

CHAPTER 4

AQUEOUS ORGANIC GEOCHEMISTRY AT HIGH TEMPERATURE/HIGH PRESSURE

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1. Introduction

The discovery in 1977 of active hydrothermal venting and associated mineralization at the seafloor spreading center of the Galapagos (Corliss *et al.*, 1979) initiated extensive surveys of global ridge-crests. Hydrothermal systems associated with ocean spreading centers are now recognized as a relatively common phenomenon and are thus one of the most actively researched topics in geology, biology and geochemistry. The morphology, mineralization, and fluid chemistry of the active systems in spreading centers has been reviewed (e.g. Barrett and Jambor, 1988; Rona, 1988; Rona *et al.*, 1983; Von Damm, 1990) and related to ancient deposits (e.g. Franklin *et al.*, 1981; Scott, 1985). Other non-rift areas with analogous hydrothermal systems are tectonically active subduction zones, fracture zones, and back-arc basins. The active seafloor systems are a major niche for fauna carrying out chemosynthetic biochemistry. This and the characterization of new species is now a main topic in biology (e.g. Childress, 1988; Grassle, 1985; Jones, 1985; Tunnicliffe, 1991). The geochemistry of vent fluids, interstitial fluids in sediments, and organic matter associated with hydrothermal systems are also a major research effort (e.g. Edmond and Von Damm, 1983; Gieskes *et al.*, 1982a,b, 1988; Simoneit, 1990; Simoneit *et al.*, 1984; Von Damm, 1990).

It is the purpose of this chapter to provide a description of the fate and chemical alterations of organic matter under hydrothermal conditions, with a brief overview of the geographic localities where these processes have been studied to date. Two major but overlapping aspects will be considered: (a) Alteration and degradation processes and reactions, both reductive and oxidative, and (b) synthesis processes and reactions that are primarily reductive.

Petroleums generated in high temperature and high fluid flow regimes are defined here as hydrothermal because the agent of thermal alteration and mass transfer, hot circulating water (temperature range – warm to > 350°C), is responsible for organic matter alteration (generally reductive), and product expulsion and migration from the source rocks or unconsolidated sediments (Didyk and Simoneit, 1989, 1990). These oils generally contain disequilibrium reaction products comprised of reduced and oxidized species (e.g. benzene vs. methylcyclopentane, cholestane vs. Diels' hydrocarbon). In contrast, conventional oils are derived products of basin evolution and are generated contemporaneously

with sediment compaction and heating (temperature window – warm to ~150°C). Generation of hydrothermal oils and gases is a geologically rapid process, taking place within 100's to 1000's of years (Peter *et al.*, 1991), whereas geothermal oils are generated at a rate that is tied to basin subsidence occurring over millions of years (Tissot and Welte, 1984; Hunt, 1979; Hunt *et al.*, 1991).

2. Alteration/Degradation Processes and Reactions

2.1. GEOLOGICAL LOCALES WITH HYDROTHERMAL ORGANIC PRODUCTS

2.1.1. Marine sedimented systems

The locations with known hydrothermal activity and associated mineralization at seafloor spreading centers (divergent plate boundaries) currently number about 100 and are catalogued in the reviews by Rona (1984, 1988). Those with associated organic matter alteration are indicated on the tectonic sketch map in Fig. 1. Both of these lists are expected to expand as exploration continues. Two continental systems are also shown in Fig. 1.

Guaymas Basin (Fig. 1) is an actively spreading oceanic basin (2000 m water depth in the rifts) where sedimentation is rapid (> 2 m/1000 yr) covering the rift floors to a depth of ~300-500 m (Curry *et al.*, 1982). The organic matter of these recent sediments is derived primarily from diatomaceous and microbial detritus and averages about 2% organic carbon. Numerous hydrothermal mounds rise to 20-30 m above the south rift floor and most are actively discharging vent fluids with water temperatures ranging from warm up to 350°C at ~200 bars (e.g. Fig. 2; Lonsdale, 1985; Lonsdale and Becker, 1985; Sayles *et al.*, unpublished data). The mounds are composed of complex deposits of sulfide, sulfate, silicate and carbonate minerals, and petroleum (Peter, 1986; Koski *et al.*, 1985; Simoneit, 1985a,b). They are covered with colonies of tube worms, bacterial mats and other chemosynthetic organisms (Jones, 1985). Typical oils from this basin are depleted in aliphatic hydrocarbons compared to normal crude oils (Didyk and Simoneit, 1990). The *n*-alkane distributions (e.g. Fig. 3a) have diverse ranges and carbon number maxima, generally from CH₄ to > C₄₀, with usual maxima in the mid-C₂₀ region and no carbon number predominance (CPI, carbon preference index = 1.0) (Kawka and Simoneit, 1987). The generation of the complete suite of saturated (reduced) biomarkers (tracer compounds) from their biological precursors is additional evidence for the strongly reductive process operating during initial organic matter alteration. The major resolved peaks in the aromatic/naphthenic fraction are unsubstituted polynuclear aromatic hydrocarbons (PAH, Fig. 3c), a group of compounds uncommon in petroleum but ubiquitous in high temperature (> 250°C) pyrolysates (Geissman *et al.*, 1967; Blumer, 1975; Hunt, 1979). The dominant analogs are the pericondensed aromatic series (e.g. phenanthrene I, chemical structures are given in Fig. 4, pyrene II, chrysene III, etc.) (Kawka and Simoneit, 1990), and their pyrolytic origin is further supported by the presence of PAH with five-

