Chapter 4 Organic Acids from Petroleum Source Rocks

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Summary

The vastness and dynamics of sedimentary basins make it difficult to assess organic acid generation from petroleum source rocks on the basis of the limited subsurface data currently available. An alternative approach involves simulating the natural process in laboratory pyrolysis experiments that maintain a liquid-water phase, utilize whole rock, avoid extreme temperatures, and minimize reactor-wall effects. Appropriately conducted laboratory pyrolysis experiments show that saturated acyclic monocarboxylic acids are the dominant organic acids generated, that C_2–C_5 monocarboxylic acids dominate the aqueous phase assemblages, and that acetic acid (C_2) is typically the dominant aqueous organic acid. Low activation energies derived from laboratory pyrolysis experiments indicate that these organic acids are retained in sedimentary organic matter by weak noncovalent bonds. Thus, the organic acid potential of a source rock is largely dependent on the amount of C_2–C_5 monocarboxylic acids assimilated by noncovalent bonds into sedimentary organic matter during its early development into kerogen. Significant quantities of these acids may be released from petroleum source rocks by diffusion during early diagenesis. However, the sluggishness of this diffusion process is only likely to cause local enhancement of porosity within a source rock and in rocks immediately adjacent to it. Release of the remaining organic acids is most likely to occur during the expulsion of petroleum from a source rock. Dissolved organic acids in the expelled petroleum will redistribute themselves within the associated formation waters as the migrating or entrapped petroleum cools, degasses, or encounters lower salinity waters. As a result, enhanced porosity may occur within carrier beds during secondary petroleum migration or within reservoirs during or after petroleum entrapment.

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1 Introduction

Subsurface waters associated with petroleum accumulations have been shown to have organic acid concentrations as high as 5000 mg/l (Carothers and Kharaka 1978). Saturated aliphatic carboxylic acids with two to five carbon atoms are the most commonly observed organic acids in subsurface waters (Fisher 1987). Distributions of these short-chain carboxylic acids are usually dominated by acetic acid (C_2), with propionic (C_3), butyric (C_4), and valeric (C_5) acids being subordinate in varying proportions. Petroleum engineers in the mid- and late-1940s recognized that these short-chain carboxylic acids significantly contributed to the internal corrosion of well-head equipment and production pipes in gas-condensate fields (Menaul 1944; Greco and Griffin 1946; Holmberg 1946; Shock and Hackerman 1948). The serious impact of these corrosive organic acids on the economics of producing fields was sufficient to initiate field and laboratory studies that were collectively published by the Natural Gasoline Association of America (Prange et al. 1953). Geologists and geochemists over the following two decades became more aware of these acids in subsurface waters and their effect on alkalinity measurements (Obukhova and Kutovaya 1968; Shvets and Shilov 1968; Bykova et al. 1971; Willey et al. 1975). However, it was not until the mid-1980s that organic acids were considered responsible for the generation of secondary porosity (Surdam et al. 1984; Surdam and Crossey 1985). The resulting hypothesis proposed that organic acids are released from petroleum source rocks prior to petroleum generation. These expelled acids generate secondary porosity during their migration away from the source rock, thereby enhancing the potential of carrier and reservoir beds for later expelled oil.

This hypothesis continues to be critically questioned (Giles and Marshall, Chap. 14, this Vol.), but it also continues to be used in explaining occurrences of secondary porosity in the subsurface (Hansley and Nuccio 1992; Mazzullo and Harris 1992). A pivotal concern of this hypothesis is whether organic acids can be generated and expelled from petroleum source rocks in sufficient quantities and in the appropriate time frame. Addressing this concern solely from available subsurface data is difficult because of the dynamics of fluid flow within the vastness of sedimentary basins. In addition, subsurface data from a specific petroleum source rock are either limited to a narrow range of thermal maturities or are not comparable over broader ranges of thermal maturities due to regional variations in types and amounts of organic matter. These uncertainties and lack of subsurface data may be alleviated in part by conducting laboratory experiments designed to simulate the natural process. Using results from such experiments within natural constraints defined by available subsurface data, a reasonable evaluation of the hypothesis and related natural processes may be undertaken. This chapter will employ this approach by (1) examining experimental considerations germane to simulating the natural process, (2) reviewing the types and quantities of organic acids recovered from laboratory experiments, and (3) evaluating the generation and expulsion of organic acids in sedimentary basins on the basis of experimental results and natural constraints.

2 Experimental Considerations

The simple heating of a sample to determine its ability to generate organic acids may appear straightforward from a chemistry perspective, but from a geochemistry perspective, there are experimental constraints that must be considered in order to understand the natural process. These experimental considerations include temperature and time conditions, presence of water, type of sample, reactor wall composition, oil/water partitioning, pressure, and water chemistry.

2.1 Time and Temperature Conditions

The time and temperature at which a sample is heated are obvious considerations in any experiment, but they are particularly important in kinetically controlled reactions. Reactions involving organic matter in subsiding sedimentary basins under low to moderate temperatures (i.e., 50 to 150 °C) are typically kinetically controlled. The degree of kinetic control is variable, with some reactions being more time-dependent than others (e.g., petroleum generation relative to vitrinite reflectivity). The problem that this time dependence poses is that natural reactions occurring at low temperatures (<200 °C) over long periods of geologic time (1 to 100 m.y.) cannot be *duplicated* in laboratory experiments. As a result, laboratory experiments must use higher temperatures to achieve measurable amounts of reaction products within reasonable durations (i.e., days to months).

An inherent assumption in this type of substitution is that the mechanisms and their relative rates of occurrence are not significantly altered at the higher experimental temperatures. Assessing the reality of this assumption is difficult and requires a thorough kinetic understanding of the elementary mechanisms making up the overall reaction. Some degree of comfort in this assumption may be obtained from compositional similarities between the products derived experimentally at higher temperatures and those derived naturally at lower temperatures. The reality of this assumption is also more approachable by conducting experiments at the lowest possible temperatures to reduce the possibility of high temperature artifacts and reversals in the relative rates of elementary reactions. In addition, the use of higher temperatures increases the likelihood of product destruction or modification by less time-dependent and more temperature-dependent reactions.

The experimental studies by Kawamura and Ishiwatari (1981, 1985a,b) best illustrate the futility of generating organic acids from sedimentary organic matter at temperatures comparable to those experienced by source rocks in sedimentary basins (i.e., <150 °C). Their experiments involved isothermally heating wet surface sediments from Lake Biwa in borosilicate glass tubes at 65 and 83 °C for 24 to 5952 h (Kawamura and Ishiwatari 1985a), 120 to 198 °C for 48 h (Kawamura and Ishiwatari 1981), and 68 to 325 °C for 24 h (Kawamura and Ishiwatari 1985b). Organic acids with 12 through 32 carbon atoms (i.e., C_{12}–C_{32}) extracted from the wet sediments showed no significant increase in concentration after being heated at 83 °C for 5952 h, 120 °C for 48 h, and 129 °C for 24 h. A small but detectable increase in acid concentrations was first observed after heating at 140 °C for 24 h, and a 50% increase relative to the concentration of the unheated sample required heating temperatures of 300 and 325 °C for 24 h.

Subsequent experimental investigations indicate that optimum conditions for the generation of organic acids from sedimentary organic matter ranges from 200 to 350 °C over durations of a few days to several weeks. Barth et al. (1987, 1989) have shown that concentrations of organic acids generated from Kimmeridgian shales and lower Jurassic coal increased in experiments for 72-h durations from 200 to 350 °C. Similarly, Eglinton et al. (1987) observed the concentration of organic acids generated from organic matter isolated from a Kimmeridgian shale to increase in experiments for 72-h durations from 200 to 330 °C. Cooles et al. (1987) also reported concentrations of organic acids generated from Cretaceous and Kimmeridgian mudstones to increase in experiments for 72-h durations from 300 to 350 °C. No obvious high-temperature artifacts nor peculiar compositional distributions were observed in these experiments. Therefore, experimental conditions of 200 to 350 °C for 72-h durations appear to provide a reasonable *simulation* of organic acid formation at lower temperatures and longer durations in the subsurface of sedimentary basins.

2.2 Presence of Water

Water is ubiquitous in the interstices of subsurface sedimentary rocks. Those interstices include intergranular voids as well as fractures. Although the specific role of water in geologic reactions remains an active area of research, its presence has been shown to be critical to granite melts (Goranson 1932), metamorphism (Rumble et al. 1982), clay-mineral transformations (Whitney 1990), coalification (Schuhmacher et al. 1960), and petroleum generation (Lewan et al. 1979). Eisma and Jurg (1969) showed that the thermal decomposition rate of behenic acid to low-molecular-weight hydrocarbons at 250 °C in the presence of bentonite was 1.5 orders of magnitude higher in the absence of water than in its presence. Kawamura et al. (1986) found that heating kerogen isolated from the Green River Shale at 300 °C for 2 to 100 h generated twice as much organic acid in the presence of water than in its absence. Mechanisms responsible for these effects of water on organic acids have not been established, but the ubiquity of water in the subsurface and its significant enhancement of organic acid preservation or generation make inclusion of water in laboratory experiments imperative to simulating the natural system.

In addition to conducting experiments in the presence of water, it is also important to consider the water phases present in the experiments. With the exception of localized occurrences of supercritical water fluid in contact metamorphic regimes and water vapor in shallow hydrothermal vents, liquid water is the prevailing phase in sedimentary basins. Therefore, maintaining a liquid-water phase in contact with heated samples is preferred considering the significantly different properties and reactivities of the other two nonsolid phases of water. As discussed by Lewan (1993a), the volume of liquid water (V_l^T) present at a given experimental temperature (T) may be calculated with the following equation,

$$V_l^T = \frac{(M_w^o \gamma_v^T - [V_r - V_s])\gamma_l^T}{\gamma_v^T - \gamma_l^T}$$

by knowing the reactor volume (V_r), sample volume (V_s), specific volumes of water liquid (γ_l^T) and vapor (γ_v^T) at the experimental temperature (Meyer et al. 1983), and mass of liquid water (M_w^o) orginally added to the reactor at room temperature. The critical aspects of this determination is that sufficient water is used in an experiment to insure that the heated sample is submerged in liquid water at the desired experimental temperature. Supercritical conditions should also be considered. Although the supercritical temperature for pure water is 374 °C, the introduction of CO_2 from a heated sample may result in supercritical temperatures less than 300 °C (Takenouchi and Kennedy 1964).

2.3 Type of Sample

Experiments designed to understand the generation of organic acids from sedimentary organic matter have used either samples of whole rock or isolated insoluble organic matter (i.e., kerogen). Whole rock samples provide an overall evaluation of the natural process including organic acid generation within, migration through, and expulsion from, the rock. Possible catalytic and absorption effects caused by the rock matrix may also be represented in the final results because the embedded organic matter thermally matures in contact with natural mineral assemblages, rock fabrics, and intergranular porosities. One consideration in this approach is the size of the whole rock used in the experiments. Oil-prone organic matter in thermally immature rocks usually has dimensions in the order of tens of micrometers. Therefore, pulverizing rock samples to grain sizes less than sand size (i.e., $<62\,\mu m$) risks reducing the amount of natural contact between minerals and organic matter and increasing the amount of contact between water and organic matter to an unnatural level.

A variation in the use of whole rocks is to preextract soluble organic matter (i.e., bitumen) from a rock with nonpolar organic solvents prior to experimentation (e.g., Lundegard and Senftle 1987). The intent of this treatment is to allow the distinction between preexisting organic acids from those generated during the experiment. Bitumen (i.e., soluble organic matter) in thermally immature rocks typically comprises less than 5 wt% of the sedimentary organic matter. The significance of the removal of this minor amount of organic matter remains to be evaluated, but its removal is clearly a deviation from the natural system.

The use of isolated kerogen (i.e., insoluble organic matter) in experiments provides an evaluation of the amount of organic acids that may be generated without the influence of a rock matrix. Experiments of this type are important in evaluating the effects of rock matrices when compared with whole-rock experiments, but by themselves they are not particularly relevant to evaluating the natural system. Surdam et al. (1984) provide an example of a study utilizing both whole rock and isolated organic matter from the Green River Formation. Although an experimental temperature of only 100 °C was employed for 336 h, the results showed that oxalate concentrations were in trace but measurable quantities in the isolated-kerogen experiments (6 ppm) and below detection limits in the whole-rock experiments.

Consideration should also be given to the methods employed to isolate kerogen from its host rock, and how these methods may affect the ability of a kerogen to generate organic acids. Most isolation procedures remove the mineral matter through a series of HCl and HF treatments (e.g., Lewan 1986) that expose the kerogen to atmospheric oxygen. Whether this exposure influences organic acid generation remains to be determined, but its potential to do so should be considered. Experiments have also been conducted on isolated kerogen that has been mixed with different mineral powders, with the intent of evaluating rock matrix effects (Kawamura et al. 1986). Unfortunately, in the presence of liquid water, these unconsolidated powdered mixtures are not representative of the natural system due to the development of water films, which prevent contact between mineral grains and the organic matter.

2.4 Reactor Wall Composition

Some reactor wall compositions have been shown by Palmer and Drummond (1986) to catalyze the thermal degradation of acetic acid at temperatures ranging from 300 to 400 °C. Their study indicates the catalytic effect to be a heterogeneous interaction between the reactor wall and aqueous acetic acid. This catalytic effect is dependent on the composition of the reactor wall. The rate of thermal degradation is not significantly enhanced by gold surfaces, but is enhanced by an order of magnitude by stainless steel surfaces. The obvious concern that emerges from these experimental results is that the rate at which organic acids are destroyed by surface catalysis may approach the rate at which they are generated. As a result, the true potential of the organic-acid generating capability of sedimentary organic matter could be underestimated. Using whole rock instead of isolated kerogen significantly minimizes the contact between the reactor walls and organic acids generated within the rock matrix. However, as generated organic acids are expelled into the surrounding water phase, their access to reactor walls is greatly enhanced and must be considered.

