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The Kinetics of Specific Organic Reactions in the Zone of Catagenesis [and Discussion]

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The kinetics of specific organic reactions in the zone of catagenesis

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Recently it has been shown that the measured extent of reactions in sedimentary biological marker compounds during catagenesis (for example, steroid aromatization, sterane isomerization) can assist in providing information about the extent of maturation of sedimentary organic matter before and during oil generation and also the thermal history of sediments. In the present study, aromatization of a C_{27} C-ring aromatic steroid and isomerization at the chiral centres of an isoprenoid alkane, 6(*R*),10(*S*)-pristane, have been brought about under laboratory conditions, elemental sulphur being used as the source of radicals. Precise rate laws have been determined and rate coefficients measured at different temperatures. The pre-exponential factors and activation energies were found to be $6.7\times10^{12}\ \mathrm{s^{-1}}$ and $145\ \mathrm{kJ\ mol^{-1}}$ for the aromatization, and $2.1\times10^{7}\ \mathrm{s^{-1}}$ and $120\ \mathrm{kJ\ mol^{-1}}$ for the configurational isomerization of pristane. These values reflect the relative behaviour of the two types of reactions in sediments, the aromatization being the more temperature-dependent reaction.

1. INTRODUCTION

Biological marker compounds occur widely in sediments and petroleums; their molecular structures suggest a link with those of natural products biosynthesized by organisms present at the time of deposition. It has become apparent in recent years that many of the biological compounds contributed to sediments are altered in a systematic way by reaction pathways which occur progressively with increasing burial depth.

The evidence for these pathways comes mainly from two independent, but complementary, approaches. First, the availability of computerized gas chromatography–mass spectrometry (g.c.–m.s.) systems allows changes in the distributions of a variety of compound types to be monitored. These changes can be followed in suites of samples ranging from bottom aquatic sediments containing active microbial communities to sediments in the zone of catagenesis, where thermal effects are important. Second, it is often possible, in simulation experiments, to bring about in the laboratory some of the specific reactions thought to occur naturally in the sedimentary column.

One example is seen in the sedimentary fate of sterols, such as cholesterol. These compounds, contributed mainly to bottom sediments by plankton, are dehydrated to Δ^2-sterenes after reduction of the Δ^5 double bond (figure 1); the alkenes are in turn isomerized to the more stable Δ^4- and Δ^5-sterenes, which undergo further rearrangement to backbone-rearranged sterenes (diasterenes). Reduction to the corresponding alkanes completes this pathway of defunctionalization occurring during low-temperature diagenesis (Dastillung & Albrecht 1977; Mackenzie *et al.* 1982). There is good evidence that these alkene rearrangements are acid-catalysed ionic reactions brought about by the clay minerals present. First, the proposed $\Delta^2\rightarrow\Delta^4+\Delta^5\rightarrow$ diasterene transformation can be mimicked by treating the Δ^2-sterene with acid

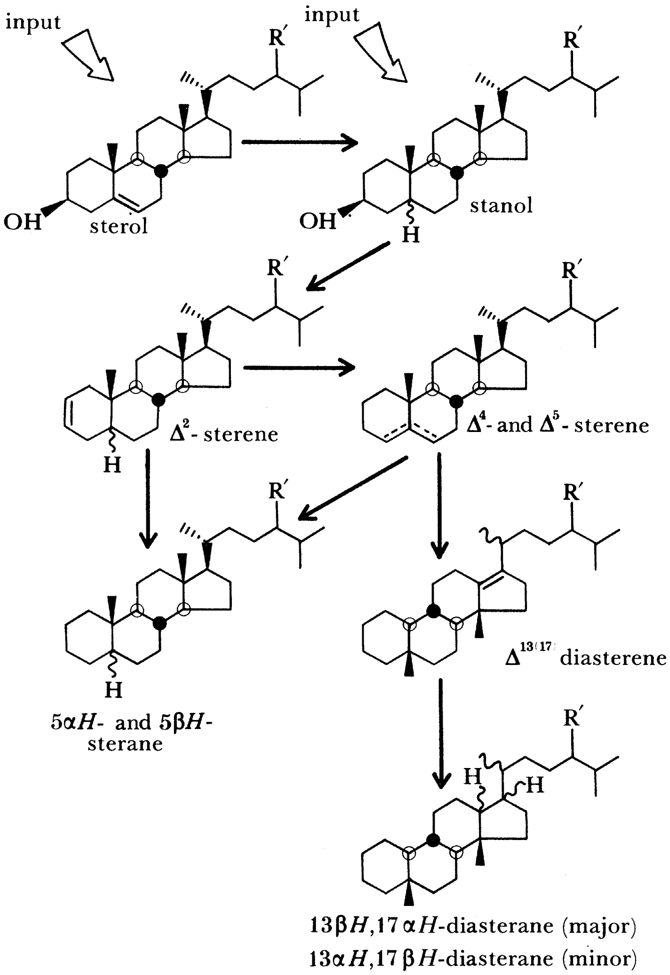

FIGURE 1. Proposed early stage diagenetic transformations leading from sterols and their nuclear saturated analogues, stanols, to steranes and diasteranes (after Dastillung & Albrecht 1977; Mackenzie *et al.* 1982).

(Turner *et al.* 1957; Kirk & Shaw 1975). Second, the appropriate alkene products can be generated by heating the stanol with acidic clay minerals (Rubinstein *et al.* 1975; Sieskind *et al.* 1979). In addition, diasterenes are often not observed in, or are in very low abundance in, immature 'pure' carbonate sediments (see, for example, Comet *et al.* 1981); the same situation is often seen for diasteranes in more mature 'pure' carbonate sediments (Maxwell, unpublished observations).