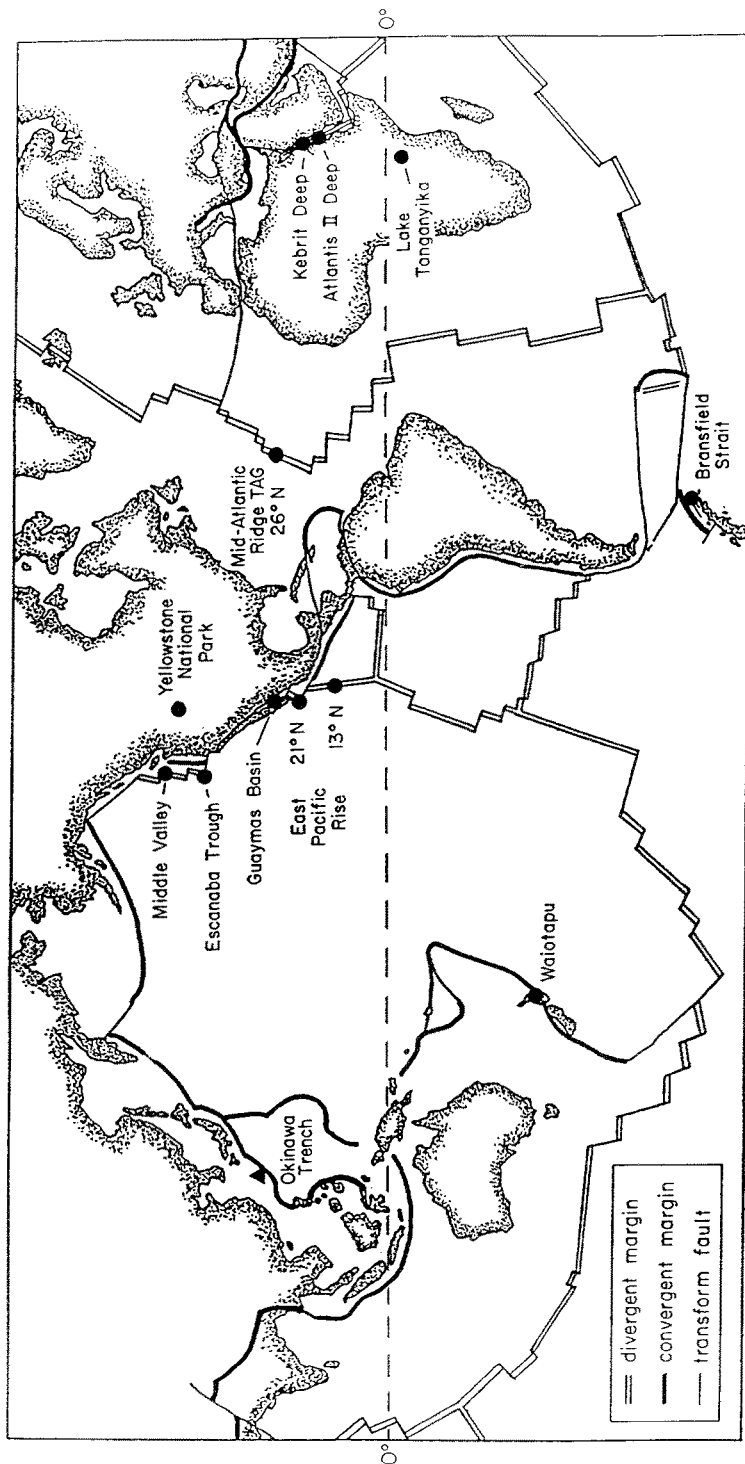


Fig. 1. General location map of the hydrothermal vent fields discussed here with the sketched global tectonics.

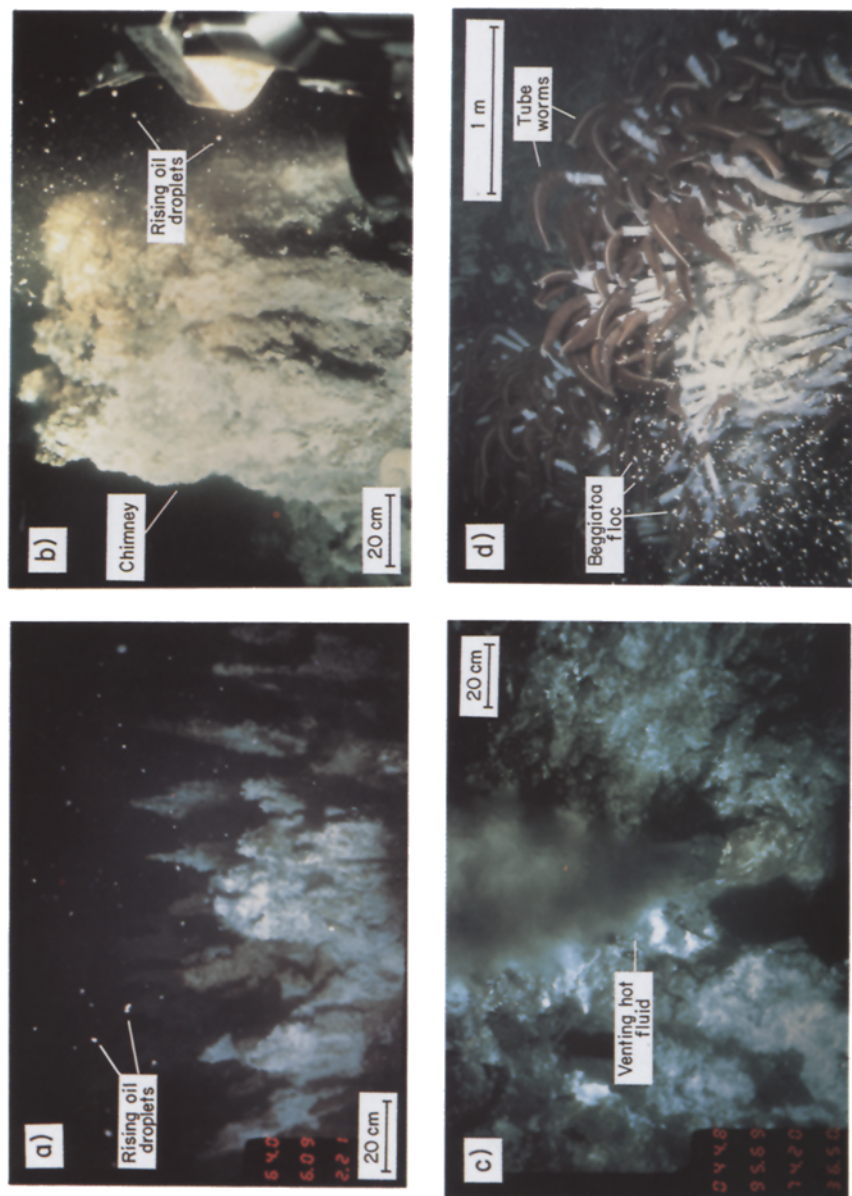


Fig. 2. Photographs of examples of Guaymas Basin vent systems: (a) petroleum rising from top of mound with small chimneys, (b) petroleum rising from base of chimney, (c) vent discharging hot fluid, (d) mound macrofauna (tube worms and *Beggiatoa* floc).