In order to more fully evaluated this potential experimental problem, a series of experiments were conducted in the authors' laboratory. The experiments involve isothermally heating 300-g aliquots of a thermally immature sample of Monterey Shale (MR-216) with liquid water at 330 °C for 72 h in 1-l reactors with walls of different surface compositions. The six surface compositions used include fresh stainless steel-316, carburized stainless steel-316, gold-plated stainless steel-316, fresh Hastelloy C-276, carburized Hastelloy C-276, and borosilicate glass (Pryex liner). After the experiments cooled to room temperature, the expelled oil floating on the water surface was removed (Lewan 1993a) and the recovered water was decanted from the reactor. The recovered water was immediately filtered through a 0.45-μm filter and analyzed for dissolved inorganic and organic species, which are given in Tables 1 and 2. Recovered waters from these experiments had pH's between 6.7 and 7.1 and Eh's between −402 and −420 mV.

Stainless steel-316 is an iron-based alloy with subordinate amounts of chromium, nickel, and molybdenum. Hastelloy C-276 is a nickel-based alloy with subordinate amounts of molybdenum, chromium, iron, and tungsten. Comparison of the inorganic species dissolved in the waters recovered from the fresh-metal surfaces of these two alloys shows no significant differences (Table 1). However, dissolved organic species (Table 2) show the fresh-metal stainless steel-316 reactor to have significant reductions in total acid, butyric acid, and propionic acid relative to the fresh-metal Hastelloy C-276 reactor. These results indicate that butyric acid is preferentially degraded in fresh-metal stainless steel-316 reactors.

The bright silvery surfaces of the fresh-metal walls of both alloys dull and darken with successive experiments utilizing sedimentary organic matter (Lewan 1993a). This surface seasoning is the result of carbon from hydrocarbon and CO_2 degradation at the metal surface diffusing into the alloy (Stanley 1970). This process is referred to as carburization and typically extends several μm into the reactor wall in these types of experiments where expelled oils and generated gases are produced. Dissolved inorganic species show no significant differences between the fresh-metal and carburized surfaces with the exception of chlorine, which has a significantly higher concentration in the carburized reactors of both alloys. Salts in the original sample are the source of this chlorine, and its increased concentration in the

Table 1. Dissolved inorganic species released from a sample of Monterey Shale (MR-216) into the surrounding water after heating for 72 h at 330 °C in 1-l reactors with different surface compositions. Concentrations are given in mg/l and were determined by AA or ICP-AES

Reactor surface composition	Li	Na	K	Mg	Ca	Sr	B	C	Al	Si	S	Cl	Cr	Mn	Fe	Total dissolved solids
Stainless steel-316																
Fresh metal	2.0	2189	98	41	1199	3.2	13.1	1865	1.0	118	571	3865	0.06	0.06	0.15	10 660
Carburized	2.1	2177	93	44	1275	3.0	13.2	1875	1.1	122	586	4163	0.06	0.06	0.14	10 780
Gold plated	2.1	2229	85	16	1311	3.1	16.6	2015	1.0	115	563	4095	0.06	0.06	0.19	10 530
Hastelloy C-276																
Fresh metal	2.1	2229	88	43	1290	3.2	14.8	1888	1.2	125	545	3922	0.06	0.06	0.15	11 430
Carburized	2.0	2203	90	44	1387	3.2	13.6	1982	1.1	121	570	4210	0.06	0.06	0.13	11 350
Borosilicate glass	1.6	1979	59	31	813	2.3	515.0	1776	0.7	180	423	3021	0.06	0.15	0.19	10 090

Table 2. Dissolved organic species released from 300 g of crushed (0.5–2.0 cm) Monterey Shale (MR-216) into 365 g of water after heating for 72 h at 330 °C in 1-l reactors with different surface compositions. Aliphatic acids were determined by ion exclusion chromatography[a] and dissolved organic carbon (Org. C) was determined with a UV photooxidation carbon anayzer[b]

Reactor surface composition	Acetic (mg)	Propionic (mg)	Butyric (mg)	Total (mg)	Org. C (mg)	Normalized percentage			% Org. C as acid C
						Acetic	Propionic	Bytyric	
Stainless Steel-316									
Fresh metal	245	123	201	569	607	43.1	21.6	35.3	44.7
Carburized	235	128	246	609	603	38.6	21.0	40.4	48.8
Gold plated	254	128	255	637	648	39.9	20.1	40.0	47.4
Hastelloy C-276									
Fresh metal	245	128	310	683	613	35.9	18.7	45.4	54.5
Carburized	235	137	301	673	627	34.9	20.4	44.7	52.5
Borosilicate glass[c]	266	91	161	518	611	51.3	17.6	31.1	39.6

[a] Dionex 2120: ion chromatograph with 0.001 M HCl eluant, 0.8 ml/min flow, AS-3 separator, Ag-H+ resin suppressor, and conductivity detector.

[b] Astro resources model 1850.

[c] Full-length Pyrex glass liner with bottom in stainless steel-316 1-l reactor.

carburized reactors suggests that more chloride reacts with the fresh-metal surfaces. Acetic acid concentrations decreased and propionic acid concentrations increased slightly in the carburized reactors of both alloys (Table 2). Butyric acid concentrations increased significantly in the carburized stainless steel-316 reactor, but decreased slightly in the carburized Hastelloy C-276 reactor. Although the differences between the fresh-metal and carburized Hastelloy C-276 reactors may not be significant, it is evident from the data in Table 2 that under either condition this alloy has less effect on the amount and distribution of acids than either fresh-metal or carburized stainless steel-316.

Lewan (1993a) noted that the amount of H_2S present in the gases generated by the experiments conducted in stainless steel-316 reactors was inversely proportional to the amount of pyrrhotite that formed on the reactor walls. Pyrrohite coatings were most apparent on the fresh-metal reactor and least apparent on the carburized reactor. The intermediate degree of pyrhotite coating and notable deterioration of gold plating in the gas-phase portion of the gold-plated reactor suggest the existence of an imperfect gold barrier between the underlying fresh-metal stainless steel-316 and dissolved acids. As a result, the amounts and proportionality of the acids in the gold-plated reactor are intermediate to the Hastelloy C-276 reactors and the carburized stainless steel-316 reactor (Table 2). Significant quantities of gold (i.e., 2538 to 7224 mg/kg H_2O) are soluble in near-neutral, H_2S-enriched waters at temperatures between 300 and 350 °C (Shenberger and Barnes 1989). This high susceptibility to dissolution under commonly employed experimental conditions and the ability of some types of sedimentary organic matter to generate high concentrations of H_2S make the utility of gold-plated stainless steel-316 reactors uncertain and less advantageous than Hastelloy C-276 reactors.

Some investigators have conducted their experiments in borosilicate glass tubes under the presumption of minimizing catalytic surface effects (Tannenbaum and Kaplan 1985). Contrary to this presumption, data on the use of borosilicate glass tubing for reactors are more detrimental to simulating the natural system than the use of carburized metal reactors (Lewan 1993a). Palmer and Drummond (1986) showed that the established first-order rate of acetic degradation is altered to a zero-ordered rate when experiments are conducted in fused quartz or borosilicate glass tubes. In addition, Dawidowicz et al. (1984, 1986) have shown that boron within silica glass leads to the formation of unreactive carbon during the heating of alcohols. The amount of unreactive carbon formed was found to be proportional to the amount of boron in the silica glass. Lewan (1993a) suggested this process to be responsible for the reduced yields of expelled oil obtained in an experiment using a borosilicate glass liner in a metal reactor. The glass liner recovered at the conclusion of this experiment was completely frosted and contained carbon deposits where the expelled-oil layer occurred at the experimental temperatures. Dissolved inorganic species in the waters recovered from this experiment are similar to the waters from the metal reactors, with the exception of anomalously high boron and elevated silicon concentrations (Table 1). However, the dissolved organic species show significant reductions in propionic and butyric acids, and an increase in acetic acid relative to the waters from the metal reactors (Table 2). These data and the data from Palmer and Drummond (1986) clearly discourage the use of borosilicate glass in simulating the natural system at temperatures in excess of 300 °C.

2.5 Partitioning Between Oil and Water

The dichotomous chemical character of most organic acids, resulting from their hydrophobic hydrocarbon group and hydrophillic hetero-atom acid group, allows them to occur in varying degrees as dissolved species in both water and organic liquids. Their distribution as dissolved species in coexisting immiscible organic liquid and water phases is expressed as a dimensionless ratio referred to as the partition coefficient (Leo et al. 1971). This parameter is conventionally defined as the concentration of a solute in an organic liquid divided by its concentration in a coexisting water phase. Partition coefficients for organic acids may vary significantly depending on structural configurations and the relative abundance of hetero-atom acid groups to hydrocarbon groups. Figure 1 shows that as the hydrocarbon group of monocarboxylic acids increase in length with addition of aliphatic carbons, there is an increased preference for their occurrence in organic liquids rather than water. These partition coefficients indicate that C_1 through C_4 monocarboxylic acids will preferentially concentrate in water rather than coexisting oils, benzene, or chloroform. Conversely, monocarboxylic acids with five or more carbon atoms will preferentially concentrate in the organic liquids rather than in water. Organic liquids that are more polar in character have higher partition coefficients for the same acids are shown in Fig. 1 by the greater preference for C_3 and C_4 monocarboxylic acids to occur in octanol than in coexisting water.

Hydrous pyrolysis experiments generate two types of organic liquids: (1) bitumen that is retained within the rock and (2) expelled oil that accumulates on the water surface. The expelled oil is rich in hydrocarbons and is likely to have partition coefficients for organic acids similar to those for benzene, chloroform, or oils, as shown in Fig. 1. Bitumen retained in the rock is more polar in character and is likely to have partition coefficients for organic acids between those for octanol and chloroform (Fig. 1). Most hydrous pyrolysis studies conducted to date only determined the amount of organic acids dissolved in the recovered water at room temperature. Depending on the final ratio of organic liquids (bitumen + oil) to water, the results obtained from this procedure may be misleading. This dependence is illustrated in Fig. 2 for acetic, propionic, and butyric acids. As the mass ratio of organic

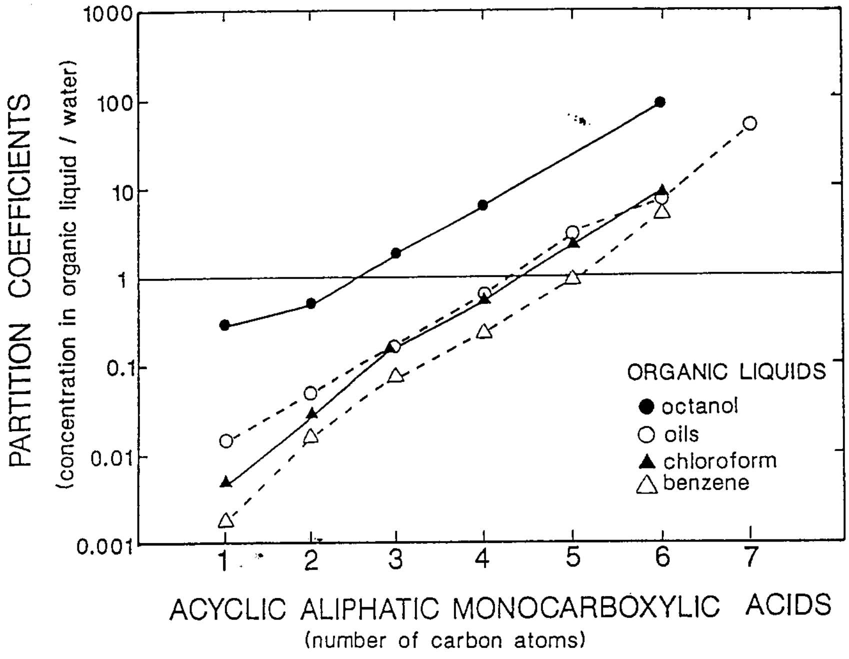

Fig. 1. Partition coefficients of acyclic aliphatic monocarboxylic acids dissolved in organic liquids and coexisting water at 25 °C. Values are from Leo et al. (1971)

liquid to water increases, the percent of the total organic acid dissolved in the water diminishes significantly. This decrease becomes more apparent as the number of carbon atoms in the organic acid increases. At an expelled oil/water ratio of one, only 95% of the acetic acid, 85% of the propionic acid, and 62% of the butyric acid are present in the water at room temperature. This effect becomes more pronounced with bitumen, which would give results somewhere between the octanol and chloroform lines in Fig. 1. It is apparent from Fig. 2 that the amounts as well as the proportionality of the organic acids may be influenced at organic liquid/water ratios greater than 0.1. Therefore, partitioning of dissolved organic acids between organic liquids and water is an important consideration in designing experiments and in interpreting experimental results.