At the stage of sterane formation, the major non-rearranged steranes present retain the original biological configuration of the precursor sterols at the chiral centres at C-8, C-9, C-14, C-17 and C-20 (i.e. 8β*H*, 9α*H*, 14α*H*, 17α*H*, 20(*R*); the most abundant isomer has the 5α*H* configuration, the 5β*H* isomer being present in lower abundance (figure 1 and Mackenzie *et al.* 1982). With the onset of catagenesis and the associated increase in temperature, apparently ubiquitous changes are observed in the sterane distributions. For example, a gradual decrease is seen in the abundance of the above major isomer with the 20(*R*) configuration in favour of its 20(*S*) counterpart (originally absent), until a slight preference for the latter isomer is found (figure 2). From such observations it is presumed that the 20(*R*) compound isomerizes to the

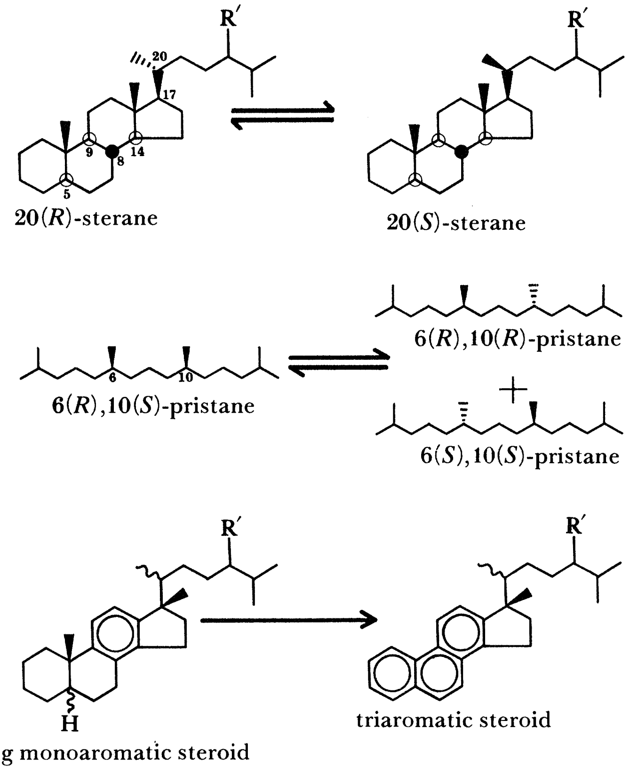

FIGURE 2. Examples of reactions proposed to occur in sediments during catagenesis and which have been observed in the laboratory.

20(*S*) compound, this proposed reaction occurring before and during the early stages of oil generation (Mackenzie *et al.* 1980). Other changes include an increase in the abundance of steranes with the 5α*H*,14β*H*,17β*H* configuration (20(*R*) and 20(*S*); Petrov *et al.* 1976; Seifert & Moldowan 1979; Mackenzie *et al.* 1980).

The thermal maturity of sedimentary organic matter is often assessed by using well established methods such as vitrinite reflectance, spore coloration, Rock Eval pyrolysis or gross chemical composition (Tissot & Welte 1978). More recently, the extent of specific chemical transformations in biological marker alkanes in solvent extracts have also been used successfully in this respect (Ensminger *et al.* 1977; Seifert & Moldowan 1978, 1980; Mackenzie *et al.* 1980). An example of this approach is shown in figure 3, which is a plot against depth from the sea floor, of the percentage of the C_{29} 20(*S*),5α*H*,14α*H*,17α*H*-sterane isomer (figure 2, with $R' = C_2H_5$) relative to the sum of itself and the 20(*R*) isomer in a number of Jurassic sediments from the U.K. sector of the northern North Sea (Mackenzie *et al.* 1984). The progress of the isomerization from a low abundance of the 20(*S*) isomer to *ca.* 55% can be clearly seen; in addition, the values in the sediments begin to correspond to the values for the oils (delineated by the dotted lines) at a depth of *ca.* 3 km. These results supported earlier conclusions that the oils originate from the Jurassic Kimmeridge source rock buried more deeply than 3 km (Mackenzie *et al.* 1984); i.e. the main expulsion zone is deeper than 3 km.

Another reversible isomerization has been proposed to occur in the acyclic alkane pristane (figure 2). Here, the original biological 6(*R*),10(*S*) isomer appears to be converted to a 1:1 mixture of itself and the 6(*R*),10(*R*) plus 6(*S*),10(*S*) isomers (Maxwell *et al.* 1972; Patience

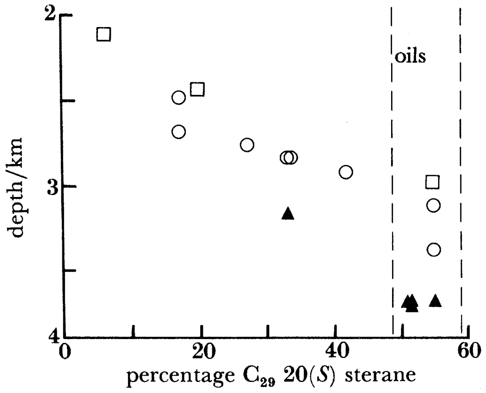

FIGURE 3. Percentage of C_{29} 20(S)-5αH,14αH,17αH-sterane (figure 2, $R' = C_2H_5$) relative to itself plus 20 (R) isomer against depth from sea floor for North Sea Jurassic sediments (taken from Mackenzie *et al.* 1984). Vertical dotted lines show the limits measured for associated oils. (○), N Viking Graben–East Shetland Basin; (▲), S Viking Graben; (□), Witchground Graben.

et al. 1978; Mackenzie *et al.* 1980). This reaction takes place at a greater rate than the 20(R)–20(S) isomerization in steranes (Mackenzie *et al.* 1980). The extents of pristane isomerization and other molecular measurements in a number of Toarcian shales from the Paris Basin provided the first pieces of evidence that such measurements might be of value in assessing the thermal history of sedimentary basins. The values for a number of outcrop or very shallow core samples from the SE of the basin were inconsistent (Mackenzie *et al.* 1980) with the maturity trends expected from maximum burial depths proposed previously (Deroo 1967). On this basis (Mackenzie *et al.* 1980; note added in proof) and from sonic log data (Goy 1979), it was suggested that the maximum burial depths were greater (i.e. these samples have experienced a greater uplift than supposed previously; see Mackenzie & McKenzie 1983).