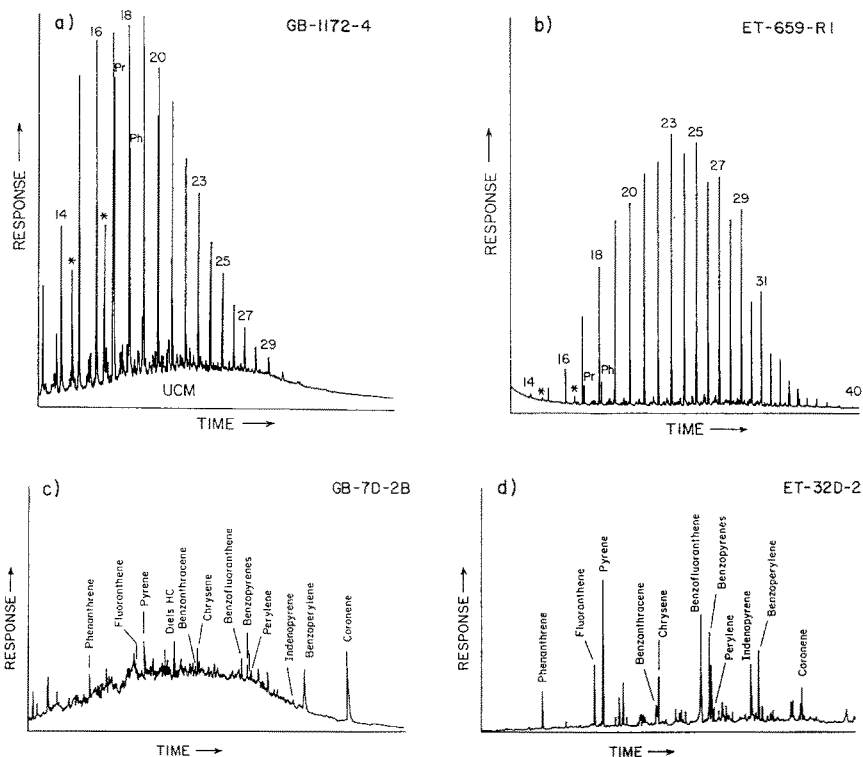


Fig. 3. Gas chromatograms of saturated (a, b) and aromatic (c, d) hydrocarbons in: (a-c) Guaymas Basin (GB) and (b, d) Escanaba Trough (ET) oils (Kvenvolden and Simoneit, 1990). (numbers refer to carbon chain length of *n*-alkanes, Pr = pristane, Ph = phytane, asterisk = other isoprenoids; UCM = unresolved complex mixture; PAH are labeled).

membered alicyclic rings (e.g. fluorene IV, methylenephenanthrene V, etc.), which are found in all pyrolysates from organic matter and once formed do not easily revert to the pericondensed PAH (Blumer, 1975, 1976; Scott, 1982). PAH become the dominant species due to their high thermal stability as well as enhanced solubility in near- and supercritical water (e.g. Sanders, 1986). The aromatic/naphthenic fractions of the Guaymas oils also contain significant amounts of N,S,O hetero-PAH (e.g. Gieskes *et al.*, 1988) and Diels' hydrocarbon, VI (Simoneit *et al.*, 1992). The chemical compositions of the aromatic fractions suggest an origin from oxidative alteration at high temperatures in the system (> 300°C).

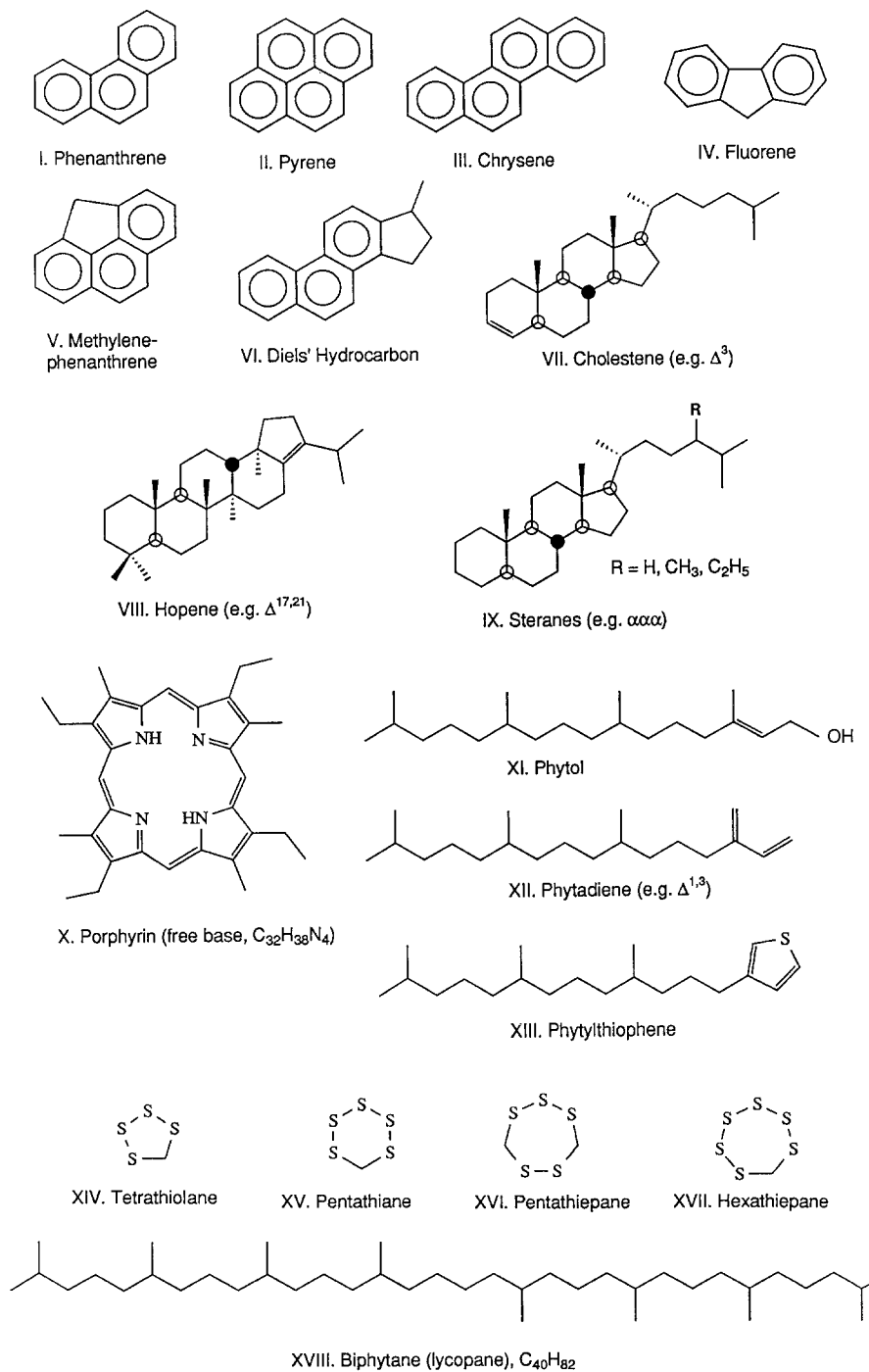


Fig. 4. Chemical structures cited in the text.

The Escanaba Trough in the northeastern Pacific (Fig. 1) is an active oceanic spreading center about 300 km long and bounded on the north and south by the Blanco and Mendocino fracture zones, respectively. It is filled with up to 500 m of Quaternary turbidite sediments (Kvenvolden *et al.*, 1986). The petroleum which saturates the sediments and mineral ores is derived from hydrothermal alteration of sedimentary organic matter primarily from terrestrial sources (Kvenvolden *et al.*, 1986, 1990). Middle Valley is another sediment covered hydrothermal system in the northeastern Pacific (Fig. 1), with associated hydrothermal organic matter alteration. Examples of the compositions of the saturated and aromatic hydrocarbon fractions of a hydrothermal petroleum from Escanaba Trough are shown in Fig. 3b,d. The *n*-alkanes range from C₁₄ to C₄₀, with a carbon number maximum at *n*-C₂₇ and a significant odd carbon number predominance > *n*-C₂₅ (CPI = 1.25), compared to conventional crude oils (CPI = 1.0). This is typical of a catagenetic (thermal alteration) product from organic matter of a terrestrial, higher plant origin (Kvenvolden *et al.*, 1990; Kvenvolden and Simoneit, 1990). The PAH are more concentrated relative to the UCM in the aromatic fraction when compared to the example from Guaymas Basin (Fig. 3c), although the relative yields are similar. This may be due to the deposition of more oxidized terrestrial organic matter and precursor biomarkers in Escanaba Trough than in Guaymas Basin.