2.6 Pressure and Water Chemistry

Other experimental considerations that may prove to be important in simulating natural organic-acid generation include pressure and water chemistry. Experimental studies have shown pressure (Michels et al. 1992) to have significant effects on petroleum generation. Most experiments concerned with organic-acid generation use pressures generated by the vapor pressure of water at the experimental temperature. An exception is the experimental study by Knauss et al. (1992) in which petroleum source rocks were heated at 330 °C with water in a flexible gold-bag reactor at 30 and 60 MPa for

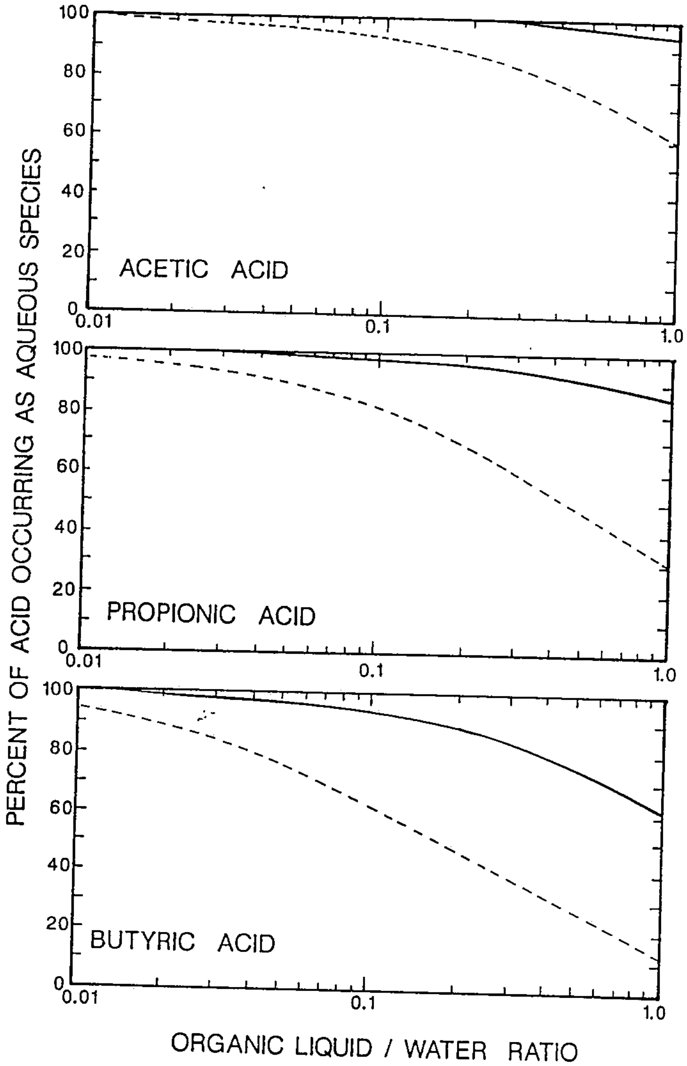

Fig. 2. Graphs showing influence of organic liquid/water ratios on percent of total acetic, propionic, and butyric acids dissolved in water coexisting with oils (*solid curves*) or octanol (*dashed curves*). Curves are calculated from partition coefficients given by Leo et al. (1971)

durations up to 65 days. No significant variations were observed in the concentrations of acetic and propionic acids over this pressure difference. Water chemistry has been shown to significantly enhance petroleum formation (Soldan and Cerqueira 1986), but most experiments concerned with organic-acid generation use distilled or fresh water. An exception is the experimental study by Thornton and Seyfried (1987) in which organic-rich sediment was heated with its original seawater at 350 °C in a flexible titanium reactor with a fixed pressure of 50 MPa. Acetic acid was released under these conditions, but no comparative experiments with different water chemistries were conducted to evaluate their effect. The importance of water chemistry on organic-acid generation remains to be determined.

3 Acid Types and Quantities

Organic acids detected in waters associated with petroleum may be classified as aliphatic carboxylic acids or aromatic carboxylic acids. With respect to generation of these acids from thermally maturing sedimentary organic matter, the aliphatic carboxylic acids have been the most studied. These acids may consist of straight, branched, or cyclic aliphatic groups that are either saturated or unsaturated and contain one or more carboxylic acid groups. Acyclic, saturated, mono- and di-carboxylic acids are the most commonly detected and emphasis will be placed on these acid types.

3.1 Saturated Acyclic Aliphatic Monocarboxylic Acids

These acids are described by their number of carbon atoms and structural configuration (i.e., presence or absence of branch chains). Straight-chain acids with 1 to 32 carbon atoms are the most common acids of this type that are generated from experimentally heated sedimentary organic matter. C_{12} to C_{32} acids of this type in surface sediments of Lake Biwa have been monitored through a series of isothermal heating experiments at temperatures from 68 to 325 °C for 24-h durations (Kawamura and Ishiwatari 1985b). As shown in Fig. 3, there is an initial decrease in their total concentration up to 100 °C, which is attributed to their assimilation into insoluble organic matter during early diagenetic formation of kerogen (Kawamura and Ishiwatari 1985a). At experimental temperatures in excess of 100 °C, these assimilated acids once again become extractable as the kerogen thermally decomposes. The total concentration of these acids continues to increase beyond their original concentration with increasing temperatures until a constant concentration is maintained between 179 and 279 °C. This concentration level is followed by another increase in concentrations at 300 and 325 °C. Assuming a 65 wt% carbon content for the original organic matter, the maximum yield of these acids accounts of 0.83 wt% of the organic matter. Although these long-chain monocarboxylic acids in rock bitumens and crude oils have been used to evaluate sources and transformations of sedimentary organic matter (Parker 1969), they are not likely to be significant in geologic processes mediated by water. Large partition coefficients (>1; Fig. 1), resulting from the large aliphatic groups in these acids, limit their occurrence to source-rock bitumens and expelled oils of a source rock. Concentrations of $C_{14}-C_{30}$ aliphatic monocarboxylic acids have been reported in subsurface waters associated with petroleum accumulations, but their concentrations seldom exceed one μmol/l (Cooper and Bray 1963).

C_2 to C_8 acids of this type are also generated from sedimentary organic matter by hydrous pyrolysis at temperatures from 250 °C for 72 h to 330 °C for 168 h (Eglinton et al. 1987). These experiments used kerogen isolated

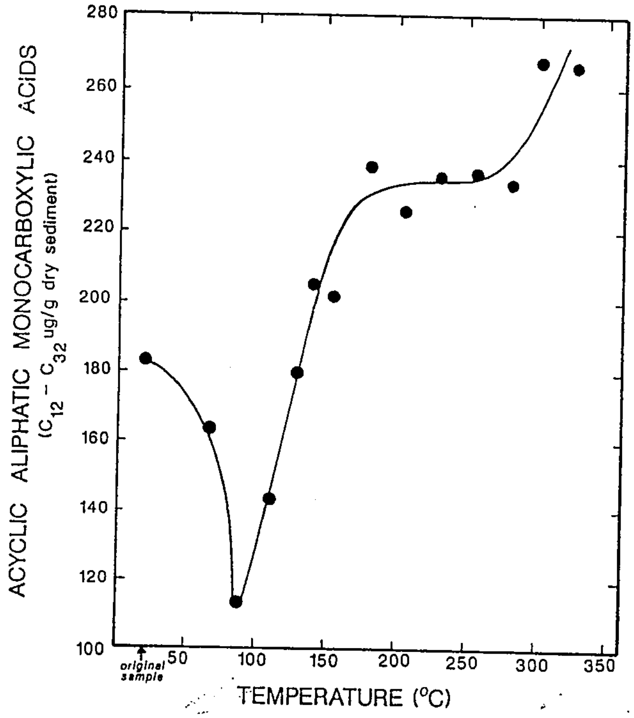

Fig. 3. Concentration of C_{12}–C_{32} acyclic aliphatic carboxylic acids extracted from aliquots of Lake Biwa surface sediments after isothermal heating at temperatures from 68 to 325 °C for 24 h. (Kawamura and Ishiwatari, 1985a)

from an oil shale in the Kimmeridge Clay Formation. A maximum yield of C_2 to C_8 monocarboxylic acids from this kerogen was reached at 330 °C after 168 h. At this maximum, 0.66 wt% of the original kerogen was converted to straight- and branched-aliphatic C_2–C_8 monocarboxylic acids. Straight-chained C_2–C_5 acids comprise nearly 95% of this maximum yield, with branched C_4 and C_5 acids comprising most of the remaining 5%. Small partition coefficients (<1; Fig. 1) for these C_2–C_5 acids insure their occurrence as aqueous species that may be significant in geological processes mediated by water. C_2–C_5 acids are the prevalent aliphatic monocarboxylic acids detected in subsurface waters associated with petroleum accumulations (Carothers and Kharaka 1978; Fisher 1987). Although formic acid (C_1) is also favored to occur as an aqueous species (Fig. 1), it only occurs as a minor component in waters reacted with source rocks during hydrous pyrolysis (Lundegard and Senftle 1987) and in subsurface waters associated with petroleum accumulations (MacGown and Surdam 1988).

Acetic acid (C_2) is typically the most abundant of the monocarboxylic acids and comprises more than 50 mol% of the total acids generated from source rocks during hydrous pyrolysis. Barth et al. (1989) conducted a series of hydrous pyrolysis experiments on aliquots of a powdered shale sample from the Kimmeridge Clay Formation. The aliquots were isothermally heated for 72 h at temperatures ranging from 200 to 350 °C. Acetic acid in the reacted waters increased with increasing temperature. The percent of acetic acid comprising the total acid concentration also increased from 56% at temperatures between 200 and 270 °C to 65% at temperatures between 330 and 350 °C. The maximum amount of kerogen converted to acetic acid was 1.06 wt% at 350 °C after 72 h. Compared with other experimental results (Table 3), maximum conversion of organic matter to acetic acid usually requires experimental temperatures equal to or in excess of 350 °C for 72-h durations. Maximum generation of expelled oil also occurs under these experimental conditions, which will be elaborated on later.

Notable exceptions to the results presented in Table 3 are from hydrous pyrolysis experiments conducted on peats by Pickering and Batts (1992a). Forest and grass peats were heated isothermally for 72 h at temperatures between 95 and 330 °C. Maximum yields of acetic acid occurred at 200 °C with organic matter conversions of 0.15 wt% for the forest peat and 1.18 wt% for the grass peat. In addition to these maximum yields occurring at an anomalously low temperature, the distribution of the C_1–C_5 carboxylic acids was peculiar and not representative of subsurface waters. The weight percentages of the total C_1–C_5 carboxylic acids were 1.1 to 4.9 for formic acid, 9.3 to 12.1 for acetic acid, 32.5 to 64.4 for propionic acid, 6.2 to 24.1 for normal- and iso-butric acids, and 16.2 to 29.2 for normal- and iso-valeric acids. Pickering and Batts (1992b) also reported peculiar distributions with anomalously high percentages of valeric acid from hydrous pyrolysis experiments on Australian coals at 120 °C for 72-h durations. No explanations for these anomalous distributions are given by the investigators. If these peculiar distributions are not a result of the neutralization procedure (i.e., addition of NaOH) imposed on the sample-water system before the experiments, then they may indicate that some coals are not typical sources of these acids in subsurface waters.

The maximum conversions of organic matter to acetic acid in Table 3 are variable. Maximum conversion to acetic acid varies for coals from 0.45 to 2.01 wt% and for marine source rocks from 0.51 to 2.05 wt% (Table 3). All the experiments in Table 3, except for those by Cooles et al. (1987), were conducted in stainless steel-316 reactors, and therefore, the influence of reactor wall composition is not likely to be responsible for these variations. Another factor unlikely to be responsible for this variation is mineral oxides within the rocks. Eglinton et al. (1987) enhanced the generation of acetic acid nearly fourfold by including limonite ($HFeO_2$) with isolated kerogen in a hydrous pyrolysis experiment at 330 °C for 72 h. Kerogen oxidation by oxygen from the reduction of ferric oxide during the experiments is the most likely cause of this enhanced generation of organic acids. The problem with applying this observation to petroleum source rocks like those given in Table 3 is that ferric oxides are not present in the reducing depositional environments under which sedimentary organic matter accumulates. Under these conditions, reduced species like ferrous sulfides (e.g., pyrite) occur rather than ferric oxides. The only exception is if weathered source rock samples containing hematite or jarosite were used in the experiments.

Table 3. Experimental conditions and the weight percent of original organic matter converted to acetic, propionic, butyric, and valeric acids at the maximum for acetic acid generation from organic matter in samples of whole rock (WR), solvent-extracted rock (ER) and isolated kerogen (IK)

Rock unit	Sample type	Kerogen type	Range of conditions	Conditions for maximum acetic acid	Acetic acid (% org. matter)	Propionic acid (% org. matter)	Butyric acid (% org. matter)	Valeric acid (% org. matter)	Total (% org. matter)
Green River Shale[a] (Mahogany Zone)	WR	I	260–361 °C/ 72–144 h	361 °C/72 h	0.53	0.18	0.21	0.05	0.97
Kimmeridge Clay[b] (Blackstone Band)	IK	II	250–330 °C/ 7.2–168 h	330 °C/168 h	0.47	0.14	0.05	0.01	0.67
Kimmeridge Clay[a] (Blackstone Band)	WR	II	300–366 °C/ 72 h	350 °C/72h	0.51	0.15	0.08	n.d.	0.74
Kimmeridge Clay[c] (Oil Shale)	ER	II	200–350 °C/ 72 h	350 °C/72 h	1.06	n.r.	n.r.	n.r.	1.06
Kimmeridge Clay[d] (Oil Shale)	WR	II	250–350 °C/ 72 h	340 °C/72 h	0.73	0.20	n.r.	n.r.	0.93
Phosphoria Fm.[a] (Retort Shale)	WR	II	240–361 °C/ 72 h	355 °C/72h	0.51	0.19	0.21	0.03	0.94
Monterey Shale[a] (Phosphatic mb.)	WR	II	240–360 °C/ 72 h	355–360 °C/ 72 h	1.35	0.31	0.17	0.03	1.86

Kreyenhagen Shale[a] (Siliceous unit)	WR	II	270–365 °C/ 72 h	360 °C/72 h	2.19	0.38	0.09	0.08	2.74
Non-Marine Shale[e] (TOC = 4.41%)	ER	II	250–350 °C/ 72 h	350 °C/72 h	0.54	0.16	0.04	n.r.	0.74
Non-Marine Shale[c] (TOC = 7.71%)	ER	II/III	250–350 °C/ 72 h	350 °C/72 h	0.36	0.09	0.02	n.r.	0.47
Non-Marine Shale[e] (TOC = 4.05%)	ER	III/II	250–350 °C/ 72–360 h	350 °C/72 h	0.71	0.17	n.d.	n.r.	0.88
Norwegian Coal[f] (Lower Jurassic)	WR	III	290–350 °C/ 72 h	350 °C/72 h	0.45	n.r.	n.r.	n.r.	0.45
Australian Coal WR[d] (Cretaceous-Paleogene)	WR	III	300–350 °C/ 72 h	350 °C/72 h	2.01	0.63	n.r.	n.r.	2.64

n.r., not reported; n.d., not detected.

