

THERMODYNAMIC CONSTRAINTS ON THE GENERATION AND MATURATION OF PETROLEUM IN SEDIMENTARY BASINS

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ABSTRACT

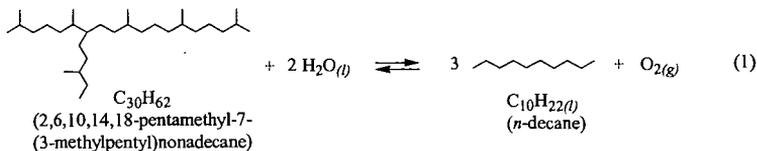
Preliminary Gibbs free energy minimization calculations indicate that high molecular weight compounds in kerogen may be in metastable equilibrium with hydrocarbon species in petroleum during the incongruent partial melting process responsible for the generation and maturation of petroleum, which is accompanied by progressive oxidation of kerogen with increasing depth of burial. It appears that H₂O plays a crucial role in the process, which may be driven by escape from the system of methane as the ultimate product of the irreversible hydrolytic disproportionation of the light paraffins.¹

INTRODUCTION

Although the overall process responsible for the generation of bitumen from kerogen and the chemical evolution of high molecular weight compounds in bitumen to the lower molecular weight species that predominate in petroleum is irreversible (Tissot and Welte, 1984; Béhar *et al.*, 1992; Helgeson *et al.*, 1993; Planche, 1996), thermodynamic calculations indicate that metastable equilibrium states probably prevail among liquid hydrocarbon species with carbon numbers $\geq 6-15$ and carbon-bearing aqueous species such as CO₂ and CH₃COOH at the oil-water interface (Helgeson *et al.*, 1993). In addition, it appears from the results of recent calculations that mature kerogen may be in metastable equilibrium with maturing crude oil in hydrocarbon source rocks. Thermodynamic calculations lead to the conclusion that the maturation process may be driven by the extent to which methane escapes from the system as the ultimate product of the irreversible hydrolytic disproportionation of hydrocarbons with carbon numbers $\leq 6-15$. The large chemical affinities of these reactions are an attractive energy source for thermophilic microbes, which may then mediate the maturation process if the system is open at the hydrocarbon-water interface (Helgeson *et al.*, 1993).² It follows that irreversible hydrolytic disproportionation reactions among the light hydrocarbons should perturb to the right reversible reactions representing hydrolytic reduction of the higher molecular weight compounds to form lighter species.

HYDROLYTIC OXIDATION/REDUCTION AND DISPROPORTIONATION REACTIONS

To illustrate the hydrolytic oxidation/reduction process in a maturing source rock, reversible reaction of the highly branched isoprenoid liquid species corresponding to 2,6,10,14,18-pentamethyl-7-(3-methylpentyl)nonadecane (C₃₀H₆₂) in kerogen or bitumen to form a light paraffin species such as liquid decane (C₁₀H_{22(l)}) in petroleum can be described in terms of the overall reaction represented by

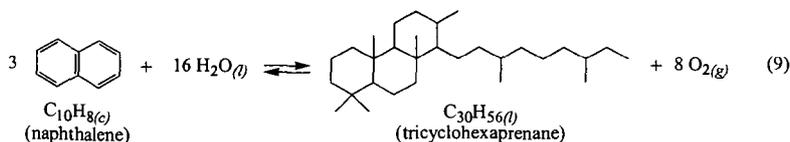
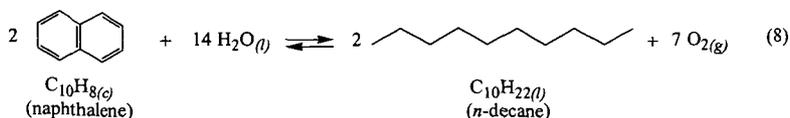
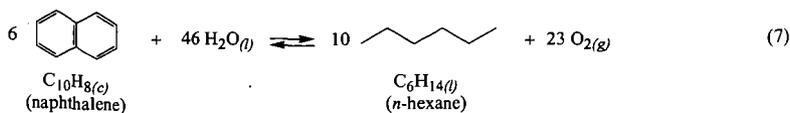


¹ The term hydrolytic disproportionation refers to reaction of a given hydrocarbon with H₂O to form a lighter hydrocarbon and oxidized carbon-bearing species.