The Bransfield Strait, Antarctica (Fig. 1) is a typical example of a back-arc rift, which is tectonically active with extensional features such as dip-slip faults and intrusives, and is also heavily sedimented (Whiticar *et al.*, 1985; Suess *et al.*, 1992). Hydrothermal activity is evidenced by mineral alteration and a slight petroliferous odor of the sediments. However, the bitumen compositions indicate only mild and localized heating from intrusions, which resulted in accelerated diagenesis and limited product migration (Brault and Simoneit, 1988).

The Atlantis II Deep (Fig. 1) contains stratified brine layers, the deepest of which is at a temperature of 62°C (Hartmann, 1980, 1985). Bulk organic matter and hydrocarbons have been analyzed in two sediment cores from the Deep and the results indicate mild hydrothermal alteration (Simoneit *et al.*, 1987). The reductive products, i.e. saturated hydrocarbons, are predominant and the oxidative products, i.e. PAH, are not detectable, confirming that hydrothermal alteration commences at low temperatures. Related data on hydrothermal petroleum from the Kebrut and Shaban Deeps of the Red Sea have also been reported; however, these systems appear to be at higher temperatures (Michaelis *et al.*, 1990).

Volatile compounds (mainly CH₄-C₁₀ hydrocarbons) are not effectively retained with the heavy petroleum as it solidifies at the vents on the seafloor of Guaymas Basin. Upon exiting at the seabed the fluids are often saturated with a broad range of volatile hydrocarbons (CH₄ to *n*-C₁₀) as well as lower concentrations of heavy ends (> C₁₅) (Simoneit *et al.*, 1988). Interstitial gas in sediments of Deep Sea Drilling Project (DSDP) cores consists of biogenic methane (CH₄) overprinted by thermogenic CH₄ to C₅ hydrocarbons near the sills and, to a lesser extent, at increasing subbottom depths. These are of

a similar composition as the venting volatile hydrocarbons (Simoneit *et al.*, 1988; Whelan *et al.*, 1988). Guaymas Basin vent water samples contain high amounts of light hydrocarbons, with CH₄ at corrected concentrations of about 150 cm³ (STP)/kg (Welhan and Lupton, 1987). For comparison, the CH₄ concentrations in vent fluids from the East Pacific Rise at 21°N, a sediment-starved rift system, have been reported to be 1-2 cm³ (STP)/kg (Welhan and Lupton, 1987). Sedimented hydrothermal systems generate higher amounts of natural gas. The headspace gases of a Guaymas Basin mound sample (1629-A3, Fig. 5a) can be compared with the hydrocarbon content of a 308°C vent water, which is highly enriched in the lower alkanes (< C₇, Fig. 5b; Simoneit *et al.*, 1988). The hot water has an enhanced content of aromatic (benzene, toluene, ethylbenzene and xylenes – i.e. more water soluble) versus aliphatic hydrocarbons (Fig. 5b). Hydrogen gas is a major

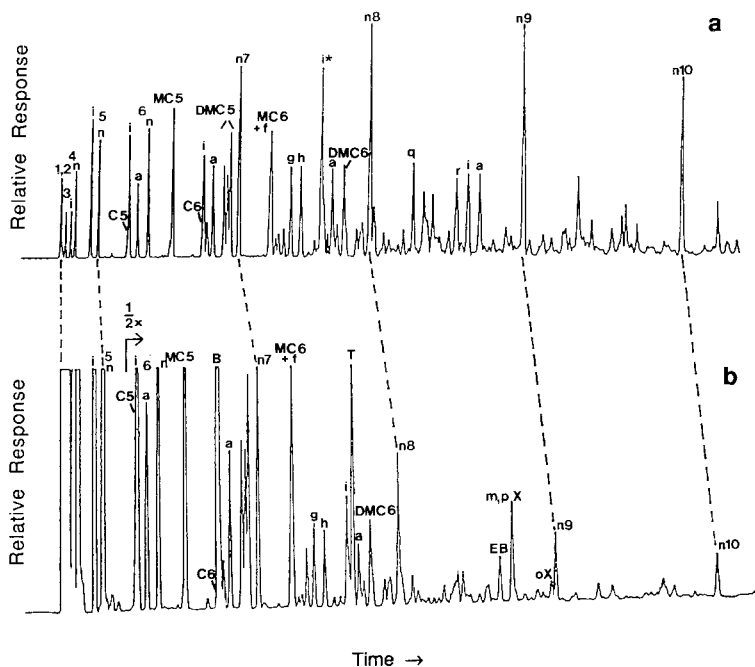


Fig. 5. Gas chromatograms of headspace analyses for comparison of the volatile hydrocarbons from: (a) hydrothermal crust, 1629-A3; (b) hot venting water, 1620-2C (T=308°C) (Simoneit *et al.*, 1988). Numbers refer to carbon chain length with n = normal, i = iso- (2-methyl-) and a = anteiso- (3-methyl-) of corresponding chain length. Other acyclic compounds are q = 2,6-dimethylheptane; r = 2,3-dimethylheptane; and s = 2,6-dimethyloctane. Cyclic compounds are the C = cyclo-, MC = methylcyclo-, DMC = dimethylcyclo- alkanes. The DMC5 triplet contains the c = *cis*-1,3-; d = *trans*-1,3-; e = *trans*-1,2- isomers. Other individual alkylcyclopentanes are f = 1,1,3-trimethyl-; g = 1,2,4-trimethyl-; and h = 1,2,3-trimethyl-. The aromatics are B = benzene, EB = ethylbenzene, T = toluene and X = xylenes (with (o) ortho-, (m) meta- and (p) para- isomers). The * indicates a coeluting unknown and the symbol 1/2x reflects a signal attenuation by a factor of 2.

component of the vent fluids in Guaymas Basin (Welhan and Lupton, 1987). Acetate and propionate ions are highly enriched in the hydrothermally altered sediments of Guaymas Basin relative to normal marine sediments (Martens, 1990). These volatile and water soluble acids are important as complexing agents for metals, substrates for heterotrophic microbial processes, buffers, and possibly in CO₂, CH₄ and C₂H₆ generation.