[a] Authors' data.

[b] Eglinton et al. (1987).

[c] Barth et al. (1989).

[d] Cooles et al. (1987).

[e] Lundegard and Senftle (1987).

[f] Barth et al. (1987).

Barth and Bjørlykke (1993) used mulivarient statistics in an attempt to establish correlations between acetic acid yields from hydrous pyrolysis experiments and the organic carbon contents, open-system pyrolysis data (i.e., Rock-Eval parameters), and vitrinite reflectances of the pyrolyzed source rocks. As reported by these investigators, the principal component analysis was inconclusive. Other investigators have suggested a general relationship between the original oxygen content of the organic matter and the amount of acetic acid generated (Cooles et al. 1987; Lundegard and Senftle 1987). Although high acetic acid concentrations are usually generated from oganic matter with high oxygen contents, all organic matter with high oxygen contents does not generate high acetic acid concentrations (Eglinton et al. 1987). Data from hydrous pyrolysis experiments conducted in the authors' laboratory on Phosphoria Retort, Monterey, Kimmeridge Clay, and Kreyenhagen Shales (Table 3) indicate that maximum yields of C_2–C_5 monocarboxylic acids only account for 5 to 10 mol% of the oxygen in the original kerogens. A more direct control on the amount of kerogen converted to acetic acid is the amount of acetic acid originally incorporated into the organic matter during early diagenesis, when insoluble kerogen is forming. As previously discussed, C_{12}–C_{32} monocarboxylic aliphatic acids are initially assimilated into insoluble organic matter (i.e., kerogen) of recent sediments at experimental temperatures below 100 °C (Fig. 3). Therefore, the amount of acetic acid available during early diagenesis may dictate the amount of acetic acid that can be generated from a kerogen during the latter stages of diagenesis and petroleum formation. Availability of assimilable acetic acid would depend on the balance between their generation and consumption by microbial activity in the original sediment.

The bonding types responsible for the assimilation of acetic acid into the insoluble kerogen during early diagenesis are not known. However, the low activation energy of 5.4 kcal/mol determined by Barth et al. (1989) for the generation of acetic acid from an oil shale indicates weak noncovalent bonding. It has been well documented that prior to petroleum formation, the oxygen content of a kerogen decreases relative to its carbon content (Tissot et al. 1974). This relationship has been expressed on a van Krevelen diagram in which the atomic H/C ratio of a kerogen is plotted against its atomic O/C ratio (Fig. 4). In addition to loss of CO_2 through decarboxylation, loss of acetic acid through the cleavage of noncovalent bonds may also contribute to the initial decrease in the atomic O/C ratio. As a result, the amount of acetic acid generated by a kerogen in hydrous pyrolysis experiments may depend on its thermal maturity with respect to its atomic O/C ratio prior to experimentation. Figure 4 shows that the rocks with the most thermally immature Type II kerogens (i.e., Monterey Shale and Kreyenhagen Shale), based on high atomic O/C ratios, have generated the most acetic acid during the hydrous pyrolysis experiments (Table 3).

The resulting implication is that the maximum amounts of acetic acid generated from sedimentary organic matter are best assessed in hydrous

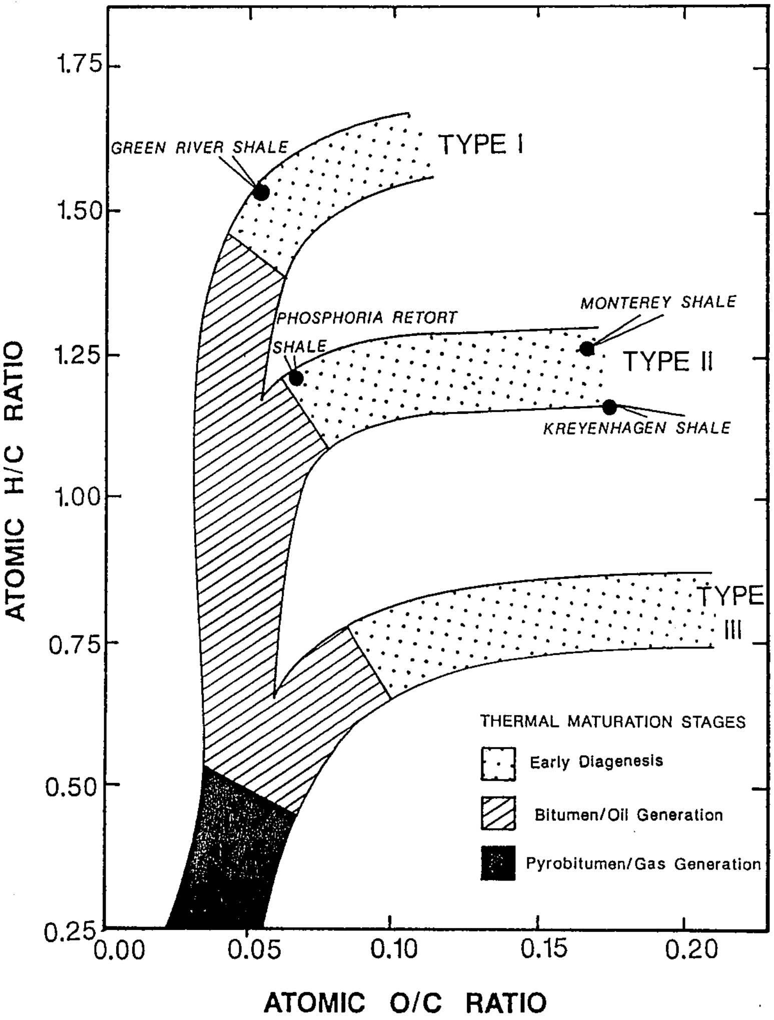

Fig. 4. Modified van Krevelen diagram after Tissot et al. (1974) showing the three major kerogen types based on their atomic hydrogen/carbon and oxygen/carbon ratios. *Labeled points* refer to kerogens isolated from rocks used to study organic acid generation by hydrous pyrolysis in the authors' laboratory

pyrolysis experiments conducted with samples that are thermally immature relative to the oxygen loss during early diagenesis. Samples of Paleozoic age, like the Phosphoria Formation (Permian) in Fig. 4, are immature with respect to petroleum generation (Lewan 1985), but thermally mature with respect to oxygen loss during early diagenesis. It should not be inferred from this implication that all kerogens with high atomic O/C ratios will generate large amounts of acetic acid, but rather these kerogens provide the best assessment of maximum acetic acid generation from maturing source rocks. Accordingly, maxima for acetic acid generation from Type II kerogen are best represented by the experiments on samples from the Monterey Shale and Kreyenhagen Shale, which are 1.35 and 2.17 wt% (Table 3), respectively.

Although these conversions of sedimentary organic matter to acetic acid are an acceptable maximum range for Type-II kerogens, sufficient experimental data are not available to assess the maximum range of conversion for Type-III and Type-I kerogens. Elemental analyses (i.e., C, H, O, and N) are not given for the Type-III kerogens of the two coal samples studied (Table 3), but the Australian coal generates the most acetic acid with a conversion of 2.01 wt%. This amount of conversion may not be representative of a maximum for Type-III kerogen, because the vitrinite reflectance of 0.4% Ro given for this coal (Cooles et al. 1987) suggests that it is of subbituminous C rank. More representative maximum conversions for Type-III kerogens are most likely to be obtained from future hydrous pyrolysis experiments on lignites, which are more thermally immature with respect to oxygen loss during diagenesis. Similarly, more experimental work is needed to determine the maximum conversions of Type-I kerogens to acetic acid. A complete set of hydrous pyrolysis data is only available on one source rock bearing Type-I kerogen (i.e., Green River Shale), and the original sample is not immature with respect to oxygen loss during early diagenesis (Fig. 4).

Although all of the C_2 through C_5 monocarboxylic acids typically increase with increasing thermal stress (Fig. 5), the amount each acid increases is not always at a constant proportion to the other acids. This variable proportionality among the C_2 through C_5 acids with increasing thermal stress is shown in Fig. 6. Acetic acid becomes more dominant relative to the other acids with increasing thermal stress for the Kreyenhagen Shale. Conversely, butyric acid plus valeric acid becomes more dominant relative to the other acids with increasing thermal stress for the Phosphoria Retort Shale. Intermediate between these two opposite trends are the acids generated from the Monterey Shale, which show no change in proportionality among one another with increasing thermal stress. One explanation for these differences (Fig. 6) may be the preferential loss of acetic acid and to a lesser extent propionic acid during the early diagenetic loss of oxygen, which is at a higher level (i.e., lower atomic O/C ratio) for the original organic matter in the Phosphoria Retort Shale than in the Kreyenhagen Shale (Fig. 4). Implications of this explanation are discussed in the following section concerning generation and expulsion of organic acids.

3.2 Saturated Dicarboxylic Aliphatic Acids

These acids consist of a saturated aliphatic group bearing two carboxylic groups. The saturated aliphatic group may have a straight, branched, or cyclic structural configuration. Straight and to a lesser extent branched configurations are the most commonly reported acids of this type generated in laboratory heating experiments involving sedimentary organic matter. Similar to monocarboxylic aliphatic acids, high-molecular-weight dicarboxylic

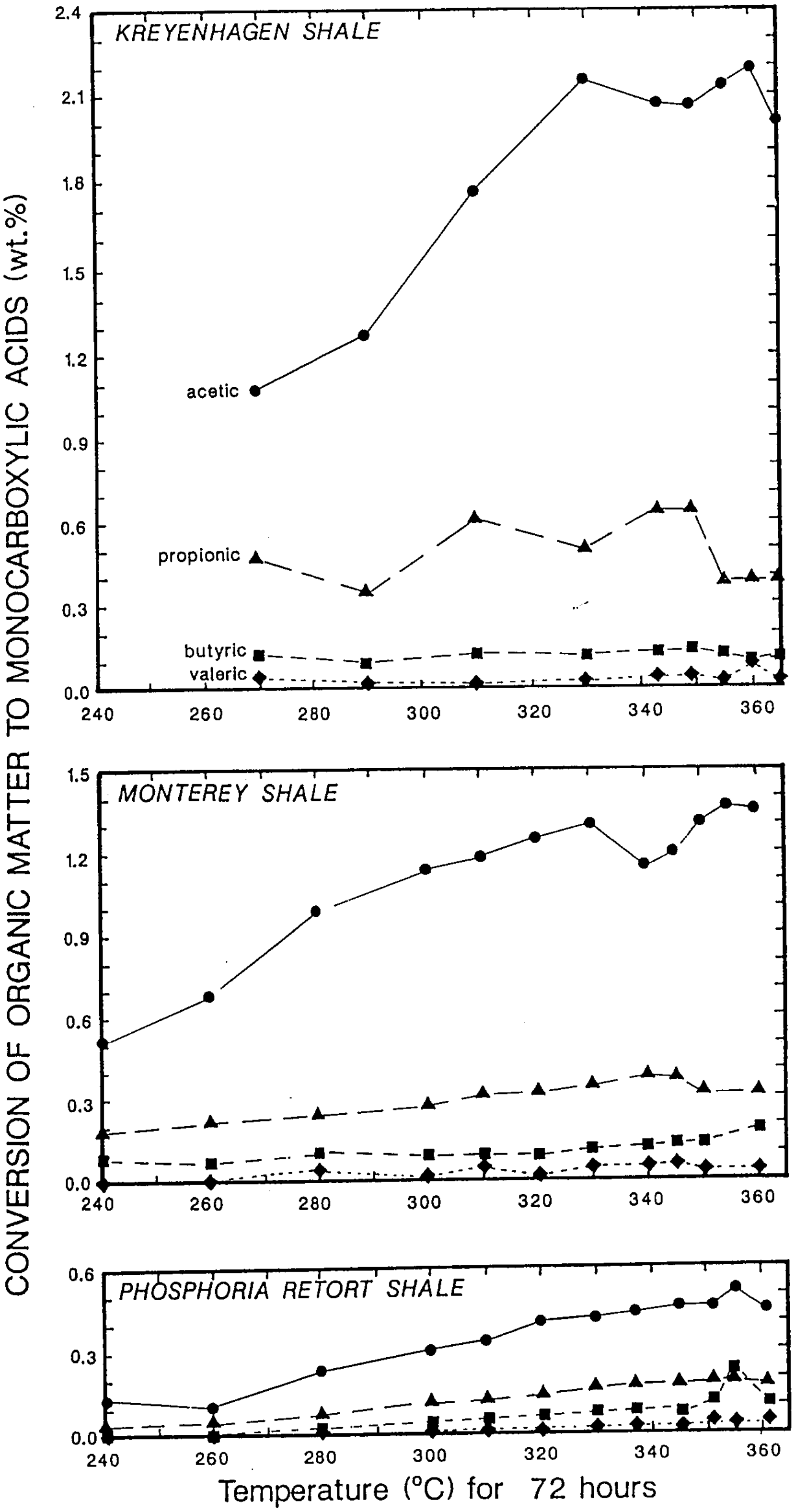

Fig. 5. Weight percent of original organic matter converted to aqueous C_2–C_5 monocarboxylic acids after hydrous pyrolysis of aliquots of Kreyenhagen, Monterey, and Phosphoria Retort shales isothermally heated at temperatures from 240 to 365 °C for 72-h durations. Experiments were conducted in carburized stainless steel-316 reactors in the authors' laboratory