Another change with increasing maturation occurs in the distributions of aromatic steroid hydrocarbons. Here, the most abundant triaromatic steroids in sediments, with a base peak of $m/z = 231$ in their mass spectra, increase in abundance relative to their C-ring monoaromatic counterparts with a base peak of $m/z = 253$ (Ludwig *et al.* 1981; B. Ludwig, G. Hussler, P. Wehrung & P. Albrecht 1981, unpublished results; Mackenzie *et al.* 1981*a*; Seifert *et al.* 1983). This can be seen in figure 4, which shows a plot against depth of the percentage of the C_{28} triaromatic with the 20(R) configuration in the side chain (figure 2; 20(R), $R' = C_2H_5$) to itself plus the monoaromatic (figure 2; 20(R), $R' = C_2H_5$) with the same side chain (5αH- and 5βH-isomers) for the same samples as in figure 3. These and similar results suggest that an irreversible aromatization (figure 2) occurs (Ludwig *et al.* 1981*b*; Mackenzie *et al.* 1981*a*).

When the extents of aromatization and of sterane isomerization at C-20 were plotted (a.–i. plots) against each other for sediments from different basins, it was observed that there were significant differences in some cases. For example in figure 5, which shows a.–i. plots for a sequence of Pliocene samples from the Pannonian Basin in SE Hungary and for the E Shetlands Basin–N Viking Graben samples shown in figures 3 and 4, two distinct ‘pathways’ are apparent (Mackenzie *et al.* 1982). The Pannonian Basin sediments, as a result of rapid sedimentation, have experienced a high heating rate and have high aromatization values for a given isomerization value in comparison with the colder North Sea sediments. In both cases, the samples have experienced continuous burial, and it was proposed that the aromatization reaction is accelerated relative to the isomerization in the Pannonian samples in comparison with the North Sea samples (Mackenzie *et al.* 1982). In other words, the aromatization appears to be the more temperature dependent of the two reactions, as suggested previously from heating an immature Toarcian shale from the Paris Basin at elevated temperatures in the laboratory (Mackenzie *et al.* 1981*b*).

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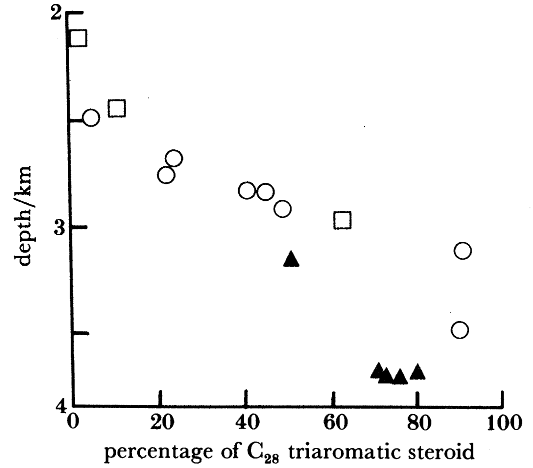

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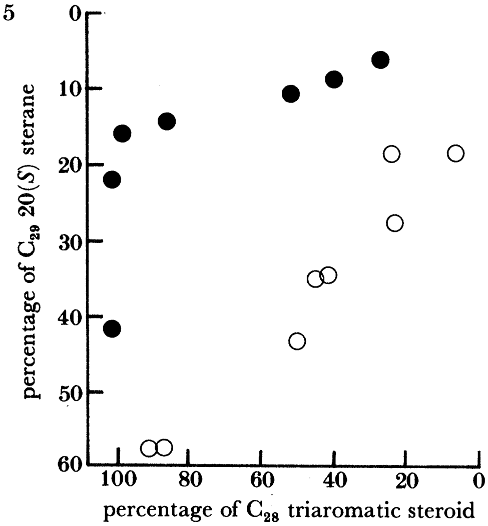

FIGURE 4. Percentage of C_{28} 20(*R*)-triaromatic steroid (figure 2, $R' = C_2H_5$) relative to itself plus C_{29} 5α*H* and 5β*H* 20(*R*) monoaromatic steroids against depth from sea floor for North Sea Jurassic sediments (taken from Mackenzie *et al.* 1984). (○), N Viking Graben–East Shetland Basin; (▲), S Viking Graben; (□), Witchground Graben.

FIGURE 5. Percentage of C_{29} 20(*S*)-5α*H*,14α*H*,17α*H*-steranes (figure 2, $R' = C_2H_5$) against percentage of C_{28} 20(*R*)-triaromatic steroid (figure 2, $R' = C_2H_5$). (●), Pannonian Basin, Hungary (Pliocene); (○), N Viking Graben–East Shetland Basin, northern North Sea (Jurassic).

So that the differences in the rates of the two presumed reactions could be rationalized, a quantitative description of the temperature history of a sedimentary basin was required. This came from a model of basin formation by lithospheric extension proposed by McKenzie (1978).

The temperature dependence of the rate constant of a reaction is governed by the Arrhenius law,

$$k = A \exp(-\Delta E/RT), \tag{1}$$

where A is the frequency or pre-exponential factor, ΔE is the activation energy of the reaction, R is the gas constant and T is the temperature in kelvins. This equation provides the link between the modelling of temperature history and the resulting effect on the extents of the aromatization and isomerization reactions. To derive rate constants and thereby ΔE and A for the aromatization and sterane isomerization, Mackenzie & McKenzie (1983) have used the measured extents of the two reactions (figure 5) in conjunction with the geophysical model. Here, it was assumed that each reaction is described by (2),

$$\mathrm{A} \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \mathrm{B}, \tag{2}$$

where $k_1 = 0$ for the aromatization.