2.1.2. Marine non-sedimented systems

The examples of sediment-starved hydrothermal systems are located on basaltic rift areas as for example 26°N on the Mid-Atlantic Ridge and 13° and 21°N on the East Pacific Rise (Fig. 1). At 13°N (Hekinian *et al.*, 1983) aliphatic hydrocarbons have been analyzed in hydrothermal plumes and in metalliferous sediments near active vents and at the base of an inactive chimney (Brault *et al.*, 1985, 1988; Simoneit *et al.*, 1990). Hydrocarbons from metalliferous sediments have distributions characteristic of immature organic matter, which has recently been biosynthesized and microbiologically degraded, as might be expected from the low temperature environment in the surrounding talus of a vent system. Thermally mature compounds, such as *n*-alkanes with no carbon number predominance (CPI = 1.0) and biomarkers (17 α (H)-hopanes, steranes), are present at trace levels in waters collected within ~1 km above the hydrothermal vents at 13°N. The hydrocarbon patterns of these waters are indicative in many cases of pyrolysis of bacterial matter entrained in ocean water mixed with the discharging high temperature fluids. Extensive hydrothermal activity occurs at the EPR in the region of 21°N (Fig. 1) in unsedimented oceanic crust with associated abundant faunal communities (Spiess *et al.*, 1980). Various samples of massive sulfides from vent chimneys have been analyzed for hydrocarbon contents, which are extremely low but from hydrothermal alteration (Brault *et al.*, 1989). All samples contain *n*-alkanes with no carbon number predominance (CPI = 1.0) and PAH, supporting evidence for an origin from high temperature alteration. A sample with pyritized tube worm residues also contains hydrothermally altered derivatives (e.g. cholestenes VII, hopenes VIII, Fig. 4) of biomarkers from this vent biota. However, these biomarkers may also have formed by acid-catalyzed, low temperature processes.

The Trans-Atlantic Geotraverse (TAG) hydrothermal field on the Mid-Atlantic Ridge crest at 26°N (Fig. 1) is an active vent system on a slow-spreading mid-oceanic ridge (Rona *et al.*, 1984). Various hydrothermal ores deposited directly on oceanic crust have been dredged from the area (TAG 1985-1) and four types of samples have been examined for lipid/bitumen content (Brault and Simoneit, 1989). A sample consisting of predominantly ferric oxide contained no hydrocarbons attributable to hydrothermal alteration of associated organic detritus. They were probably oxidized and lost. However, three other samples (consisting of mainly anhydrite, sphalerite and chalcocopyrite, respectively) did contain minor amounts of lower molecular weight (C₁₀-C₂₂) hydrothermal petroleum, consisting of *n*-alkanes and PAH.

2.1.3. Continental systems

Continental systems are in volcanic or failed rift terranes as for example Yellowstone National Park, Lake Tanganyika and Waiotapu (Fig. 1). In most cases the thermal processes cause remobilization of organic matter in the form of bitumen as illustrated with the examples of oils from Yellowstone National Park (Love and Good, 1970; Clifton *et al.*, 1990). However, the following two cases are petroleum generated within continental hydrothermal systems. In the Waiotapu geothermal region of New Zealand small amounts of oil are presently being generated from volcanic sedimentary rocks of Lower Pleistocene age (Czochanska *et al.*, 1986). The source material is terrigenous organic matter present in vitric tuff which has been rapidly buried by volcanic overburden. The associated breccias serve as regional aquifers and surround the tuff with high temperature water. The generated oil, however, lacks the disequilibrium reaction products seen in the typical hydrothermal petroleum. The north Tanganyika trough in the East African Rift is another occurrence of massive sulfides and petroleum (Tiercelin *et al.*, 1989, 1992). Hydrothermal fluids pass through ~2 km of organic-rich lacustrine sediments (algal detritus), mobilizing asphaltic petroleum and venting with temperatures of 65-80°C at the lake bed in a water depth of ~20 m (the site described is in proximity to shore; vents at higher temperatures are suspected to occur in deeper water of the lake). The vent waters also contain thermogenic hydrocarbons (Tiercelin *et al.*, 1989). Hydrothermal activity can generate and migrate petroleum from continental source rocks, both lithified and unconsolidated. The invasion of hydrothermal fluids into mature source rocks will result in migration by remobilization with some alteration of the bitumen in the formation.

2.2. TEMPERATURE/PRESSURE CONSTRAINTS

Conventional petroleum formation is believed to occur in the temperature window of ~60-150°C and above that temperature the organic compounds are inferred to go to CH₄ and graphite (Hunt, 1979; Tissot and Welte, 1984). Geologically "instantaneous" (e.g., days-years) organic matter alteration in hydrothermal systems is a widespread process occurring over a temperature range from ~60°C to about 400°C. Formation of hydrothermal petroleum seems to commence in low temperature regions, generating products from weaker bonds and as the temperature regime rises, additional products are derived from more refractory organic matter and are even "reformed" (e.g. PAH). The products are continuously removed by fluid flow. The process progresses from reductive to more oxidative reactions of the residual organic matter as the temperature increases. At very high temperatures, organic matter is only partly destroyed, probably because the thermogenic products are soluble in the ambient fluid (Connolly, 1966; Sanders, 1986) and are thus rapidly removed from the hot zone by convection of fluids.

The aqueous solubility of petroleum and various hydrocarbon fractions has been determined experimentally (Price, 1976) and their solubility increased exponentially from

100°C to 180°C. It has also been demonstrated that CH₄ in the presence of water is an even better carrier for petroleum than water or methane alone (Price *et al.*, 1983). Both increases in pressure (to about 1800 bar) and temperature (to 250°C) raised the solubility of petroleum, and cosolubility was found at rather moderate conditions. Pure hydrocarbons, both aliphatic and aromatic, are soluble in all proportions in near critical water, as tested for low molecular weight compounds (Connolly, 1966), and for high molecular weight compounds (> 400 dalton, Sanders, 1986). Bitumen/tar solubility in supercritical water (400°C, 14–24.5 MPa) ranged as high as 90%, with little decomposition for Athabasca tar sand (Berkowitz and Calderon, 1990). All these laboratory experimental conditions are generally observed in the natural hydrothermal systems.

The thermal alteration products of organic matter in hydrothermal systems can be considered to be in a metastable equilibrium state (e.g. Shock, 1988, 1989, 1990b) during their brief formation and residence times at high temperatures. In this state not all of the stable equilibrium species are present due to kinetic constraints, but theoretical evaluations of the distributions of species at metastable equilibrium are analogous to those for stable equilibrium. Thus, Guaymas Basin vent fluids for example, concurrently contain reduced species (e.g. hydrogen, hydrogen sulfide and CH₄-C₄₀ hydrocarbons), and oxidized species (e.g. CO₂, acetate, PAH).

The interactions of the fluid medium in terms of chemistry and solvent properties are not well understood. The dominant fluid is water, and in the example locales of Guaymas Basin and Escanaba Trough it is under temperatures approaching 350° and 400°C, respectively, with pressures exceeding 200 and 300 bar (20 and 30 MPa), respectively. Reduced density of hydrothermal fluids due to heating results in convective circulation, which in effect makes hydrothermal systems semi-open (a flow-through system) rather than closed as in most laboratory simulation experiments to date. These T and P conditions are in the near-critical domain of water (Fig. 6; Bischoff and Pitzer, 1989; Bischoff and Rosenbauer, 1984, 1988; Chen, 1981; Josephson, 1982; Pitzer, 1986). Supercritical water has enhanced solvent capacity for organic compounds and reduced solvation properties for ionic species due to its loss of aqueous hydrogen bonding (Fig. 6; Connolly, 1966; Shaw *et al.*, 1991; Tödheide, 1982). It is also a reactive medium for either reductive or oxidative reactions (Ross, 1984; Ross *et al.*, 1986) and some specific chemical reactions have been described by Ferris (this volume). Thus, the near-critical domain of water in hydrothermal systems is expected to aid reaction rates and enhance the solvation capacity for organic matter.