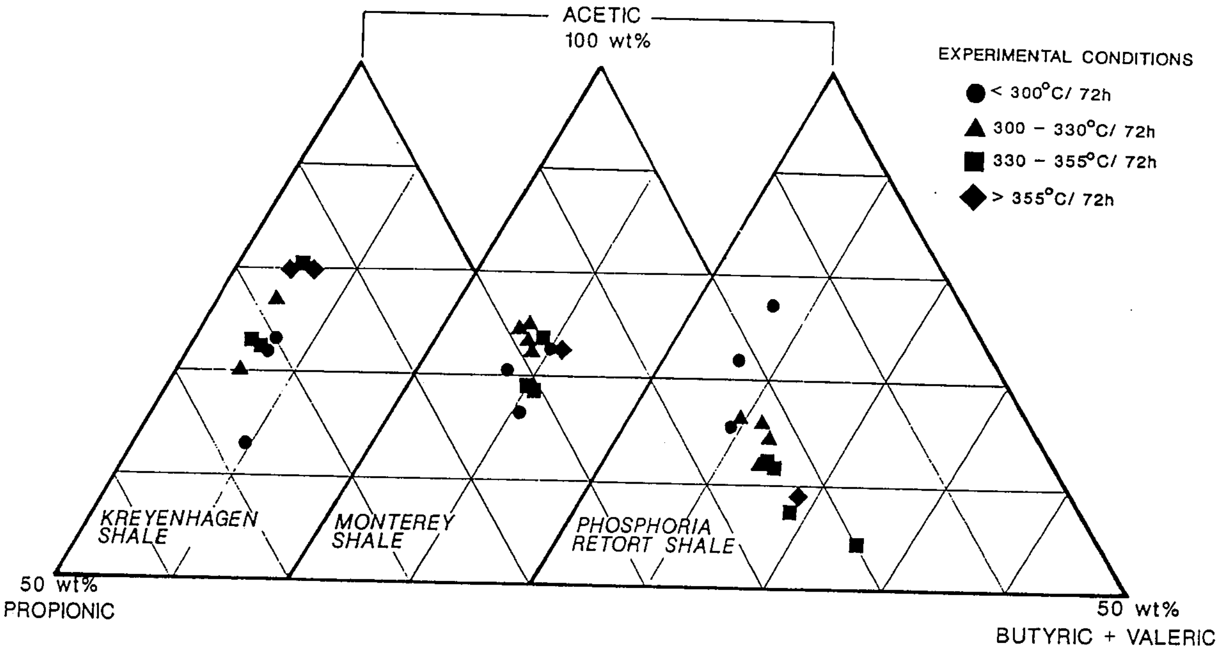

Fig. 6. Ternary diagrams showing the proportionality of C_2–C_5 monocarboxylic acids generated by hydrous pyrolysis of Kreyenhagen, Monterey, and Phosphoria Retort shales as shown in Fig. 5

aliphatic acids with 9 to 30 carbons have been generated from Lake Biwa surface sediments in laboratory heating experiments (Kawamura and Ishiwatari 1985b). Isothermal experiments conducted for 24-h durations generate a steady increase of these acids from 129 °C to a maximum at 279 °C, which is followed by a decrease at 300 and 325 °C. The maximum amount of organic matter converted to C_9–C_{30} dicarboxylic aliphatic acids is 0.11 wt%. It is unlikely that this amount of high-molecular-weight dicarboxylic acids would have a role in geological processes mediated by water because of their positive partition coefficients between organic liquids and water (Leo et al. 1971). Expelled oil and source-rock bitumen would retain most of the C_9 through C_{30} dicarboxylic aliphatic acids with only trace amounts in the associated formation water.

Conversely, the negative partition coefficients for the low-molecular-weight dicarboxylic acids with 2 through 9 carbon atoms makes them more relevant to geological processes mediated by water. Although these C_2 through C_{10} acids have been reported in waters heated with sedimentary organic matter during hydrous pyrolysis experiments (Eglinton et al. 1987), their thermal stability is less than that of the monocarboxylic aliphatic acids (Crossey 1991). Hydrous pyrolysis experiments on Type-II kerogen isolated from the Kimmeridge Clay Formation yielded maximum dicarboxylic acid concentrations at 250 °C after 720 h (Eglinton et al. 1987). Kawamura and Kaplan (1987) also generated dicarboxylic acids with 2 through 10 carbon atoms from sedimentary organic matter in hydrous pyrolysis experiments at

Table 4. Experimental conditions and weight percent of original organic matter converted to oxalic (C_2), succinic (C_4), pyrotartaric (C_5), glutaric (C_5), iso-adipic (C_6), adipic (C_6), pimelic (C_7), suberic (C_8), azelaic (C_9), and sebacic (C_{10}) acids at maximum generation of total dicarboxylic aliphatic acids

Rock unit	Kimmeridge Clay[a]	Monterey Shale[b]	Green River Shale[b]	Tanner Basin Recent Sediment[b]	Recent Bog Sediment[b]
Sample type	Isolated kerogen	Isolated kerogen	Isolated kerogen	Isolated kerogen	Extracted humic acid
Kerogen type	II	II	I	II(?)	III(?)
Range of conditions	250–330 °C/ 7.2–168 h	270 °C/2 h	270 °C/2 h	270 °C/2 h	270 °C/2 h
Conditions at maximum generation	250 °C/720 h	270 °C/2 h	270 °C/2 h	270 °C/2 h	270 °C/2 h
Oxalic acid (% org. matter)	n.r.	0.152	0.238	0.895	0.844
Malonic acid (% org. matter)	n.r.	n.d.	n.d.	n.d.	n.d.
Succinic acid (% org. matter)	0.016	0.032	0.050	0.444	0.256
Pyrotartaric acid (% org. matter)	0.006	0.035	0.057	0.272	0.073
Glutaric acid (% org. matter)	0.014	0.006	0.010	0.055	0.025
Iso-adipic acid[c] (% org. matter)	n.r.	0.007	0.010	0.016	0.005
Adipic acid (% org. matter)	n.d.	0.002	0.004	0.016	0.006
Pimelic acid (% org. matter)	0.001	n.r.	n.r.	n.r.	n.r.
Suberic acid (% org. matter)	0.019	0.004	0.026	0.027	0.022
Azelaic acid (% org. matter)	0.002	n.d.	0.004	0.019	n.d.
Sebacic acid (% org. matter)	tr.	n.d.	0.003	0.008	n.d.
Total dicarboxylic aliphatic acids (% org. matter)	0.058	0.238	0.402	1.752	1.231

n.r., not reported; n.d., not detected

[a] Eglinton et al. (1987).

[b] Kawamura and Kaplan (1987).

[c] 2,3-Dimethyl succinic acid.

270 °C after 2 h. The results of these experiments (Table 4) indicate that oxalic acid accounts for more than half of this type of acid.

Similar to the monocarboxylic aliphatic acids, the most thermally immature samples should provide the best assessment of maximum conversion of organic matter to dicarboxylic aliphatic acids. The assumed Type-II kerogen from recent sediment in the Tanner Basin is the most thermally immature and generates the highest yield. However, some caution is warranted in using this yield as a maximum because the organic matter in this unconsolidated sediment may undergo further microbial alteration before it is buried in the subsurface. In addition, this value and the others given by Kawamura and Kaplan (1987) were determined at only one experimental condition (i.e., 270 °C/2 h), which may not be representative of maximum yields attainable under other experimental conditions. Although concerns over this limited data inhibit establishing a maximum conversion of organic matter to dicarboxylic aliphatic acids, it may be stated that at least 0.40 wt% of Type-I kerogen and 0.24 wt% of Type-II kerogen may be converted to C_2–C_{10} dicarboxylic acids.

Minimum conversions of Type-III kerogen to dicarboxylic acids are more difficult to determine. The high conversion of 1.23 wt% given in Table 4 for a humic acid is not representative because this organic extract may only account for 2 to 42 wt% of Type-III kerogens in peats (Vandenbroucke et al. 1985). Similar to the peculiar results on monocarboxylic acids, the same experimental data reported by Pickering and Batts (1992a) on maximum conversions of peats to dicarboxylic acids also occurred at the anomalously low temperature of 200 °C for a 72-h duration. These maximum conversions of extremely immature Type-III kerogens to C_2–C_4 dicarboxylic acids are 0.49 wt% for forest peat and 2.96 wt% for grass peat. Unlike distributions in subsurface waters, succinic acid (C_4) accounted for more than 62 wt% of these maximum yields. Anomalously high concentrations of succinic acid were also observed in their experiments on Australian coals (Pickering and Batts 1992b). More experimental work is clearly needed to fully appreciate the experimental results reported by these investigators.

3.3 Unsaturated Aliphatic Carboxylic Acids

These acids have an aliphatic group that contains one or more double carbon bonds, which determines the degree of unsaturation. More than half of the aliphatic carboxylic acids in most living organisms are unsaturated (Parker 1969). However, double carbon bonds are highly reactive sites and at burial of less than 1-m unsaturated carboxylic acids are typically absent in recent sediments (Rosenfield 1948; Parker and Leo 1965; Rhead et al. 1971). This loss of unsaturated carboxylic acids at low temperatures is considered to be related to bacterial activity within sediment pore waters (Johnson and Calder 1973). Some of these acids survive early diagenesis as indicated by their occasional detection in some sedimentary rocks (Parker 1969). However, their generation from organic matter or persistence with increasing burial depth into the subsurface is not likely to be significant due to their low thermal stability.

Kawamura and Ishiwatari (1985a,b) showed that unsaturated aliphatic carboxylic acids with 16 and 18 carbon atoms rapidly decreased in concentration from samples of Lake Biwa surface sediments with increasing temperatures from 68 to 279 °C for 24 h. Unsaturated C_{18} carboxylic acids were undetectable at 279 °C after 24 h if they contained one double carbon bond, at 229 °C after 24 h if they contained two double carbon bonds, and at 204 °C after 24 h if they contained three double carbon bonds. This decrease in thermal stability with the increasing number of double carbon bonds in the aliphatic group of carboxylic acids is also supported by laboratory heating experiments conducted on green algae (Abelson 1962). In these experiments, the di- and tri-unsaturated C_{18} carboxylic acids were absent after 18 days at 190 °C, but the mono-unsaturated C_{18} carboxylic acid was present.

Two unsaturated aliphatic carboxylic acids generated from sedimentary organic matter in laboratory heating experiments are fumaric acid and maleic acid (Kawamura and Kaplan 1987). Both of these dicarboxylic acids have four carbon atoms with the former having a *trans* configuration and the latter having a *cis* configuration. Fumaric acid is generated in significantly higher concentrations than maleic acid, and accounts for 0.35 to 0.58 wt% conversion of organic matter from Recent sediments (Tanner Basin) and humic acids, respectively at 270 °C after 2 h (Kawamura and Kaplan 1987). This unsaturated acid and its isomer are essential to the metabolism of most plants and animals, which makes its survival past microbial activity during early diagenesis unlikely. This inference is supported in part by the low conversions of 0.007 to 0.008 wt% of organic matter from indurated rock samples of the Monterey and Green River shales, which have passed through early diagenesis (Kawamura and Kaplan 1987). Some analyses of subsurface waters have reported the occurrence of maleic acid but not fumaric acid (Surdam et al. 1984) despite its higher generation yields from heated sedimentary organic matter. This discrepancy may be related to maleic acid being more soluble in water by two orders of magnitude (March 1985, p. 112) and having a significantly lower partition coefficient than fumaric acid (Leo et al. 1971).

3.4 Aromatic Carboxylic Acids

These acids consist of one or more carboxyl groups bound to an aromatic hydrocarbon. The simplest of these acids is benzoic acid (C_6H_5COOH), which has been reported in the reacted waters from hydrous pyrolysis experiments on sedimentary organic matter. Kawamura et al. (1986) observed that only 0.006 wt% of isolated kerogen from Green River Shale occurred as benzoic acid in the reacted water after heating at 300 °C for 10 h. Similarly, Eglinton et al. (1987) observed that isolated kerogen from the Kimmeridge Clay Formation generated only trace amounts (~<0.005 wt%) of benzoic acid in reacted waters after 168 and 720 h at 250 °C. At higher experimental temperatures (i.e., 280 and 330 °C) for 7.2 to 720 h, no benzoic acid was detected in the reacted waters. Hydrous pyrolysis of isolated kerogens in the presence of illite, montmorillonite, and calcite showed no appreciable increase in conversion to benzoic acid after 10 h at 300 °C (Kawamura et al. 1986). However, 0.01 to 0.02 wt% of isolated kerogen converted to benzoic acid when heated in contact with limonite after 7.2 to 720 h at 250 to 330 °C (Eglinton et al. 1987). In addition, minor amounts (0.002 to 0.0066 wt%) of the kerogen were also converted to toluic acid [$H_3C(C_5H_4)CO$] under these conditions. As previously stated, the unlikelihood of ferric oxide minerals occurring under reducing depositional conditions makes this source of aromatic carboxylic acids from petroleum source rocks unlikely.

Other aromatic carboxylic acids that have been reported in trace quantities of subsurface waters associated with petroleum accumulations include phthalic and salicylic acids (Fisher and Boles 1990; Harrison and Thyne 1992). Currently, no heating experiments involving sedimentary organic matter have reported these acids in reacted waters. An important consideration in evaluating the potential of these two acids, as well as benzoic acids, is that their partition coefficients at 25 °C indicate their occurrence is favored in an organic liquid rather than in water (Leo et al. 1971).