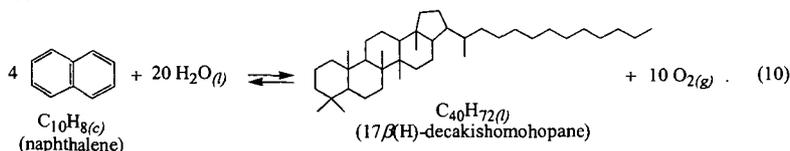
² The chemical affinity of the *r*th irreversible reaction (*A_r*) can be expressed as $A_r = 2.303RT \log(K_r / Q_r)$, where *A_r* stands for the chemical affinity of the *r*th reaction, *R* refers to the gas constant, *K_r* represents the equilibrium constant for the reaction, and *Q_r* designates the activity quotient for the subscripted reaction, which is given by

$$Q_r = \prod_i a_i^{\hat{n}_{i,r}}$$

where *a_i* denotes the activity of the *i*th species in the system and $\hat{n}_{i,r}$ stands for the reaction coefficient of the *i*th species in the *r*th reaction, which is positive for products and negative for reactants. Although *K_r* is computed from the standard molal thermodynamic properties of the species in the reaction, *Q_r* is evaluated from compositional data. Hence, if $Q_r = K_r$, *A_r* = 0 and the reaction is reversible. Otherwise, $A_r d\xi_r > 0$ where ξ_r stands for the progress variable for the *r*th reaction.



and



The logarithmic analogs of the law of mass action for these reactions can be written for unit activity of crystalline naphthalene as

$$\log a_{\text{C}_6\text{H}_{14}(l)} = (\log K_{(7)} - 23 \log f_{\text{O}_2(a)}) / 10 \quad (11)$$

$$\log a_{\text{C}_{10}\text{H}_{22}(l)} = (\log K_{(8)} - 7 \log f_{\text{O}_2(a)}) / 2 \quad (12)$$

$$\log a_{\text{C}_{30}\text{H}_{56}(l)} = \log K_{(9)} - 8 \log f_{\text{O}_2(a)} \quad (13)$$

and

$$\log a_{\text{C}_{40}\text{H}_{72}(l)} = \log K_{(10)} - 10 \log f_{\text{O}_2(a)} \quad (14)$$

where $K_{(7)}$, $K_{(8)}$, $K_{(9)}$, and $K_{(10)}$ stand for the equilibrium constants for the subscripted reactions. Equations (10)–(14) represent the curves shown in Fig. 2, where it can be seen that the curves in each of the four diagrams cross each other over narrow temperature intervals at log activity values which are slightly below zero. It follows that the liquid hydrocarbons represented by these curves can coexist with appreciable concentrations in a single liquid phase in metastable equilibrium with crystalline naphthalene at the temperatures and fugacities of oxygen corresponding to those of the curve-crossings in Fig. 2. A $\log f_{\text{O}_2(a)}$ – temperature profile consistent with this observation is depicted in Fig. 3, where it can be compared with the profile in the hydrocarbon reservoirs of the Texas Gulf Coast (Helgeson *et al.*, 1993). It can be seen in Fig. 3 that the two curves are separated by only 2 log units or $\sim 10^\circ\text{C}$.