It was also assumed that the reactions obey first-order rate laws and that the total concentration of reactant plus product remains constant during each reaction or that, if degradation reactions occur, both reactant and product are depleted at the same rate. The first-order rate laws were then integrated analytically to provide initial estimates of A and ΔE for the aromatization and isomerization reactions, which were then used in a numerical integration to obtain refined values.

In the analytical integration, kinetic expressions were derived (Mackenzie & McKenzie 1983) and rearranged into a form where the rate constant (k_A for aromatization, k_I for isomerization) was expressed as a function of the respective reaction extents (x, y) and the effective heating time (t_{eff}); t_{eff} is taken to be the time spent within 15 °C of maximum temperature of each sample (Hood *et al.* 1975). The samples used to provide x and y measurements were those shown in figure 5. One value of each rate constant (k_A or k_I) was obtained for each sample from the measured value of x and y, by using the analytical expressions. The rate constants were then plotted against the inverse of the present-day temperature for each sample and, by using (1), estimates of A and ΔE were derived for each reaction.

These initial estimates were then used in the numerical integration of the rate laws, in combination with the Arrhenius equation (1), with the temperature history obtained from the model of basin formation by extension, to generate an a.–i. curve (figure 5). The initial estimates of A and ΔE were then adjusted until the calculated curves matched the field observations of x and y (figure 5) for the Pannonian samples. It was noted, however, that for the North Sea samples, the observed values fall systematically above the predicted curve when $x \geqslant 0.5$ (Mackenzie & McKenzie 1983). The reasons for this discrepancy are not obvious.

The values of A and ΔE derived in this way for the aromatization, sterane isomerization and an analogous isomerization in the pentacyclic hopanes are shown in table 1 (Mackenzie & McKenzie 1983).

TABLE 1. REACTION CONSTANTS WITH THE USE OF THE GEOPHYSICAL MODEL†

	activation energy, $\Delta E/(\text{kJ mol}^{-1})$	pre-exponential factor, A/s^{-1}
steroid aromatization	200	1.8×10^{14}
hopane isomerization at C-22	91	25×10^{-3}
sterane isomerization at C-20	91	7×10^{-3}

† From Mackenzie & McKenzie (1983) and Mackenzie *et al.* (1985).

These values have subsequently been used in conjunction with the extensional model, to estimate thermal conductivities of sediments from the Nova Scotian continental shelf and the amount of uplift and erosion experienced by sediments in the Paris and Lower Saxony Basins (Mackenzie *et al.* 1985). In addition, the geographical variation in heat flow in the foreland basin of Alberta was estimated by using a lithospheric flexure model (Mackenzie *et al.* 1985). In this work, the very low pre-exponential factors for the isomerization reactions were noted, indicating that the transition states are more constrained than the reactants.

The aim of the present study was to measure ΔE and A values for specific aromatization and isomerization reactions brought about in the laboratory. This has been achieved by heating pure organic substrates on powdered extracted sediments with elemental sulphur. In both cases the substrate occurs in sediments and is a precursor in each of the reactions proposed to occur in the sedimentary column. Although this type of approach has the potential disadvantage that it might not simulate exactly the proposed reactions in sediments, it has a number of advantages.

First, product formation is an unambiguous result of a specific chemical reaction; hence, the approach can provide independent evidence that the observed changes in the distributions of sedimentary hydrocarbons do result from reactions of the types proposed. Second, the rate law for each reaction can be determined precisely. Absolute concentrations rather than reaction extents derived from product:reactant ratios can be measured; it need not be assumed, therefore, that the total concentration of reactant plus product remains constant during the course of the reaction.

If laboratory-derived activation energies are to be capable of extrapolation to the sedimentary column, then the same type of mechanism must be followed in both cases. Previous authors have suggested the importance of free-radical mechanisms in petroleum generation and associated processes (see, for example, Eisma & Jurg 1969; Amon & Johns 1977; Seifert & Moldowan 1980; Alexander *et al.* 1981, 1983). Furthermore, significant concentrations of free radicals have been measured in many kerogens (Marchand & Conrad 1980). Because elemental sulphur at moderate temperatures (*ca.* 150 °C) undergoes thermal scission to sulphenyl and polysulphenyl radicals, it will initiate free-radical pathways for the reactions of interest. It is also a well known aromatizing agent and, indeed, has been suggested as playing a role in the genesis of petroleum hydrocarbons (Douglas & Mair 1965).

2. MATERIALS AND METHODS

(*a*) *Preparation and workup of heating experiments*

Trial experiments with a C_{29} C-ring monoaromatic steroid substrate made from treatment of 24-ethylcholesta-3,5-diene with acid (cf. Mackenzie *et al.* 1982) and containing a mixture of isomers, were done. Heating *in vacuo* (see below) on a number of different matrices was performed; these were (i) alumina (Brockman activity II, BDH Limited), (ii) bentonite (technical grade, BDH Limited), (iii) a solvent-extracted Toarcian shale (Semécourt, Paris Basin, France), and (iv) a solvent-extracted Middle Cretaceous carbonate (Bida Hamama-1, Abu Dhabi). Elemental sulphur was also added to some experiments under (iii) and (iv) above. Formation of triaromatic steroid hydrocarbons with base peak $m/z = 231$ in their mass spectra, the most abundant triaromatic steroid series in sediments, was only observed in the presence of sulphur under the conditions used. The reaction was more efficient on the carbonate and this was selected as the inorganic matrix for subsequent kinetic experiments.

A similar series of experiments with the use of 6(*R*),10(*S*)-pristane as substrate revealed that, under the conditions investigated, the isomerization reaction was only observed on the solvent-extracted Toarcian shale heated with added sulphur.

In the kinetic experiments for aromatization, the powdered matrix (500 mg of Abu Dhabi carbonate) was heated in pyrex tubes with sulphur (0.43 mg of reagent grade (BDH Limited) was added via hexane or 2,2,4-trimethylpentane solution) and 0.176 mg substrate (C_{27} C-ring monoaromatic steroid hydrocarbon added via 2,2,4-trimethylpentane solution). Before heating, the solvents were removed by nitrogen blowdown, the tubes were evacuated and flushed with nitrogen four times and sealed *in vacuo* (*ca.* 0.1 Torr†).