4 Organic Acid Generation and Expulsion

Organic acid generation within and expulsion from a petroleum source rock are two additional factors that must be evaluated when considering the effectiveness of these acids as agents of secondary porosity formation. The timing of acid generation and expulsion relative to petroleum generation are of particular importance. If generation of organic acids and petroleum involves independent processes, the experimental observations may not reflect their relative relationships at the higher temperatures and shorter time conditions employed in hydrous pyrolysis experiments. This variation is especially true if the overall reaction rate constants significantly diverge or converge with one another as temperature increases. It is therefore important to understand the relationships between organic acid and petroleum formation under the experimental conditions, and to evaluate these relationships through extrapolations to subsurface conditions in sedimentary basins. Before embarking on this type of evaluation, it is first important to review the current understanding of petroleum formation (i.e., generation and expulsion) as simulated in hydrous pyrolysis experiments.

4.1 Petroleum Formation

An important attribute of hydrous pyrolysis that distinguishes it from anhydrous pyrolysis (i.e., absence of liquid water) is its ability to generate an immiscible oil phase that is expelled from a source rock in a manner considered operative in subsiding sedimentary basins (Lewan 1987, 1992a,b). The expelled oil accumulates on the overlying water surface within the reactor where it may be quantitatively collected at the end of an experiment (Fig. 7). Petroleum formation may be described by this experimental approach in terms of four stages: (1) pre-generation; (2) bitumen generation; (3) oil generation; and (4) pyrobitumen generation (Fig. 8). Organic matter of a source rock in the pre-generation stage consists predominantly (i.e., >95 wt%) of an aggregate of macromolecular organic compounds that are insoluble in organic solvents (e.g., benzene, dichloromethane, and chloroform). This insoluble fraction is referred to as kerogen and the remaining (i.e., <5 wt%) solvent-soluble fraction is referred to as bitumen. As the thermal stress experienced by a source rock increases, the bitumen-

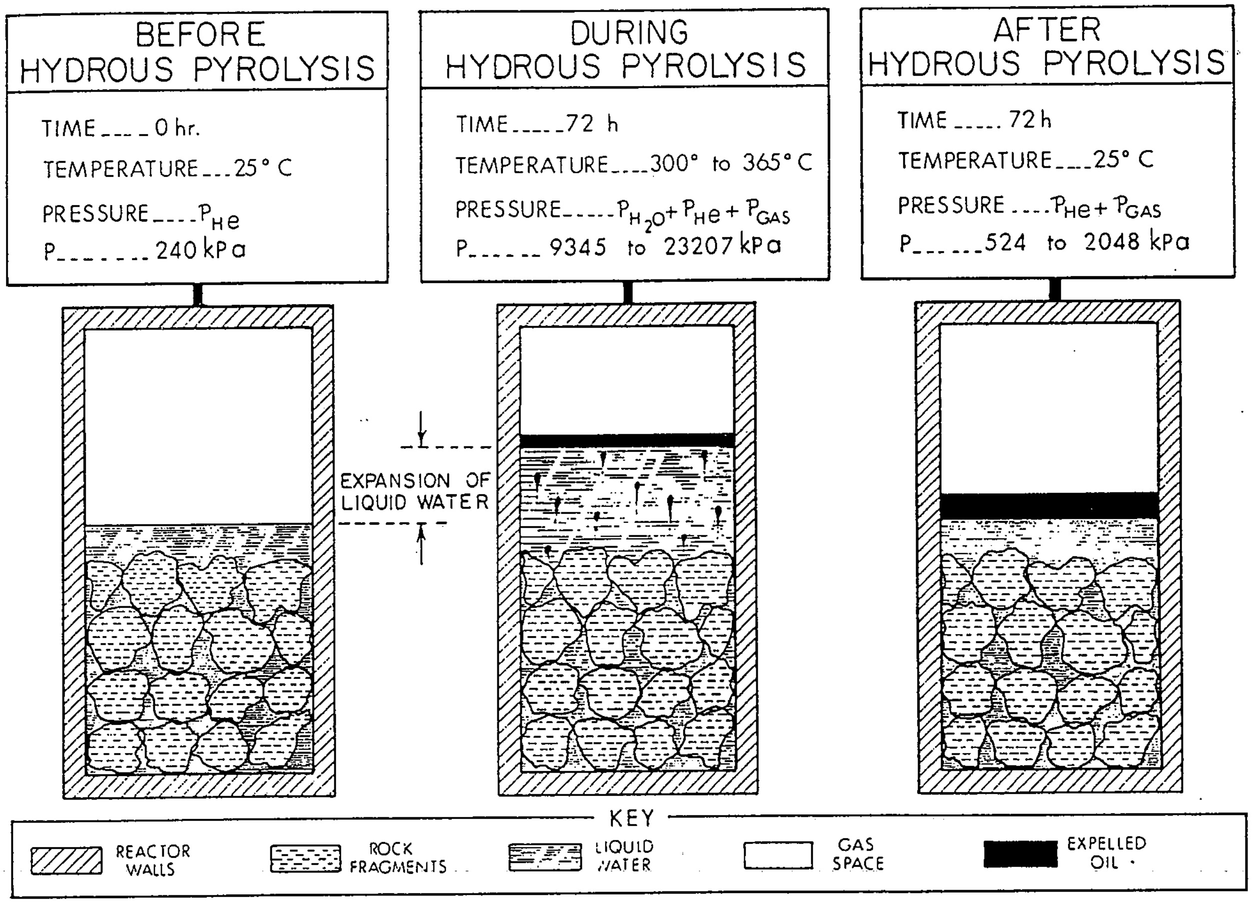

Fig. 7. Diagramatic cross section of physical conditions before, during, and after hydrous pyrolysis of a petroleum source rock (Lewan 1992a). Specifics on experimental procedures are given by Lewan (1993a)

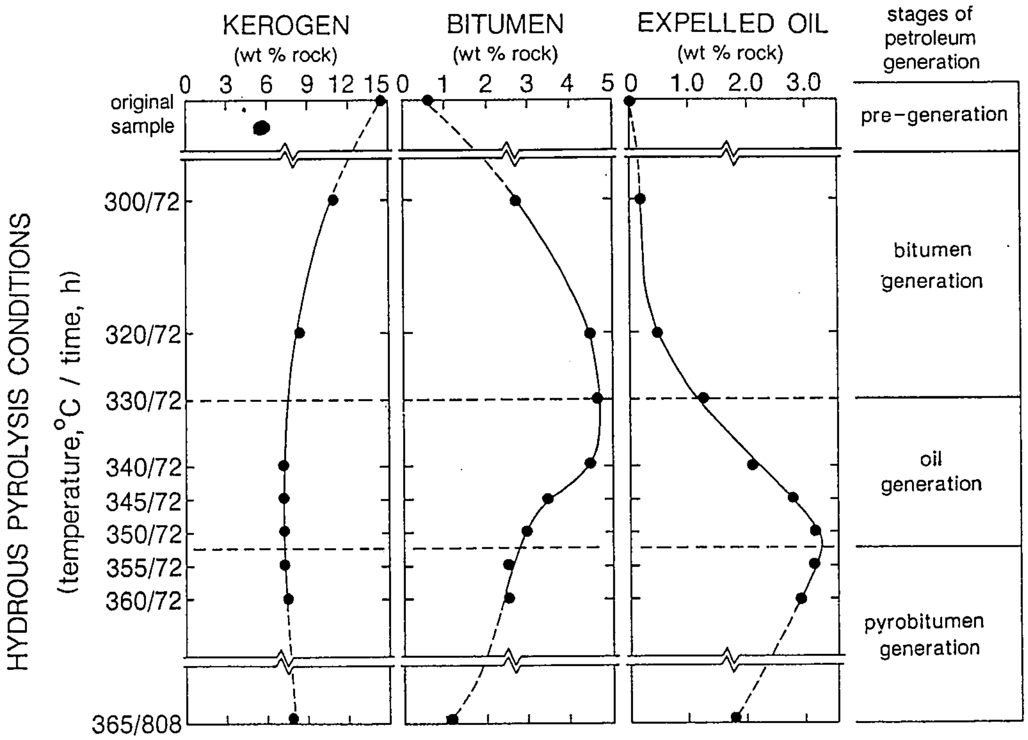

Fig. 8. Changes in kerogen, bitumen, and expelled oil through an isothermal heating series of hydrous pyrolysis experiments conducted on aliquots of Woodford Shale

generation stage commences with the partial decomposition of kerogen to bitumen (Fig. 8). The generated bitumen consists predominantly of high-molecular-weight organics that were originally held in the kerogen by weak noncovalent bonds (e.g., hydrogen bonds, chemical sorption, and electron donor-acceptor complexes). A net volume increase accompanying this overall reaction causes the generated bitumen to expand into the micropores and along bedding-plane partings to form a continuous bitumen network within the source rock. In addition to displacing some of the interstitial water within the rock, several mole percent of the interstitial water is dissolved in the bitumen network (Lewan 1992a).

The amount of interstitial water that may be dissolved in bitumen increases with increasing temperature and is two orders of magnitude greater than the amount of hydrocarbon that may be dissolved in water (Lewan 1992a). A water-saturated bitumen network within a source rock is maintained during hydrous pyrolysis by the excess water surrounding the rock sample within the reactor. This excess water in the natural system occurs in fractures and faults that dissect source rocks, and in porous strata adjacent to source rocks. As discussed by Lewan (1992a,b), dissolved water is chemically and physically important to the oil-generation stage, which involves partial decomposition of the bitumen network to an expelled immiscible oil (Fig. 8). Data suggest that the dissolved water acts as a hydrogen donor to terminate free-radical sites and as an oxygen donor, to generate excess carbon dioxide (Lewan 1992a). Termination of free-radical sites with water derived hydrogen retards thermal cracking, carbon-carbon bond cross-linking, and aromatization, which reduces pyrobitumen generation (Lewan and Winters 1991). Physically, the dissolved water in the bitumen allows an immiscible oil phase to separate from the water-saturated bitumen network. Under anhydrous conditions, the lack of dissolved water in the bitumen network does not allow formation of an immiscible oil phase.

The cleavage of covalent bonds in the partial decomposition of water-saturated bitumen to an immiscible oil is accompanied by a net volume increase in the resulting organic products (Lewan 1987). If the bitumen network fills the preexisting porosity of a source rock, the volume increase caused by the generation of immiscible oil will not be accommodated within the confining rock matrix. As a result, generated immiscible oil is expelled from the bitumen impregnated rock into the surrounding water and buoys to the water surface within the reactor where it accumulates. It is envisaged in the natural system that the immiscible oil is expelled into preexisting regional fractures that typically dissect source rock. These types of fractures typically occur in orthogonal sets that are parallel to the long and short axes of the basins in which they developed (Nelson 1985). Their ubiquitous character in near-horizontal strata, early development after induration of sediment to rock, and persistence with burial depth (Lorenz et al. 1991) makes regional fracture systems excellent water reservoirs for maintaining water-saturated bitumen networks in maturing source rocks. In addition, these water-filled fractures may serve as conduits for migration of expelled oil by buoyancy through a source rock or into adjacent permeable carrier beds.

The pyrobitumen-generation stage follows the oil-generation stage as thermal stress increases (Fig. 8). Immiscible oil and remaining bitumen from the oil-generation stage thermally decompose to pyrobitumen and gas during this stage. Pyrobitumen is defined as organic matter that has become insoluble in organic solvents as a result of thermal stress. This insolubility is caused by polymerization through carbon-carbon bond cross-linking and subsequent aromatization through disproportionation of cyclic structures. It is not feasible to separate pyrobitumen from matured kerogen, and as a result, there is an apparent increase in kerogen during this stage (Fig. 8). Lewan (1992a,b) has shown that in the absence of liquid water, the oil-generation stage is reduced and the pyrobitumen-generation stage is enhanced.