Calculated changes in speciation are depicted in Fig. 4 for maturation of the hypothetical hydrocarbon liquid represented by the curve-crossings in Fig. 2 and the upper temperature – $\log f_{\text{O}_2(a)}$ profile in Fig. 3. The curves shown in this figure were generated from Eqns. (11)–(14) and the relation $\sum_i X_i = 1$ (where X_i stands for the mole fraction of the i th species in the liquid) assuming in a first approximation ideal mixing of the four hydrocarbon species in the hypothetical liquid.³ It can be deduced from Fig. 4 that increasing burial of naphthalene in kerogen coexisting with this liquid along the upper temperature – $\log f_{\text{O}_2(a)}$ profile in Fig. 3 would be accompanied by “maturation” of the liquid from ~ 90 mole percent tricyclohexaprenane ($\text{C}_{30}\text{H}_{56}(l)$) and 17 β (H)-decakishomohopane ($\text{C}_{40}\text{H}_{72}(l)$) at low temperatures to ~ 80 mole percent *n*-hexane ($\text{C}_6\text{H}_{14}(l)$) and *n*-decane ($\text{C}_{10}\text{H}_{22}(l)$) at 125°C . Preliminary calculations indicate that similar, but much more complex behavior can be expected in actual bitumen and

³ The mole fraction of the i th hydrocarbon species (X_i) in bitumen or petroleum is related to its activity (a_i) by

$$X_i = a_i / \lambda_i$$

where λ_i stands for the rational activity coefficient of the subscripted species, which is unity in the case of ideal mixing.

petroleum during burial of hydrocarbon source rocks along profiles like those depicted in Fig. 1. Although the incongruent partial melting of kerogen in source rocks may not occur to an appreciable extent at low temperatures, the metastable equilibrium calculations represented by the curves shown in Figs. 2, 3, and 4 indicate that the incongruent partial melting of kerogen species and the maturation process are simultaneous interrelated processes.

CONCLUSIONS

The fact that the curves in each of the diagrams in Fig. 2 cross each other over narrow temperature ranges is a consequence of the actuality that hydrocarbon species are members of closely related homologous series. However, the observation that they cross each other at log activities corresponding to appreciable concentrations at geologically reasonable values of $\log f_{O_2(a)}$ and temperature is a manifestation of the physical, chemical, and thermodynamic reality of metastable equilibrium states among many (but not all) hydrocarbon species in kerogen, bitumen and petroleum in the Earth. Under these circumstances, if hundreds of curves were drawn in Fig. 2 representing reversible hydrolytic reduction reactions for the multitude of hydrocarbon species found in bitumen and petroleum, all of them would be expected to cross in approximately the same narrow temperature - $\log f_{O_2(a)}$ interval shown in Fig. 3. A similar result would be expected for metastable equilibrium among these species in the liquid phase and other hydrocarbon compounds in kerogen. Gibbs free energy minimization calculations are currently being carried out to explore the extent to which these metastable equilibrium states may obtain in hydrocarbon source rocks. Preliminary results of these calculations indicate that oxidized kerogen may coexist in metastable equilibrium with crude oil in source rocks during progressive burial and maturation of the oil. Furthermore, the maturation process may persist at temperatures in excess of 200°C. Because the composition and speciation of both the kerogen and maturing oil generated in the Gibbs free energy minimization calculations are consistent with geologic reality, it appears that the process is not controlled by chemical kinetics, but instead by the thermal gradient, rate of burial, availability of H₂O, and the degree to which methane can escape from the system.

ACKNOWLEDGEMENTS

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REFERENCES

- Béhar, F.; Kressmann, S.; Rudkiewicz, J.-L.; Vandenbroucke, M. *Org. Geochem.* **1992**, *19*, 173.
- Helgeson, H.C.; Knox, A.M.; Owens, C.E.; Shock, E.L. *Geochim. Cosmochim. Acta* **1993**, *57*, 3295.
- Helgeson, H.C.; Owens, C.E.; Knox, A.M.; Richard, L. *Geochim. Cosmochim. Acta* **1998**, *62*, 985.
- Planche, H. *Geochim. Cosmochim. Acta* **1996**, *60*, 447.
- Richard, L.; Helgeson, H.C. *Geochim. Cosmochim. Acta* **1998** (in press).
- Tissot, B.P.; Welte, D.H. *Petroleum Formation and Occurrence*; Springer-Verlag: Berlin, 1984.

