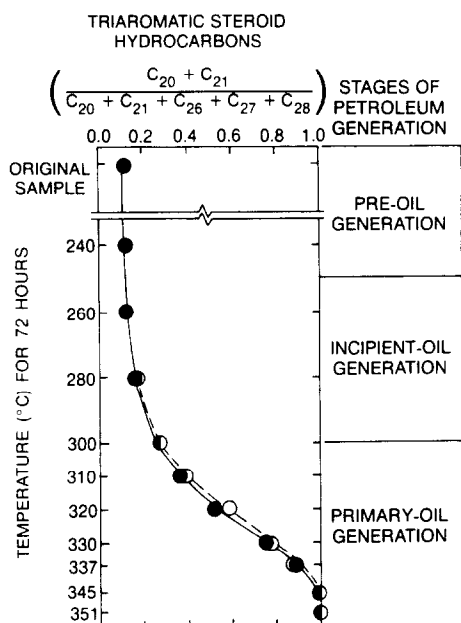
TRIAROMATIC STEROID HYDROCARBONS

FIG. 15. Changes in concentration of low-molecular weight triaromatic steroid hydrocarbons (C_{20} and C_{21}) relative to that of high-molecular weight triaromatic steroid hydrocarbons (C_{26}, C_{27}, and C_{28}) in bitumen extracts (●) and expelled oils (○) from aliquots of pyrolyzed Phosphoria Retort Shale.

1. Steroid hydrocarbons in bitumen extracts and expelled oils generated by hydrous pyrolysis have m/z 217-, 231-, and 253-ion chromatograms that are similar to those observed in bitumen extracts and crude oils from the natural system.
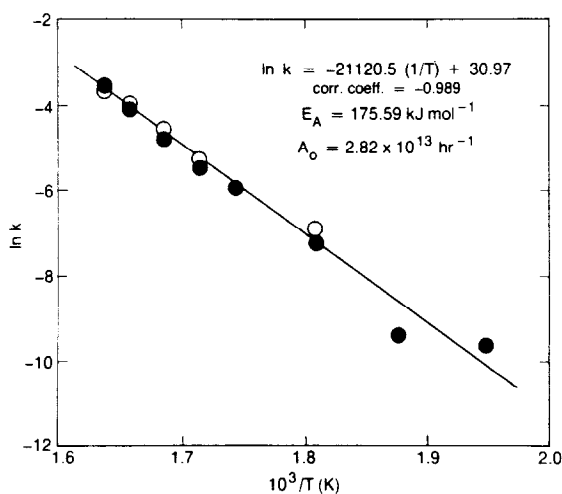

FIG. 16. Arrhenius plot for apparent cleavage of side chains from C_{26} through C_{28} triaromatic steroid hydrocarbons in bitumen extracts (●) and expelled oils (○) from the pyrolyzed aliquots of Phosphoria Retort Shale (Fig. 15). Rate constants (k) are calculated on the basis of first-order reaction rates: $k = [\ln(1 - R_0) - \ln(1 - R)]/t$, where t is the duration of the experiment and R_0 and R are the $(C_{20} + C_{21})/(C_{20} + C_{21} + C_{26} + C_{27} + C_{28})$ decimal fractions of the triaromatic steroid hydrocarbons in the original bitumen and the bitumens or expelled oils after isothermal heating, respectively.

TABLE 3. DESCRIPTION OF ABC-RING TRIAROMATIC STEROID HYDROCARBONS THAT HAVE BEEN TENTATIVELY IDENTIFIED IN THE m/z 231 ION CHROMATOGRAMS IN FIGURES 13 AND 14

Peak	Substituents *		Abbreviation of Compound
	R_1	R_2	
a	CH_3	H	C_{20} TA
b	CH_3	CH_3	C_{21} TA
c	$S(CH_3)$	C_6H_{13}	SC_{26} TA
d	$R(CH_3)$	C_6H_{13}	RC_{26} TA
d	$S(CH_3)$	C_7H_{15}	SC_{27} TA
e	$S(CH_3)$	C_8H_{17}	SC_{28} TA
f	$S(CH_3)$	C_7H_{15}	SC_{27} TA
g	$R(CH_3)$	C_8H_{17}	RC_{28} TA

* Location on Structure:
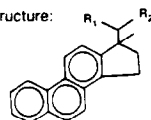
2. Similar to observations made in the natural system, the concentration of diasteranes increases relative to the concentration of regular steranes with increasing thermal stress. Diasteranes are relatively enriched in the expelled oil compared with the bitumen extract, and this enrichment increases with increasing thermal stress.

3. Proportionality of C_{27} through C_{29} steranes on the m/z 217 ion chromatogram does not change significantly with increasing thermal stress. Expelled oils are apparently enriched in C_{27} steranes relative to bitumen extracts due to co-elution of diasteranes.

4. The relative concentration of 20S- to 20R-24-ethyl-14α,17α-cholestane decreases slightly into the early part of the incipient oil generation stage, and then increases as expected into the primary oil generation stage. This is followed by another decrease, which currently has not been noted in the natural system. If this variable trend is documented in more mature samples of the natural system, its applicability as a thermal maturity index will be questionable.

5. Proportionality of C_{27} through C_{29} C-ring monoaromatic steroid hydrocarbons on the m/z 253 ion chromatogram does not change significantly with increasing thermal stress. Expelled oils are enriched in C_{27} monoaromatic steroid hydrocarbons relative to the bitumen extracts. Similar to observations made in the natural system, the monoaromatic steroid hydrocarbons are enriched in a C_{28} component relative to the steranes.

6. The concentration of dia-monoaromatic steroid hydrocarbons increases relative to regular monoaromatic steroid hydrocarbons with increasing thermal stress. This trend has also been observed in the natural system.

7. As a result of aromatization, the concentration of triaromatic- to monoaromatic-steroid hydrocarbons increases as expected with increasing thermal stress. The preferred migration of monoaromatics from bitumen extracts to expelled oils renders simple kinetic models currently employed for aromatization inappropriate.

8. As observed in the natural system, the concentration of low-molecular weight triaromatic steroid hydrocarbons increase relative to their high-molecular weight counterparts with increasing thermal stress. Assuming a first-order reaction rate, the apparent activation energy and pre-exponential factor for this apparent side-chain cleavage are 175.59 kJ mol^{-1} and 2.82×10^{13} hr^{-1}, respectively.

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