4.2 Kinetics and Bonding

Acetic acid is the most abundant and studied organic acid generated from source rocks, and therefore it will be the focus of this and subsequent discussions. Although this acid may have several different precursory link-

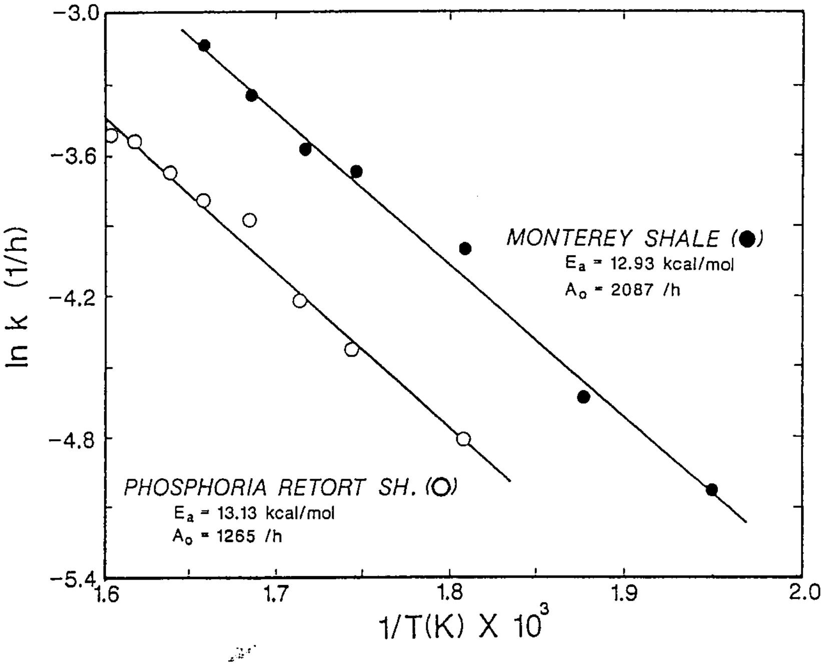

Fig. 9. Arrhenius plot for acetic acid generation from hydrous pyrolysis experiments conducted on the Monterey and Phosphoria Retort shale (Fig. 5). Calculated activation energies (E_a) and frequency factors (A_o) assume a first-order rate law

ages in sedimentary organic matter, its generation in hydrous pyrolysis experiments may initially be treated as one overall reaction. A first approximation of this type is shown by the Arrhenius plots for acetic acid generation from the Monterey and Phosphoria Retort shales in Fig. 9. First-order reaction rates are assumed and calculated on the basis of maximum yields observed in Fig. 5. The resulting linear expressions give similar activation energies (E_a) and frequency factors (A_o) for acetic acid generation from both rocks. Activation energies of 13 kcal/mol are too low to represent cleavage of covalent bonds, which typically have activation energies in excess of 40 kcal/mol for oil generation in hydrous pyrolysis experiments (Lewan 1985; Hunt et al. 1991). It should be noted that these low activation energies for acetic acid generation include energy consumed in transporting acetic acid through the bitumen network of the rock into the surrounding water. Therefore, the activation energies responsible for cleavage of these weak noncovalent bonds are likely to be lower and more in the range of hydrogen bonding for dimeric carboxylic acids (6 to 9 $\mathrm{kcal\,mol^{-1}\,bond^{-1}}$; Lewis and Randall 1960). This type of bonding is supported by the low activation energy of 5.4 kcal/mol determined for acetic acid generation from hydrous pyrolysis of Kimmeridgian oil shale by Barth et al. (1989). An integral method that did not require a maximum yield for determining first-order rate laws was used to derive this activation energy. This approach avoids the problem of underestimating maximum yield due to acid destruction, which results in higher activation energies.

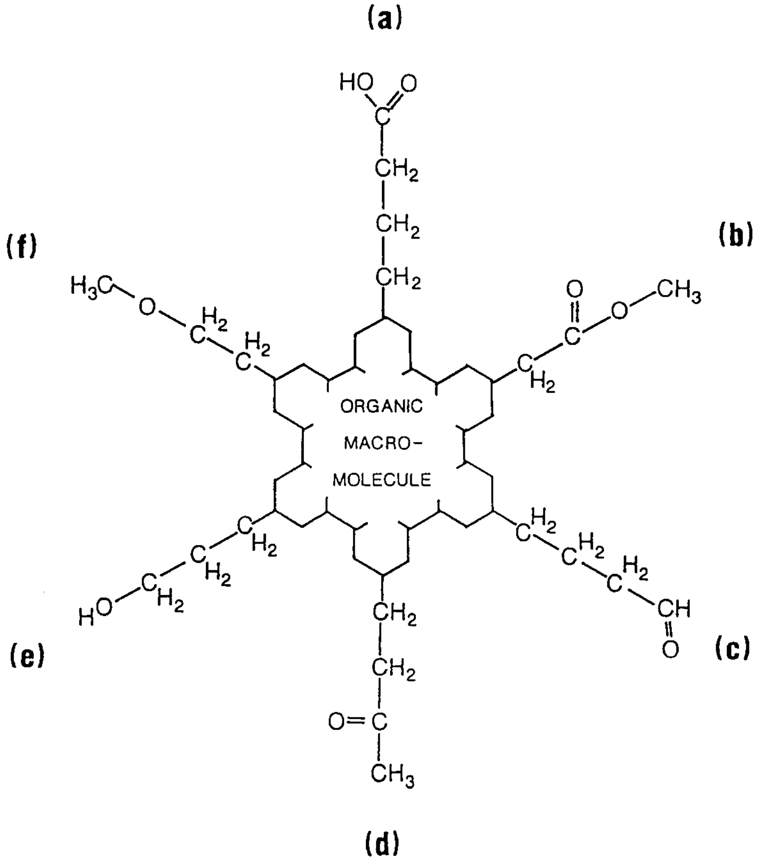

Fig. 10. Diagramatic representation of oxygen-functionalized aliphatic chains covalently bound to an organic macromolecule in bitumen or kerogen: **a** aliphatic carboxylic acid; **b** ester; **c** ketone; **d** aldehyde; **e** alcohol; and **f** ether

An important implication of these low activation energies is that carboxylic aliphatic chains covalently bound to carbon constituents in sedimentary organic matter (Fig. 10a) are not likely to be a source of acetic acid. This unlikelihood is also apparent because the covalent bond between the carboxylic carbon and the adjacent aliphatic carbon is weaker than the covalent bond between aliphatic carbon-carbon bonds in the hydrocarbon chain. Therefore, decarboxylation of the carboxylic group is more likely to occur than the cleavage of aliphatic carbon-carbon bonds. Aliphatic carboxylic-acid side chains may also result from the cleavage of a primary carbon ($\cdot CH_3$) at the end of an ester side chain (Fig. 10b). However, decarboxylation of this carboxylic group to form CO_2 is again more likely than cleavage of the stronger bond between the secondary aliphatic carbons ($\cdot CH_2 \cdot$) to form acetic acid.

Another consideration is the working hypothesis that water dissolved in the bitumen network of a source rock oxidizes carbonyl groups to form carboxylic groups, which decarboxylate with increasing thermal stress to form excess CO_2 (Lewan 1992b). Oxidation of carbonyl groups in aldehyde side chains (Fig. 10c) by water would only result in the formation of a carboxylic aliphatic chain. Similar to preexisting carboxylic-aliphatic and ester side chains, the aldehyde-derived carboxylic aliphatic chains are likely to be only a source of CO_2 and not an aliphtic carboxylic acid. However, oxidation of carbonyl groups in ketone side chains (Fig. 10d) by water may result in the formation of acetic acid. This reaction would occur due to oxidative cleavage of the weaker bond between the carbonyl carbon and their secondary aliphatic carbon ($\cdot CH_2 \cdot$), rather than the stronger bond between the carbonyl carbon and the primary aliphatic carbon ($\cdot CH_3$). Although this form of oxidation by water may source some acetic acid, the lack of an increase in the slope of the Arrhenius plots (Fig. 9) at higher temperatures suggests it is not significant.

It appears that acetic acid, as well as the other short-chain (C_3 to C_5) carboxylic acids, represent initial components formed during early diagenesis that are not covalently bound into condensing higher-molecular-weight organic components. As condensation of macromolecules proceeds to form insoluble organic matter, more favorable sites for hydrogen bonding of the unassimulated short-chain carboxylic acids become available. Covalently bound high-molecular-weight organic components with carboxylic acid groups make the most favorable sites for hydrogen bonding with the short-chain carboxylic acids, but other oxygen-bearing functional groups covalently bound into the organic matter (Fig. 10b–f) may also act temporarily as hydrogen-bonding sites. The amount of available carboxylic acid sites for hydrogen bonding is more than sufficient when one considers that Type-II kerogens have 15 to 19% of their oxygen as undifferentiated carboxylic acid groups (Tissot and Welte 1984, p. 154; Behar and Vandenbroucke 1987) and only 5 to 10% of their oxygen occurs as short-chain carboxylic acids after hydrous pyrolysis experimentation. Hydrogen bonding reactions are reversible, and the making and breaking of these bonds over time are likely to result in most of the short-chain carboxylic acids being associated with the more stable covalently bound carboxylic acid groups. Another implication of the reversibility in making and breaking of these weak noncovalent bonds is that no transport of short-chain carboxylic acids out of the sedimentary organic matter is likely without the occurrence of a diffusion gradient within or fluid expulsion from a source rock.

4.3 Expulsion Timing and Mechanisms

Although organic acids generated from source rocks have been considered to be responsible for secondary porosity, research and discussion have not focused on mechanisms by which these acids are expelled from a source rock. Three periods for expulsion of organic acids are envisaged. The first period relies on diffusion prior to bitumen generation, the second period relies on diffusion after a bitumen network has been generated, and the third period relies on bulk flow during oil expulsion. The first period of expulsion occurs after lithification of the sediment and prior to the thermal decomposition of kerogen to bitumen (i.e., early diagenesis). Organic matter in a source rock during this period consists predominantly (>95 wt%) of insoluble kerogen typically dispersed as insular domains within a mineral matrix having a water-filled pore system. Periodic cleavage of hydrogen bonds between short-chain carboxylic acids and kerogen allows the released acid to diffuse into the water-filled pore system and eventually through water-filled fractures that typically dissect source rocks. The chemical potential necessary to drive this diffusion would be the higher affinity of short-chain carboxylic acids to reside in a water phase than an organic phase, as demonstrated by their low partition coefficients (Fig. 1).

Sufficient data are not available to conduct a rigorous evaluation on the significance of this period of early diffusion. However, a general assessment may be made assuming one-dimensional diffusion in a semi-infinite homogenous pore water system, a constant concentration of acids at the kerogen-water interface, and no acids in the pore water at the start of the diffusion process. Under these assumptions, the distance (x) and time (t) required for diffusing acids to reach a given concentration (C) may be calculated using the expression

$$C = C_o erfc\left\{\frac{x}{2(Dt)^{1/2}}\right\},$$

which is derived by a Laplace transform of Fick's second law (Crank 1979, p. 20–21). D is the diffusion coefficient and C_o is the initial concentration of a diffusing acid at a given temperature. Considering the time (t) and distance (x) at which a diffusing acid front would reach half of its initial concentration (i.e., $C/C_o = 0.50$) gives the expression

$$erfc\left\{\frac{x}{2(Dt)^{1/2}}\right\} = 0.50.$$

Based on tabulated error-function complements (*erfc*; Crank 1979, p. 375), the bracketed term must equal 0.4772 in this expression, which reduces to the expression

$$x = 0.9544(Dt)^{1/2}.$$

This reduced expression allows one to calculate the distance at which diffusing species reach half of their initial concentration in a specified amount of time (t) by knowing their diffusion coefficients (D). Assuming effective diffusion coefficients of 10^{-12} to $10^{-11}\,m^2 s^{-1}$ for dissolved hydrocarbon gas diffusion through source rocks (Krooss 1987) are similar in magnitude to short-chain carboxylic acids, the significance of early diffusion prior to bitumen generation may be evaluated. For example, half of the initial organic-acid concentration will occur only 93 to 293 m from the kerogen-water interface after 300 million years at 25 °C. This approximation represents maximum distances because the calculation does not include the rate of hydrogen-bond cleavage, which may reduce the overall rate.

Although the sluggishness of this process is not likely to generate timely nor significant concentrations of organic acids to generate appreciable secondary porosity, it may account for the lower yields of short-chain carboxylic acids generated by hydrous pyrolysis of the older Phosphoria Retort Shale (Permian) relative to the younger Monterey (Miocene) and Kreyenhagen (Oligocene-Eocene) shales (Table 3). In addition, the flux of acetic acid diffusing out of a source rock is likely to be greater than that of the C_3 through C_5 carboxylic acids, because of its greater affinity for water (Fig. 1) and higher diffusion coefficient (Oelkers 1991). As a result, one would expect preferential depletion of acetic acid in a rock with increasing geologic time. This preferential depletion may explain in part the significantly lower absolute (Table 3) and relative (Fig. 6) concentrations of acetic acid generated from the Phosphoria Retort Shale of Paleozoic Age relative to the Monterey and Kreyenhagen shales of Tertiary age. Other variations in the amount of generated acetic acid may be attributed to interactions with minerals along its diffusion pathways within a source rock as suggested by Giles and Marshall (1986). It should be noted that this early diagenetic process is not simulated by hydrous pyrolysis.

The second period of expulsion is after the development of a bitumen network and before the bitumen partially decomposes to an immiscible oil. Expulsion of short-chain carboxylic acids dispersed in the bitumen network is envisaged to occur by their diffusion into water-filled fractures dissecting a source rock and adjacent rock units. Diffusion of the acids from the bitumen network at fracture surfaces into water-filled fractures is expected to be faster than diffusion during the first expulsion period because of higher effective diffusion coefficients resulting from a decrease in tortuosity. Although a two-order of magnitude increase in the diffusion coefficient may be expected (10^{-10} to $10^{-9}\,m^2\,s^{-1}$; Thomas 1989), this increase suggests that half of the initial organic acid concentration in the bitumen network will only diffuse 54 to 534 m from the interface in 10 m.y. Once again, this approximation represents maximum distances under the previously stated assumptions. In addition, the higher solubility of short-chain carboxylic acids in water than in an organic liquid (Fig. 1) indicates that the flux of these diffusing acids through a bitumen network to a fracture surface may control and lower the flux of these diffusing acids through a water-filled fracture. More experimental work is needed to fully assess this period of expulsion, but first approximations suggest that timely and sufficient concentrations of short-chain carboxylic acids from this expulsion period are only likely to be agents of secondary porosity on a localized scale in rocks immediately adjacent to maturing source rocks.