In the case of the isomerization, the matrix (solvent-extracted Semécourt shale, *ca.* 100 mg) was heated with sulphur (*ca.* 10 mg added via CS_2 solution) and about 1 mg pure 6(*R*),10(*S*)-pristane in hexane solution (Koch Light). The tubes were prepared in the same way.

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† 1 Torr = 101 325/760 Pa.

Blank experiments without added substrate showed that any pristane generated from the matrix during heating was negligible in comparison with the amounts observed when pristane was added. Blank experiments for the aromatization study revealed no detectable steroid hydrocarbons.

The tubes were heated in Perkin Elmer F11 gas chromatograph ovens in intimate contact with a chromel–alumel thermocouple. A Fluke 8600A or 8050A digital multimeter measured the e.m.f., which was converted to a temperature by using standard tables. After cooling to ambient temperature, the products were extracted (CH_2Cl_2; 3 × 3 ml) with sonication (3 × 15 min) in the presence of freshly activated precipitated copper (preparation based on that of Blumer 1957). Filtration through a small plug of alumina and solvent removal by rotary evaporation afforded the products. Combined gas chromatography–mass spectrometry (g.c.–m.s.) was used, where necessary, for product identification. Absolute quantification of reactants and products was achieved by using capillary gas chromatography (g.c.).

(*b*) *Gas chromatography–mass spectrometry* (*g.c.–m.s.*)

Analyses were performed on a Finnigan 9160 gas chromatograph fitted with a flexible silica OV-1 WCOT column (25 m × 0.3 mm i.d.), with helium as carrier, using on-column or split-splitless injection (280 °C). Temperature programming was typically 50–280 °C at 4–6 °C min^{-1}. Directly interfaced was a Finnigan 4000 mass spectrometer with electron energy, 30 eV, filament current, 350 μA, accelerating voltage, *ca.* 2 kV, and source temperature, 250 °C. Data acquisition (scan time 1 s) and processing were done on an interfaced INCOS 2300 data system.

(*c*) *Gas chromatography* (*g.c.*)

Aromatization reaction products were analysed by using a Carlo Erba FTV 4160 gas chromatograph (f.i.d. detection), fitted with a flexible silica OV-1 WCOT column (25 m × 0.3 mm i.d.) with hydrogen as carrier (inlet pressure 0.6 kg cm^{-2}) and having on-column injection and a detector temperature of 300 °C. Temperature programming was typically 60–270 °C at 4 °C min^{-1}.

Isomerization reaction products were analysed by using a Carlo Erba FTV 2150 gas chromatograph (f.i.d. detection) fitted with a diethylene glycol succinate (DEGS)–polyethylene glycol succinate (PEGS) (3:1, w:w) WCOT column (*ca.* 50 m × 0.24 mm i.d.), having hydrogen as carrier (inlet pressure *ca.* 1.8 kg cm^{-2}) and injector and detector temperatures of 225 °C. The temperature was held isothermally at *ca.* 69 °C during the analyses. An OV-1 WCOT column (*ca.* 10 m × 0.24 mm i.d.) with helium as carrier (inlet pressure *ca.* 1.0 kg cm^{-2}) and injector and detector temperatures of 300 °C was also used. Temperature programming was typically 50–270 °C at 8 °C min^{-1}. Use of the DEGS–PEGS stationary phase enables the separation of 6(*R*),10(*S*)- from 6(*R*),10(*R*)- plus 6(*S*),10(*S*)-pristane, whilst the OV-1 phase does not resolve these diastereoisomers under the conditions used.

Absolute quantification of aromatization products was obtained from g.c. peak areas (LDC 308 computing integrator) by using the internal standards method with pyrene or n-C_{24} alkane as internal standard. After correcting for the respective relative response factors, the two internal standards were found to yield the same results (within experimental error). The reproducibility of the extraction and quantification procedures was tested by performing two separate kinetic experiments at the same temperature (147.5 ± 1.5 °C), each one being quantified with a different internal standard.

Peak area measurement (LDC 308 computing integrator or VG Minichrome laboratory system) of chromatograms from DEGS–PEGS analysis of the pristane reaction products, furnished the amount (percentage) of reactant (6(*R*),10(*S*)-pristane) relative to the total reactant and product (6(*R*),10(*S*)- and 6(*R*),10(*R*)- plus 6(*S*),10(*S*)-pristane) remaining after each heating period. Absolute quantification of total pristane was obtained from g.c. peak areas (LDC 308 computing integrator) by using n-C_{16} and n-C_{18} as internal standards. Combination of these two data sets yielded the absolute amounts of the individual diastereoisomers.

3. Results

(*a*) *Aromatization of* C-*ring monoaromatics*

An isomeric mixture of C_{27} C-ring monoaromatic steroid hydrocarbons was heated on the solvent-extracted carbonate sediment with elemental sulphur at *ca.* 150 °C. The mixture comprised mainly components isomeric at C-5 and C-20 (cf. figure 2; R′ = H). The C_{26} triaromatic steroid hydrocarbons with a base peak at $m/z = 231$ in their mass spectra were observed (cf. figure 2; 20(*S*) and 20(*R*), R′ = H) and were the dominant products at *ca.* 150 °C after heating for four days (Abbott *et al.* 1985). The assignments of the 20(*S*) and 20(*R*) triaromatics were made on the basis of coinjection of the 20(*R*) compound synthesized by the method of Dannenberg & Neumann (1964). Quantification of products and reactants in experiments conducted at 147.5±1.5 °C revealed the following features; (*a*) the ratio of the triaromatics to monoaromatics increased with heating time; (*b*) the concentration of the monoaromatics decreased exponentially with increase in time and (*c*) the concentration–time function of the triaromatics passed through a maximum. These features suggested the kinetic scheme

$$A \xrightarrow{k'_A} B \rightarrow C,$$

where A = C_{27} C-ring monoaromatics (base peak $m/z = 253$); B = C_{26} triaromatics (base peak $m/z = 231$); C = unknown degradation products; k'_A = aromatization rate constant.