Fluids in hydrothermal systems also contain large concentrations of CH₄ and CO₂ (Sakai *et al.*, 1990; Simoneit and Galimov, 1984; Simoneit *et al.*, 1988; Welhan and Lupton, 1987). These gases, as well as many other possible trace components, are supercritical under the temperature and pressure conditions of the hydrothermal systems (Table 1) and their effects on the critical point of seawater are not known. Phase separation of CO₂ from water at reduced temperatures has been proposed for liquid CO₂ vents in a

TABLE 1
Critical Temperatures and Pressures for Possible Constituents of Hydrothermal Fluids¹

Name	Composition	M.W.	Critical Temperature (°C)	Critical Pressure (bar)
Water	H ₂ O	18	374.2	218
Sea water	H ₂ O + 3.2% NaCl	18	407	299
Carbon dioxide	CO ₂	44	31	73
Methane	CH ₄	16	-82	46
Hydrogen sulfide	H ₂ S	34	100	89
Hydrogen	H ₂	2	-240	13
Ammonia	NH ₃	17	132	112
Nitrogen	N ₂	28	-147	34
Ethane	C ₂ H ₆	30	32	48
Ethylene	C ₂ H ₄	28	10	51
Acetylene	C ₂ H ₂	26	36	62
Propane	C ₃ H ₈	44	97	42
Benzene	C ₆ H ₆	78	289	49
Carbonyl sulfide	COS	60	105	65
Carbon monoxide	CO	28	-139	35
Carbon disulfide	CS ₂	76	280	73
Hydrogen cyanide	HCN	27	184	49
Cyanogen	C ₂ N ₂	52	127	
Sulfur dioxide	SO ₂	64	158	78
Hydrogen chloride	HCl	36	51	82
Phosphine	PH ₃	34	51	65
Nitrous oxide	N ₂ O	44	37	72
Nitric oxide	NO	30	-93	64
Nitrogen dioxide	NO ₂	46	158	100
Helium	He	4	-268	2.3
Oxygen	O ₂	32	-118	50
Sulfur	S	32	1040	116

¹Source: CRC Handbook of Chemistry and Physics.

back-arc hydrothermal system (Sakai *et al.*, 1990). Carbon dioxide liquid is also an excellent solvent for organic compounds. Thus, hydrothermal fluids are efficient solvents for scavenging hydrothermal organic compounds (e.g. petroleum) from the source and migrating them away from the hot zone.

The reaction rates of organic matter alteration to petroleum in hydrothermal systems are rapid and fluid extraction is highly efficient. For example, carbon-14 dates have been obtained from hydrothermally-derived petroleum and calcite from the southern trough of Guaymas Basin (Peter *et al.*, 1991). The ages for petroleum range from 4240 to 5705 yBP (years before present, referenced to the year A.D. 1950 and using the ¹⁴C half life of 5570 y). These are not true ages, but rather they reflect the age of carbon within these materials. Additional ¹⁴C data on the aliphatic and aromatic hydrocarbon fractions of an

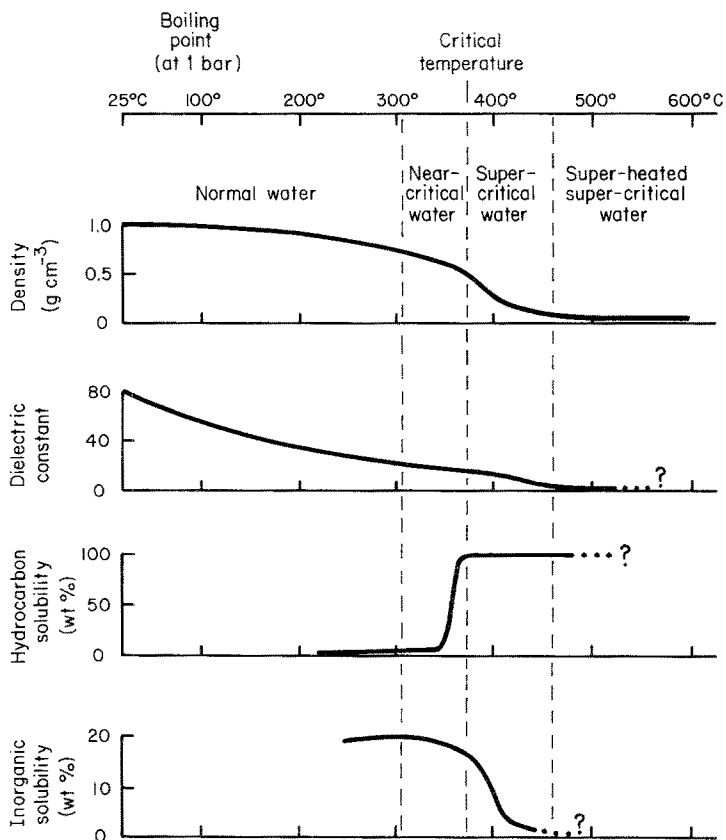


Fig. 6. Properties of water as a function of temperature at 200 to 300 bar pressure (adapted from Josephson, 1982).

oil sample from this area calculate for the same age (~4500 yBP), indicating that the PAH are generated from the same carbon pool as the saturated hydrocarbons at a subseafloor depth of ~12–30 m.

2.3. OXIDATIVE REACTIONS

Organic reactions occurring in hydrothermal systems under mild conditions of thermal stress (<150°C) have been shown to result in compound isomerizations and oxidations such as dehydration and deamination. Thus, amino acids racemize under prolonged hydrothermal stress (Silfer *et al.*, 1990) and are inferred to provide some of the ammonia in hydrothermal fluids of for example Guaymas Basin (Gieskes *et al.*, 1988). Dehydration of alcohols was inferred to occur near sill intrusions in the Guaymas Basin rift (Simoneit,

1984; Simoneit and Philp, 1982) and has been demonstrated with supercritical water in the laboratory yielding primary olefins (Ramayya *et al.*, 1987). Also, the thermally unaltered sediments of Guaymas Basin contain sterols (e.g. cholesterol) which are easily dehydrated and then both hydrogenated and dehydrogenated by hydrothermal fluids to sterane hydrocarbons (e.g. IX, Fig. 4) and Diels' hydrocarbon (VI), an aromatic compound characteristic of rapid thermal alteration (Kawka and Simoneit, 1987; Simoneit, 1985; Simoneit *et al.*, 1992). Deamination to hydrocarbons and loss of heteroatomic nitrogen to aromatic hydrocarbons have been demonstrated in supercritical water with model compounds (e.g. benzyl amine, quinolines) (Houser *et al.*, 1986; 1989).