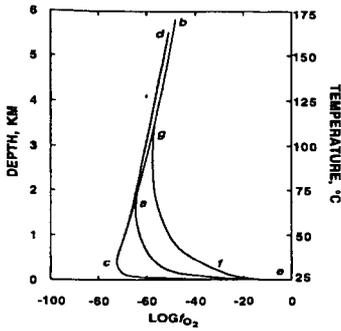


Fig.1 Temperature - $\log f_{O_{2(l)}}$ - depth profiles in hydrocarbon source rocks and reservoirs (see text). The profiles were generated for a nominal temperature gradient of 25°C/km. Curves *ea* and *ec* represent idealized profiles drawn to connect curves *ab* and *cd* at *a* and *c*, respectively, with atmospheric $f_{O_{2(a)}}$ at 25°C. Curve *efg* is a hypothetical profile representing more oxidized conditions at greater depths than those along *ea* and *ec*. Curves *cab* and *cad* are consistent with the temperature - $\log f_{O_{2(l)}}$ profiles in hydrocarbon reservoirs calculated by Helgeson *et al.* (1993).

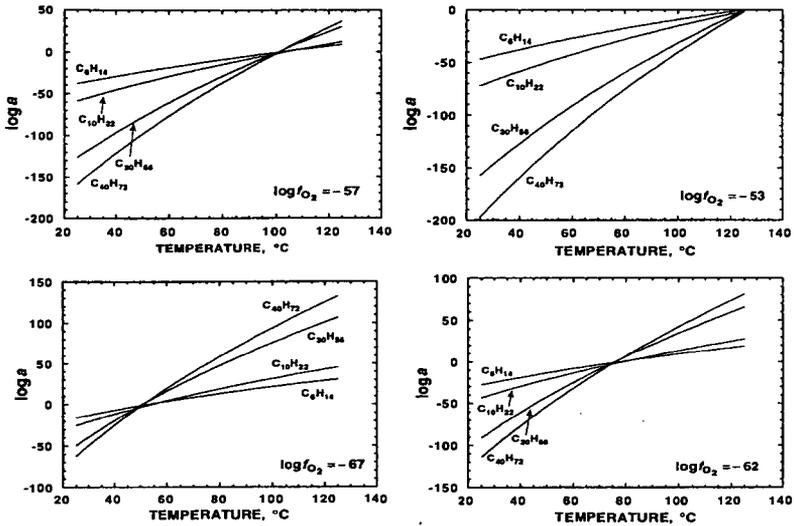


Fig.2 Graphic representation of Eqns. (11) - (14) as a function of temperature at constant pressure and $\log f_{O_{2(l)}}$ (see text).

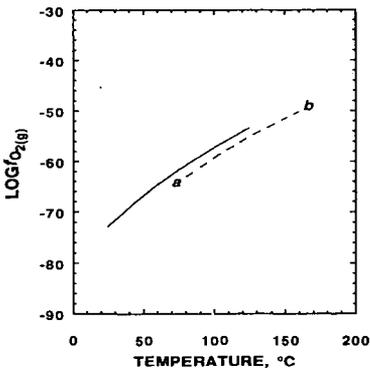


Fig. 3 Temperature - $\log f_{O_{2(l)}}$ profile consistent with the curve-crossings in Fig. 2 (upper curve) and profile *ab* in hydrocarbon reservoirs in the Texas Gulf Coast taken from Helgeson *et al.* (1993).

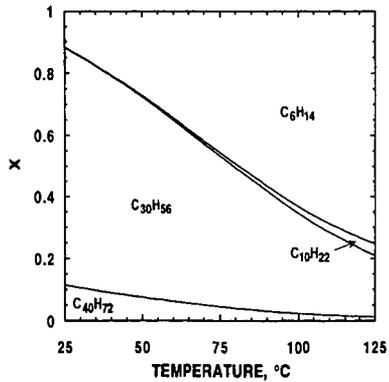


Fig. 4 Mole fraction (*X*) - temperature maturation diagram for the hypothetical hydrocarbon liquid represented by the upper curve in Fig. 3 coexisting with naphthalene in kerogen (see text).