If the aromatization obeys a first-order rate law then the following applies:

$$-\mathrm{d}[A]/\mathrm{d}t = k'_A[A]. \qquad (3)$$

Separation of the variables and integration yields

$$\ln [A]_t = \ln [A]_0 - k'_A\, t, \qquad (4)$$

where $[A]_0$ = the initial concentration of A and $[A]_t$ = the concentration of A at time *t*. Hence, if (3) is the correct rate law, a plot of $\ln [A]_t$ against time will give a straight line with intercept $\ln [A]_0$ and slope k'_A. Substitution in (4) of $[A]_t$ and *t* from two kinetic runs at 147.5±1.5 °C, and one at 165±1 °C, yielded the results plotted in figure 6.

Linear regression analysis gave 'good' straight line fits with calculated intercepts 5.20 (147.5 °C) and 5.13 (165 °C). These match satisfactorily the actual value (5.17) calculated from the initial concentration of monoaromatic steroids. The rate constants extracted from the slopes have values of 0.0228 h^{-1} (147.5 °C) and 0.1246 h^{-1} (165.0 °C). Straight-line fits were also obtained at two other temperatures (table 2).

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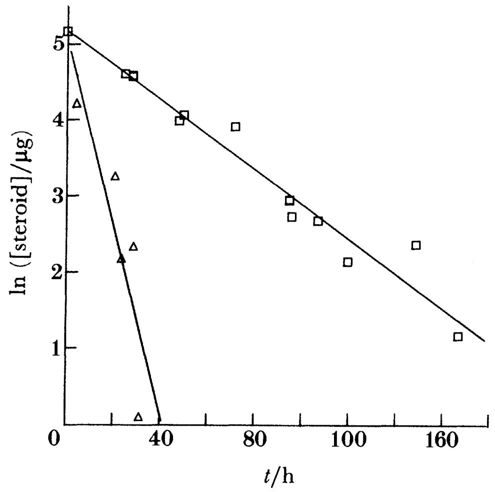

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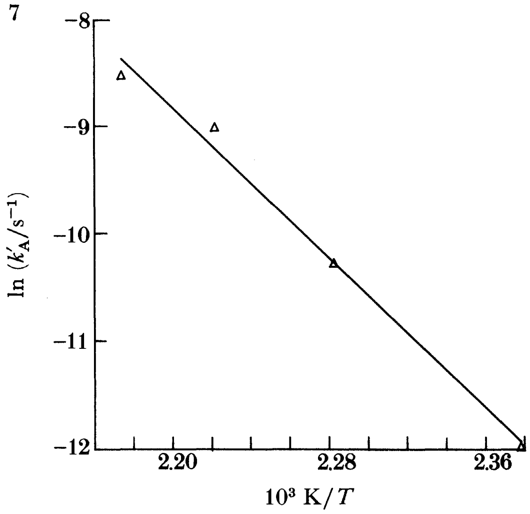


FIGURE 6. Logarithm (natural) of the concentration (w:w matrix) of C_{27} C-ring monoaromatic steroid hydrocarbons (figure 2, R′ = H) against time of heating. □, 147.5 °C (420.5 K); △, 165 °C (438 K).

FIGURE 7. Arrhenius plot for k'_A for steroid aromatization from laboratory heating experiments.

TABLE 2. AROMATIZATION AND ISOMERIZATION RATE CONSTANTS AS A FUNCTION OF TEMPERATURE AND REACTION CONSTANTS

temperature† K	steroid aromatization‡ k'_A h^{-1}	ΔE/(kJ mol^{-1})	A/s^{-1}
420.5 ± 1.5	0.0228 ± 0.0015	145 ± 10	6.7×10^{12}
438.0 ± 1.0	0.1246 ± 0.0270		
450.0 ± 1.0	0.4418 ± 0.0186		
460.0 ± 1.0	0.7206 ± 0.0575		
	pristane isomerization‡ k'_I h^{-1}		
497.4 ± 1.5	0.0173 ± 0.0015	120 ± 23	2.1×10^7
510.4 ± 1.3	0.0534 ± 0.0079		
523.4 ± 2.3	0.1063 ± 0.0080		
534.2 ± 1.9	0.1230 ± 0.0540		

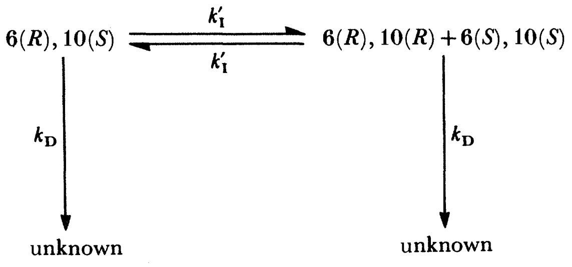
† ± Maximum observed range.
‡ Error = ± 1 standard deviation.

The temperature dependence of a rate constant may be used to deduce the activation parameters of a reaction by use of the Arrhenius expression (1). The Arrhenius plot for k'_A, constructed by using data from table 2, is shown in figure 7. The slope yields an activation energy, ΔE, of 145 ± 10 kJ mol^{-1} and a pre-exponential factor, A, extracted from the intercept, of *ca.* 6.7×10^{12} s^{-1}.

(*b*) *Isomerization of pristane*

The substrate, obtained from shark-liver oil, contains solely the 6(*R*),10(*S*) isomer (Cox *et al.* 1972). When it was heated at temperatures above 238 °C, isomerization to 6(*R*),10(*R*)- plus 6(*S*),10(*S*)-pristane was observed and an equilibrium mixture of 1:1 obtained (figure 2). Additionally, the amount of total pristane was seen to decrease, yielding unknown products.