The third period of acid expulsion is envisaged to coincide with the expulsion of immiscible oil as it is generated from the partial decomposition of the bitumen network. As shown in Fig. 11, the amount of aliphatic

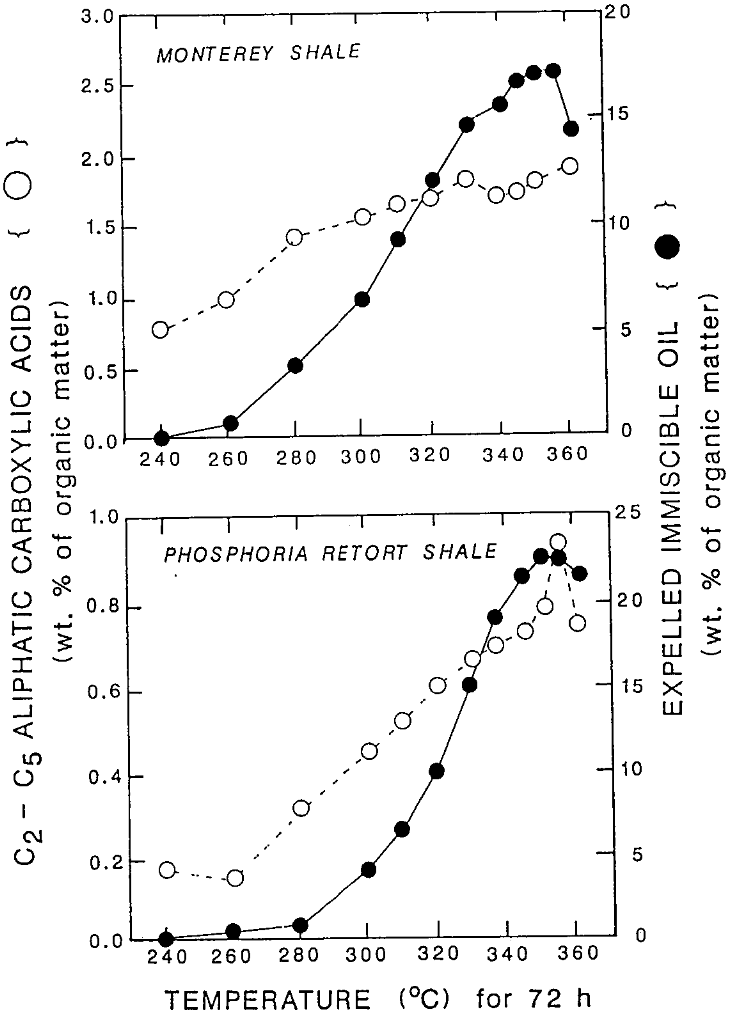

Fig. 11. Plots of expelled immiscible oil and aqueous C_2–C_5 monocarboxylic acids generated through a series of isothermal hydrous pyrolysis experiments conducted on aliquots of Monterey and Phosphoria Retort shales

carboxylic acids in the recovered water of hydrous pyrolysis experiments increases with the amount of expelled immiscible oil. Comparison of the two source rocks shows that there is no direct nor constant relationship between amounts of expelled immiscible oil and organic acids. Additional research is needed to elucidate the factors responsible for these relationships, but the amount of organic acids lost prior to this period of expulsion and the effects of mineral and organic matter composition on partitioning of organic acids between bitumen and immiscible oil are likely factors worth considering. Despite this uncertainty, mass flow of expelled immiscible oil bearing dissolved organic acids from a source rock may be a viable expulsion mechanism. Organic acids dissolved in expelled oil may repartition into formation waters during secondary migration of oil through carrier beds or during entrapment of oil in reservoir rocks as pressures, temperatures, or water salinities decrease.

The effects of temperature, pressure, and water salinity on partitioning of aliphatic carboxylic acids between oil and water phases are not currently known. However, some qualitative insights on the effects of these variables on partition coefficients may be evaluated from experiments conducted by Knaepen et al. (1990). Their experiments determined the partition coefficients for pentanol-1 and ethylacetate in isooctane/water or North Sea oil/water systems at different temperatures (22 to 150 °C), water salinities (0 to 10 wt% NaCl), and gas/oil ratios (0 to 230 v/v). An increase in temperature from 22 to 150 °C increased the partition coefficient for pentanol-1 in the isooctane/water system sevenfold. A water salinity of 10 wt% NaCl at 22 °C has a partition coefficient for pentanol-1 that is almost threefold greater than pure water. The amount of dissolved methane in North Sea oil as determined by gas/oil ratios has only a minor effect on the partition coefficient of ethyl acetate at room temperature, but at 96 °C the partition coefficient increases twofold.

Assuming similar changes in partition coefficients for short-chain carboxylic acids, these acids may be released from the source rocks during hydrous pyrolysis experiments as dissolved species in the expelled immiscible oils at the experimental temperatures (240 to 365 °C). As the experiments cool to room temperature after the 72-h isothermal heating, these acids may diffuse into the water phase as their partition coefficients decrease as a result of the falling temperature. Condensation of H_2O vapor to reduce the water salinity and the release of dissolved methane from the expelled oil would accompany this fall in temperature and further augment the decrease in the partition coefficients. Similarly, in subsiding sedimentary basins, short-chain carboxylic acids not lost to diffusion prior to oil expulsion may be released from source rocks as dissolved species in expelled oils. As these oils cool, degas, or encounter low salinity waters during migration and entrapment, the dissolved short-chain carboxylic acids may be redistributed in adjacent formation waters.

An obvious implication of this third period of expulsion is that porosity enhancement by organic acids is most likely to occur during or after oil expulsion rather than before it. As a result, oil migration pathways may be lined with enhanced porosity because of the release of organic acids into adjacent formation waters. Similarly, enhanced porosity may occur in reservoirs as a result of the release of organic acids from entrapped oil into peripheral formation waters. Amounts of organic acids within formation waters associated with oil reservoirs will be determined in part by the amount of water the reservoired oil encountered during migration and the differential in temperature, dissolved gas content, and water salinity between the source rock and the reservoir. An additional control is the amount of organic acids lost from a source rock by the first and second periods of diffusion prior to oil generation and expulsion.

4.4 Kinetic Modeling

Kinetic modeling based on laboratory experiments has become a common practice in trying to predict the occurrence of kinetically controlled reactions in sedimentary basins (Whitney and Lewan 1992). For example, kinetic parameters determined for oil formation (i.e., generation and expulsion) from hydrous pyrolysis experiments have been shown to extrapolate well to lower temperatures and longer geologic times encountered by source rocks during their subsidence in sedimentary basins (Hunt et al. 1991; Hunt and Hennet 1992). The success of these extrapolations is attributed to similar reaction mechanisms and pathways over a wide temperature range (100 to 350 °C) and to the expulsion of oil from a source rock being a direct consequence of oil generation within a source rock (Lewan 1993b). The similarity of organic acid compositions between recovered hydrous pyrolysis waters and natural subsurface waters suggests that the reaction mechanisms and pathways responsible for their generation within source rocks are also similar over a wide temperature range. However, the processes responsible for their expulsion from a source rock (i.e., diffusion and oil expulsion) are independent of organic acid generation. As a result, kinetic parameters determined from hydrous pyrolysis experiments cannot be used without taking into account these expulsion processes. This problem may be illustrated by the kinetic parameters derived from hydrous pyrolysis experiments on the Monterey Shale (Fig. 9). A simple calculation using these kinetic parameters in the Arrhenius equation for a first-order rate law indicates that essentially all of the acetic acid is generated and expelled from the Monterey Shale after 1000 years at 27 °C. Paradoxically, this sample resided at this or slightly higher temperatures for more than 5 million years before the experiments were conducted. Kinetic parameters for organic acid formation that avoid this paradox have been derived by assuming a distribution of activation energies and a single frequency factor (Braum et al. 1992; Knauss et al. 1992; Barth and Nielsen 1993). These kinetic parameters are commonly similar to kinetic parameters derived in the same manner for oil formation (Knauss et al. 1992) and may be significantly different for the same type of organic matter in different samples from the same locality and rock unit (Barth and Nielsen 1993). Although these curve-fitting methods avoid the time paradox without considering expulsion processes, their scientific reality remains questionable (Lakshmanan et al. 1991).

5 Conclusions

Laboratory pyrolysis experiments are the most effective means of assessing the amounts and types of organic acids derived from petroleum source rocks. This approach requires careful consideration of experimental conditions within the natural constraints of subsiding sedimentary basins. The role of water and its chemistry in organic acid generation is not completely understood, but experiments conducted without water result in reduced concentrations and deviate from the water-saturated state of sedimentary basins. Kinetic controls on organic acid generation require experiments to use higher temperatures for shorter durations to compensate for the lower temperatures and longer durations experienced in sedimentary basins. This substitution of temperature for time appears to be appropriate between temperatures of 200 and 360 °C for 72- to 360-h durations. Within these experimental conditions, no high-temperature artifacts are apparent and generated organic acids are similar in type and distribution to those in natural subsurface waters.

Experimentally simulating natural processes responsible for organic acid generation may best be approached with whole-rock samples that are larger than 62 μm in size and not preextracted with organic solvents. This type of sample insures natural contacts between minerals, organic matter, and pore waters, which are not simulated by experiments using isolated kerogens or unconsolidated artificial mixtures of isolated kerogens and powdered minerals. Differences in the partitioning of organic acids between water and organic liquids (i.e., bitumen and oil) require consideration of organic liquid to water ratios and product collection procedures. Another experimental consideration is the composition of reactor wall surfaces. Borosilicate glass has been shown to cause more alteration to organic acid concentrations and distributions than fresh metal surfaces of stainless steel-316. Carburized reactor walls reduce the effects of stainless steel-316 but carburized Hastelloy-C276 appears to impose the least effect on the overall water chemistry of an experiment. Experimental fluid pressures do not appear to influence organic acid generation below 60 MPa. No data are currently available on the influence of water chemistry, particularly salinity, on organic acid generation.

Acyclic aliphatic carboxylic acids are the most prevalent organic acids generated from petroleum source rocks. These acids may contain as many as 32 carbon atoms, but partition coefficients indicate that only those with fewer than five carbon atoms are likely to be important in geological processes mediated by water. Similar to organic acid concentrations in natural subsurface waters, acetic acid (C_2) usually dominates among these C_1–C_5 acids, and formic acid (C_1) usually occurs below detection limits. Changes in concentration and distributions of these generated C_2–C_5 acids with increasing experimental temperatures are variable for different rock units bearing the same kerogen types. These variations may be attributed in part to differences in the level of early diagenesis samples experienced before being subject to pyrolysis experiments. Rocks at higher levels of early diagenesis (i.e., low atomic O/C ratios of kerogen) may have preferentially lost more of their acetic acid and to a lesser extent propionic acid through diffusion than rocks at lower levels of early diagenesis (i.e., high atomic O/C ratios of kerogen). Therefore, petroleum source rocks at the lowest level of early diagenesis following the terminus of microbial activity provide the best assessment of maximum acid-generation potential. Maximum yields of these monocarboxylic aliphatic acids typically occur at 350 °C after 72-h durations, which are similar conditions for maximum oil generation. Available experimental data indicate that maximum conversions of organic matter to acetic acid are 2.17 wt% for Type-II kerogen, 2.01 wt% for Type-III kerogen, and 0.53 wt% for Type-I kerogen. Sufficient data are available to accept the maximum conversion for Type-II kerogen, but more experimental work is needed to confirm the maximum conversions for Types-I and -III kerogens. Dicarboxylic aliphatic acids are not as thermally stable as the monocarboxylic aliphatic acids, and from limited data reach maximum yields at experimental temperatures below 300 °C for durations of less than 72 h. Oxalic acid is the most dominant of the dicarboxylic acids generated. More experimental data are needed to determine maximum conversions of organic matter to these acids, but available data indicate at least 0.15 wt% of Type-II kerogen and 0.24 wt% of Type-I kerogen convert to oxalic acid. Significantly higher yields of mono- and dicarboxylic acids have been generated in experiments utilizing an iron oxide with isolated kerogen. However, it is unlikely that iron oxides would coexist with organic matter under the reducing conditions associated with depositional environments under which petroleum source rocks accumulate.

Low activation energies (<13 kcal/mol) determined for the overall generation of acetic acid indicate that it is retained in sedimentary organic matter by weak noncovalent bonds. Hydrogen bonding of carboxylic oxygens in acetic acid with other oxygen functional groups covalently bound in the sedimentary organic matter is one possibility that may also apply to the other short-chain carboxylic acids. This lack of covalent-bond cleavage in their generation implies that carboxylic aliphatic chains covalently bound to macromolecules in sedimentary organic matter are not likely sources of these acids. Instead, these carboxylic aliphatic chains are more likely to decarboxylate to form carbon dioxide than cleave from a macromolecule to form a short-chain carboxylic acid. Therefore, the potential for a source rock to generate short-chain carboxylic acids may be controlled by the amount of short-chain carboxylic acids assimilated through weak noncovalent bonding into sedimentary organic matter during its early development into kerogen.

Three expulsion periods are envisaged for the release of short-chain carboxylic acids from source rocks. The first period occurs during early diagenesis before thermal stress is sufficient to generate a bitumen network within a source rock. The higher affinity of short-chain carboxylic acids for water establishes a diffusion gradient from kerogen domains through pore-water systems within the rock matrix. This sluggish diffusion process is not likely to expel sufficient quantities of these acids in a timely manner to generate secondary porosity. However, the effectiveness of this diffusion process over long periods of geologic time may explain the low yield of these acids from pyrolysis experiments conducted on older rocks near the end of early diagenesis. The second period is also diffusion controlled and occurs after a bitumen network has been established within a rock matrix. Again, the higher affinity of short-chain carboxylic acids for water establishes a diffusion gradient from the bitumen network through water-filled fractures dissecting the source rock. This period of expulsion is also sluggish and may only enhance porosity locally in adjacent rocks.

The third expulsion period occurs during the expulsion of oil from a source rock. Short-chain carboxylic acids are released from a source rock as dissolved species in an expelled oil. As the expelled oil cools, degasses, or encounters lower salinity waters along its migration pathway or within its reservoir, these dissolved acids regain their affinity to diffuse into adjacent formation waters. If the concentrations of these diffusing acids are sufficient, secondary porosity may occur along migration pathways and near oil-water interfaces in reservoirs. Secondary porosity development envisaged for this expulsion period occurs during or after petroleum formation and not before it. Additional research addressing the effects that temperature, pressure, water salinity, and oil composition have on the partition coefficients of organic acids is needed.

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