In the intermediate temperature window (150-300°C) the alteration of organic matter in sediments under hydrothermal stress consists of cracking, reforming, sulfurization, decarboxylation and depolymerization reactions. Aliphatic biopolymers such as microbial membranes yield alkanes (e.g. van de Meent *et al.*, 1980); chlorophylls are converted to porphyrins (e.g. X, Fig. 4) with generally lower carbon number maxima (e.g. Didyk and Simoneit, 1990); phytol (XI) and/or phytadienes (XII), its dehydration products, are converted to phytylthiophenes (XIII) by reactions with H₂S, sulfur and/or SO₄⁼ (Leif *et al.*, 1991); and carboxylic acids are reduced and/or decarboxylated to alkanes. Cracking and reforming products are saturated by the excess hydrogen present in the system (Welhan and Lupton, 1987) or by dimerization of the free radical fragments, yielding aliphatic products. It has been shown that the hydrogen in the reductive processes is derived from the water by using deuterium oxide in hydrous pyrolysis experiments (Hoering, 1984; Simoneit *et al.*, unpublished data). The hydrothermal fluids of Guaymas Basin contain major amounts of short chain organic acids as the ionic species, e.g. acetate and propionate (Martens, 1990), which may be derived from breakdown by cracking/oxidation of higher molecular weight lipids.

In the high temperature window (> 300°C) organic matter residues are heavily altered and the products consist primarily of low molecular weight species (e.g. methane, H₂S, benzene). Desulfurization of organic sulfur compounds occurs in this thermal region generating H₂S (Clark *et al.*, 1983; 1986). Polynuclear aromatic hydrocarbons in the higher molecular weight range (>228 dalton) are generated probably by reforming aromatic moieties into more stable configurations, but have not been formed in laboratory simulations up to 300°C (e.g. Simoneit, 1992). The residual organic matter ("spent" kerogen) after expulsion of all the products generated by the hydrothermal activity in Guaymas Basin sediments consists of activated amorphous carbon (Simoneit, 1982b; Curray *et al.*, 1982). In deeper sedimentary sections, where the temperature is higher, this carbonaceous kerogen residue is not found, indicating that it may have reacted (e.g. with S to yield CS₂) or migrated with the fluids.

3. Synthesis/Reductive Processes and Reactions

Evidence for synthesis of organic compounds in natural hydrothermal systems is sparse (also cf. Ferris, this volume) because such potential products would be masked by the ex-

cess of the contemporary pyrolysis products (e.g. hydrocarbons derived from organic detritus). Reductive alteration of organic compounds is the prevalent process in both sedimented and sediment-starved hydrothermal systems and this can readily be demonstrated with isotope labeling.

3.1. AQUEOUS ORGANIC CHEMISTRY

The reactivity of organic compounds in hot water (200-350°C) has been studied to model the geochemical and technological implications of this chemistry (see review by Siskin and Katritzky, 1991) and the potential of supercritical water as a medium for chemistry has also been reviewed (Shaw *et al.*, 1991; Townsend *et al.*, 1988). An extensive study of the hydrothermal alteration of some simple organic compounds has been published (Katritzky *et al.*, 1990a-o, 1991; Siskin *et al.*, 1990a-c, 1991). The results are summarized in Table 2. Four reaction categories have been defined, namely condensation, bond cleavage, hydrolysis and autocatalysis reactions. Reactions catalyzed by the presence of minerals are a related category. For organic compound synthesis in hydrothermal systems it is necessary to understand the chemistry of condensation, autocatalysis, catalysis and hydrolysis reactions.

3.2. SYNTHESIS

Preliminary evidence for the synthesis of heterocyclic sulfur compounds, as for example tetrathiolane (XIV, CH_2S_4 , Fig. 4), pentathiane (XV, CH_2S_5), pentathiepane (XVI, $\text{C}_2\text{H}_4\text{S}_5$) and hexathiepane (XVII, CH_2S_6) has been reported (Kawka and Simoneit, 1987). These compounds are significant components in the Guaymas Basin samples and can be interpreted as being synthesized from formaldehyde and sulfur or HS_x^- in the hydrothermal fluids. Other products from potential synthesis reactions have not been defined in the natural systems but should be determined based on inferences from experimental interpretations. For example, more rigorous laboratory studies with model compounds should be carried out to test condensation reactions such as phytol (XI) yielding biphytane (lycopane, XVIII, Fig. 4) and dimerizations such as alkyl radicals or carbonium ions yielding extended alkanes. Since lycopane is a biomarker of bacterial origin (e.g. Albaiges *et al.*, 1985; Gillan and Johns, 1986) this experiment needs to be carried out with ^{13}C labels to test such a condensation reaction. The key indicator compounds can then be searched for in the natural hydrothermal environments. Fischer-Tropsch type synthesis also should first be demonstrated in the laboratory, because in the hydrothermal systems such products are masked by the overwhelming pyrolysates from organic matter alteration. The reaction is extensively utilized in the synthetic fuels industry. Similarly, the Strecker synthesis of amino acids is masked in hydrothermal systems by the extensive pyrolysis of proteinaceous residues from contemporary biota.

TABLE 2
 Summary of organic compounds subjected to aqueous alteration at high temperatures.¹

Reactant	Conditions ²		Major Reactions and Products
	Temperature (°C)	Time	
Aliphatic compounds:			
1-decene	250	5.5 d	ionic (acid catalysis), isomerization, dimerization
1-decyne	250	5.5 d	ionic (acid catalysis), hydrogenation
1-decanal	250	1.5 d	aldol condensation, dimers
2-decanone	250	5.5 d	aldol condensation, dimers
decyl decanoate	250	1.5 d	hydrolysis
decanenitrile	250	2.5 d	hydrolysis
1-decanol	250	13.0 d	disproportionation, trace dehydration/hydrogenation
1-decylamine	250	5.5 d	condensation
methyl 1-nonyl sulfide	250	13.5 d	dialkyl sulfide
1-decanethiol	250	13.5 d	dialkyl sulfide
methyl 1-decyl ether	250	13.5 d	N.R.
decanoic acid	250	13.5 d	N.R.
Cyclohexyl phenyl compounds:			
cyclohexyl phenyl ketone	250	5.5 d	N.R.
cyclohexyl methylbenzene	250	5.5 d	N.R.
cyclohexylbenzene	250	5.5 d	N.R.
N-cyclohexylaniline	250	5.5 d	hydrolysis/rearrangement
cyclohexyl phenyl ether	250	5.5 d	hydrolysis/rearrangement
cyclohexyl phenyl sulfide	250	5.5 d	hydrolysis/rearrangement
Ethers and Esters:			
4-phenoxyphenol	250/343	5.5 d/2 h	hydrolysis/polymer
cyclohexyl phenyl ether	250/343	5.5 d/2 h	phenol, methylcyclopentene
benzyl phenyl ether	250/343	5.5 d/2 h	phenol, benzylphenol
	284-384*	2 h	phenol, benzyl alcohol, toluene
4-(benzyloxy)phenol	250/343	5.5 d/2 h	benzyl alcohol, hydroquinone, toluene