The simplest reaction scheme suggested by these results is



where k'_{I} = first-order isomerization rate constant and k_{D} = 'degradation' rate constant.

From this scheme, and assuming that the isomerization obeys a first-order rate law, it is possible to derive the rate equation

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = (k'_{\mathrm{I}}+k_{\mathrm{D}})\,[\mathrm{A}]-k'_{\mathrm{I}}[\mathrm{B}], \tag{5}$$

where [A] = concentration of reactant and [B] = concentration of product.

Differentiation and algebraic substitution yields a linear, homogeneous second-order differential equation of the form

$$a\,\mathrm{d}^2[\mathrm{A}]/\mathrm{d}t^2+b\,\mathrm{d}[\mathrm{A}]/\mathrm{d}t+c[\mathrm{A}] = 0, \tag{6}$$

which is readily soluble, yielding the general solution

$$[\mathrm{A}] = c_1 \exp(-\lambda_1 t)+c_2 \exp(-\lambda_2 t), \tag{7}$$

where c_1, c_2 are constants, and

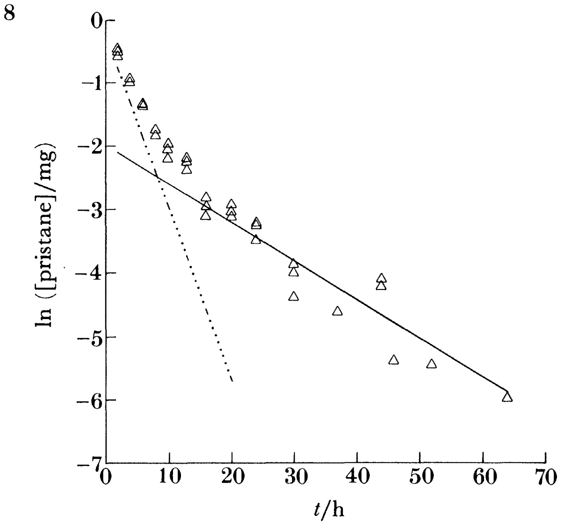
$$\lambda_1, \lambda_2 = k'_{\mathrm{I}}+k_{\mathrm{D}} \mp k'_{\mathrm{I}}.$$

The $\lambda_{1,2}$ are roots of the auxiliary equation

$$\lambda^2-2(k'_{\mathrm{I}}+k_{\mathrm{D}})\,\lambda+k_{\mathrm{D}}(2k'_{\mathrm{I}}+k_{\mathrm{D}}) = 0. \tag{8}$$

Equation (7) gives the concentration–time behaviour of 6(*R*),10(*S*)-pristane. A plot of ln [A] against time should yield two decreasing exponentials. Results obtained at *ca.* 250 °C show such behaviour (figure 8). The solid line, from linear-regression analysis of points where $t > 21$ h, represents the longer-lived component ($\lambda_1 = k_{\mathrm{D}}$). When this line is extrapolated to $t = 0$ and subtracted from the data points at early times ($t < 21$ h), a regression line (broken) through the resulting residuals yields the short-lived component that has the time constant $\lambda_2 = 2k'_{\mathrm{I}}+k_{\mathrm{D}}$. Thus, k'_{I} at 250 °C is 0.1063 h^{-1} (figure 8). Results for this and three other temperatures are collated in table 2. By using (1) and the results in table 2, the activation parameters were extracted from the Arrhenius plot (figure 9); ΔE has a value of 120 ± 23 kJ mol^{-1}, and A is *ca.* $2.1 \times 10^{7}\ \mathrm{s}^{-1}$.

Although first-order rate laws are being followed in each reaction, the overall rate of reaction appears to be dependent on sulphur concentration (unpublished results). However, sulphur was present in large excess such that the radical concentration would be expected to remain effectively constant throughout the course of each reaction. Thus, pseudo-first-order rate constants are being measured (see §4).



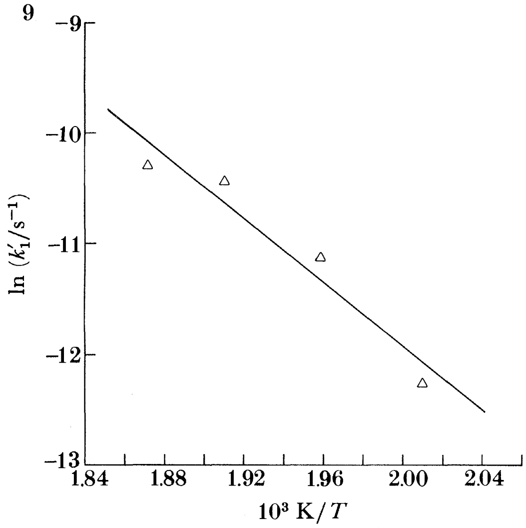


FIGURE 8. Logarithm (natural) of the concentration (w:w matrix) of 6(*R*), 10(*S*)-pristane (figure 2) against time of heating.

FIGURE 9. Arrhenius plot for k_1' from laboratory heating experiments with pristane.

4. DISCUSSION

The Arrhenius plots in figures 7 and 9 show that under laboratory conditions the aromatization reaction is more temperature dependent, i.e. it has a larger ΔE value (145 kJ mol^{-1}) than the isomerization of pristane (120 kJ mol^{-1}). This behaviour parallels that observed in sediments where, for example, the aromatization is accelerated relative to the isomerization at C-20 in steranes in the Pannonian Basin Pliocene sediments in comparison with Jurassic sediments from the North Sea (see §1).

Despite the fact that the relative behaviour of the two types of reaction is similar in the laboratory and in the sedimentary column, there are significant differences between the laboratory values of activation energy and those derived with the use of the geophysical model. There are several possible reasons for this discrepancy. For example, the mechanisms in the laboratory reactions could be different from those followed in sediments. Furthermore, it should be stated that, in this preliminary study, we have brought about the aromatization and isomerization by using two different inorganic matrices; the effect (if any) of this on the absolute values of ΔE and A is unknown at present. The discrepancy might arise in part from assumptions made in the kinetic analysis used in the geophysical model approach. For example, it is known that in over-mature samples (where vitrinite reflectance exceeds 1.5), aromatic steroids of the type in figure 2 are no longer detected, presumably having been degraded (Mackenzie 1980). If the degradation significantly alters the concentration of triaromatics at the lower maturity levels at which the extent of aromatization is measured, the kinetic constants derived from the geophysical model would be incorrect. Degradation of the triaromatic is observed in the laboratory studies, although we have not yet examined the kinetics of this step.

If the same free-radical mechanisms are followed in the laboratory and in sediments, it might be expected that the activation energies derived from the laboratory experiments would be applicable to sediments, with the following proviso. If radical species other than elemental sulphur bring about the sedimentary reactions, then it would be necessary that the activation energies are not strongly dependent on the nature of the species initiating the reactions. We are unable at present to comment, however, on whether sulphur itself is responsible for bringing about the sedimentary reactions.

It is likely that the A values measured for the laboratory reactions would be different from those in sediments. If the rate-determining step for aromatization and isomerization, both in the laboratory and in sediments, is an initial hydrogen abstraction by some radical R, then the observed rate constant will be a pseudo-first-order coefficient k', i.e.

$$k' = [\mathrm{R}]\,k,$$

provided that [R] is constant throughout the course of a specific reaction. Substitution for k from (1) results in

$$k' = [\mathrm{R}]\,A\,\exp\,(-\Delta E/RT).$$

Hence the observed pre-exponential factor will depend on the concentration of the initiating radical species. As a result of the high concentration of sulphur used in the laboratory studies, the laboratory A values would be expected to be much larger than those in sediments.

5. Future studies

There is a need for more laboratory-based studies of the kinetics of the aromatization and isomerization reaction types so that this independent approach can be extended to provide further information about the corresponding sedimentary reactions. For example, the configurational isomerization at C-20 in steranes is particularly important because of its widespread use both as a maturation parameter and in the a.–i. plots used to assess thermal history. We have brought about this reaction by heating 5αH-cholestane (figure 2, $\mathrm{R}' = \mathrm{H}$) under similar conditions to those employed for the isomerization of pristane. Isomerization also occurred, however, at C-14 and C-17 (figure 2). These qualitative results indicate that the rate law is likely to be more complex than in the case of the pristane isomerization and that its exact solution will be more difficult.

A further insight into the mechanisms of the sedimentary reactions may be obtained by testing the compatibility of the laboratory-derived activation energies with the geophysical model, by comparing the resulting predicted a.–i. plots with those observed; it is likely that the pre-exponential factors would have to be lowered (see §4).

Absolute quantification with increasing burial depth of both products and reactants in the proposed sedimentary reactions should also be attempted to test some of the assumptions used in the geophysical model approach. For example, the importance of the degradation (if any) of triaromatic steroids during aromatization should be investigated (see §4).

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Discussion

B. Durand (*Institut Français du Pétrole, Rueil Malmaison, France*). Can Dr Maxwell estimate the variation in the extent of his reactions within a sediment section of, say, 100 m thick at a depth of 2 km? Can he also estimate the likely error in the activation energy?

A. S. Mackenzie (*BP Geochemistry Branch, Sunbury-on-Thames*). I assume that Dr Durand means variation not related to higher temperature with increased depth. The problem is in deciding whether the observed variation is real or whether it is produced by contamination by migrated oil or cavings. In most cases that I know of the observed variation within 100 m which is not depth related could have been produced by contamination or by cavings.

The central question is whether the mechanism by which the reactions occur in the laboratory is the same as that in the sediments. If it is, then presumably the generation of radicals in both cases must also be similar. If this assumption is correct then the laboratory activation energies can be used for geological calculations. But this assumption remains to be properly tested. Once the rate constants are known it should be possible to unravel the thermal history of sediments in sedimentary basins.

D. P. McKenzie (*Department of Earth Sciences, University of Cambridge*). There is no straightforward way to use the observed extents of the reactions to estimate the uncertainties in the activation energies and frequency factors. The difficulty arises because we tried to find one set of constants that would not only account for the variation with depth in one basin, but would also match the variation between basins of different ages. If I am to guess what the uncertainty might be I suppose it is probably a factor of a thousand in the frequency factors, and 10% in the activation energies. But I must stress that these estimates are guesses. However, the values of these constants determined in the laboratory are not consistent with the geological observations.

What is, however, very encouraging about the laboratory experiments is that the frequency factor for the isomerization reaction is so small. Those physical chemists with whom I have talked always doubt that the small values of the frequency factors which Andrew Mackenzie and I required to match the observations from the basins are real. I have suspected that the reason why they find such low values anomalous is that their experiments are performed quickly. It is not very surprising that the slowest reactions known should occur in geological environments. Now that Dr Maxwell has found a similarly small value for the frequency factor in the laboratory experiments I hope the physical chemists will be less troubled. Furthermore, his experiments may allow the nature of the reaction that has such a large negative change in entropy to be investigated.

J. R. Maxwell. I am also encouraged that the reaction constants show the same relative behaviour as do those obtained from sediment studies. It would be surprising if all of the laboratory reaction constants matched Dr McKenzie's constants. As I said, we would expect the pre-exponential factors to differ, although the activation energies may be applicable to sediments if the same reaction mechanism is followed in both cases.

C. Beaumont (*Department of Oceanography, University of Dalhousie, Nova Scotia, Canada*). In the pristane isomerization experiments both the reactant and the product were removed by some reaction other than isomerization during the course of the experiment. Did the same behaviour occur in the aromatization experiment?

J. R. Maxwell. At the start of the conversion of the mono- to triaromatic steroid hydrocarbon the combined concentration is essentially constant, so we see no evidence for other reactions in the early stages before depletion of the triaromatic becomes important. We intend to heat the triaromatic form to try to discover what its reaction products are.