Table 2. continued

Reactant	Conditions ²		Major Reactions and Products
	Temperature (°C)	Time	
methyl 1-naphthoate	250/343	5.5 d/2 h	hydrolysis/decarboxylation/isomerization, naphthalene
1-naphthoic acid	250/343	5.5 d/2 h	decarboxylation, naphthalene
dibenzyl ether	374-412*	1 h	benzyl alcohol, benzaldehyde, toluene
phenethylphenyl ether	375-413*	1.5 h	phenethyl alcohol, phenol, styrene
Benzenes:			
benzene	250/343	5.5 d/2 h	N.R.
toluene	250/343	5.5 d/2 h	N.R.
benzoic acid	250/343	5.5 d/2 h	trace decarboxylation
benzoic acid + formaldehyde	250/343	5.5 d/2 h	methyl benzoate
benzyl alcohol	250/343	5.5 d/2 h	dibenzyl ether, minor disproportionation
benzaldehyde	250/343	5.5 d/2 h	benzoic acid
benzaldehyde + phenol	250/343	5.5 d/2 h	polymerization
dibenzofuran	500*	1 h	N.R.
diphenylmethane	405*	1 h	N.R.
N-Heterocycles:			
pyridine	250/343	5.5 d/2 h	N.R.
3-methyl pyridine	250/343	5.5 d/2 h	N.R.
pyridine-3-carboxylic (nicotinic) acid	250/343	5.5 d/2 h	decarboxylation
pyridine-3-carboxaldehyde	250/343	5.5 d/2 h	decarboxylation
3-pyridyl methanol	250/343	5.5 d/2 h	3-methyl pyridine, pyridine-3-carboxaldehyde
2-methyl pyridine	250/343	5.5 d/2 h	N.R.
pyridine-2-carboxylic acid	250/343	5.5 d/2 h	rapid decarboxylation, pyridine
pyridine-2-carboxaldehyde	250/343	5.5 d/2 h	rapid decarboxylation, pyridine
2-pyridyl methanol	250/343	5.5 d/2 h	2-methyl pyridine, pyridine
4-methyl pyridine	250/343	5.5 d/2 h	N.R.
pyridine-4-carboxylic acid	250/343	5.5 d/2 h	disproportionation
pyridine-4-carboxaldehyde	250/343	5.5 d/2 h	4-methylpyridine, pyridine-4-carboxaldehyde
4-pyridyl methanol	250/343	5.5 d/2 h	decarboxylation
pyridine-4-carboxylic acid	250/343	5.5 d/2 h	N.R.
carbazole	450-350*	1 h	

Table 2. continued

Reactant	Conditions ²		Major Reactions and Products
	Temperature (°C)	Time	
<i>C</i> ₂ -substituted benzenes:			
2-phenylethanol	250	5d	dehydration, styrene, ethylbenzene
phenylacetic acid	250	5d	N.R.
phenylacetaldehyde	250	5d	disproportionation/aldol condensation
phenylacetylene	250	5d	acetophenone, 1-phenylnaphthalene, 1,3,5-triphenylbenzene
styrene	250	5d	polystyrene
ethylbenzene	250	5d	acetophenone, toluene
1,2-diphenylethane	380-500*	3 h	N.R.
1,3-diphenylpropane	420*	1 h	N.R.
1-phenylethanol	250	5d	styrene, acetophenone
acetophenone	250	5d	traces ethylbenzene, benzaldehyde
phenylethanediol	200	6 h	condensation, phenylacetaldehyde
mandelic acid	250	1d	decarboxylation, disproportionation, condensation, dehydration
benzoylformic acid	200	1d	benzaldehyde, benzoic acid
Phenols:			
p-cresol (4-methylphenol) + NaHSO ₃	250	3d	phenol, 2,7-dimethylxanthene
4-ethylphenol + NaHSO ₃	250	56 h	phenol, 2-ethylphenol
4- <i>n</i> -propylphenol + NaHSO ₃	250	56 h	phenol, dimers
4- <i>iso</i> -propylphenol + NaHSO ₃	250	56 h	phenol, 2- <i>n</i> -propylphenol
4- <i>t</i> -butylphenol + NaHSO ₃	250	56 h	phenol
4- <i>n</i> -dodecylphenol + NaHSO ₃	250	1d	phenol, p-cresol
4-benzylphenol + NaHSO ₃	250	57 h	phenol, 2-benzylphenol, benzoic acid
5,6,7,8-tetrahydro-2-naphthol + NaHSO ₃	250	82 h	hydrogenation, 2-naphthol, 1,6-dihydroxynaphthalene
4-(hydroxymethyl)phenol + NaHSO ₃	250	6 h	phenol
4-hydroxybenzaldehyde + NaHSO ₃	250	44 h	phenol, 4-oxocyclohexanecarboxaldehyde
guaiacol	383*	45 min	o-cresol, methanol, methane

Table 2. continued

Reactant	Conditions ²		Major Reactions and Products
	Temperature (°C)	Time	
4-hydroxybenzoic acid + NaHSO ₃	250	44 h	decarboxylation
4-hydroxyacetophenone + NaHSO ₃	250	1 d	phenol, p-cresol
o-cresol + NaHSO ₃	250	11 d	phenol, 2,6-dimethylphenol
m-cresol + NaHSO ₃	250	11 d	phenol (trace)
2-ethylphenol + NaHSO ₃	250	4,6 d	phenol, o-cresol, furan
2-iso-propylphenol + NaHSO ₃	250	3 d	phenol, o-cresol, 2-ethylphenol, 2,5-dimethylfuran
3,4,5-trimethylphenol + NaHSO ₃	250	14 h	demethylation
2,4,6-trimethylphenol + NaHSO ₃	250	13 h	demethylation
anisole	250	3 d	phenol, toluene
phenol + methanol	250	3 d	anisole, o- and p-cresol
diphenyl ether	250	3 d	N.R.
n-butylphenyl ether	405*	1 h	N.R.
2,3-dihydrobenzofuran	250	3 d	trace phenol
	250	3 d	phenol, 2-ethylphenol
Aryl amines:			
o-toluidine + H ₃ PO ₄	250	3 d	deamination, o-cresol
p-toluidine + H ₃ PO ₄	250	3 d	deamination, p-cresol
o-/p-toluidine + NaHSO ₃	250	3 d	(aminophenyl)methyl/benzothiazoles
4-ethylaniiline	250	3 d	deamination/diphenylamine
4-iso-propylaniiline	250	3 d	deamination/diphenylamine
N-methylaniiline	250	3 d	disproportionation (aniiline, N,N-dimethylaniiline)
N-ethylaniiline	250	3 d	aniiline, N,2-diethylaniiline, N,4-diethylaniiline
N,N-dimethylaniiline	250	3 d	N-methylaniiline, aniiline
N,N-diethylaniiline	250	3 d	N-ethylaniiline, aniiline
1,2,3,4-tetrahydroquinoline	250	3 d	aromatization, dimers
2,4,6-trimethylaniiline	250	3 d	N.R.
benzylphenyl amine	386*	1 h	aniiline, benzyl alcohol

Table 2. continued

Reactant	Conditions ²		Major Reactions and Products
	Temperature (°C)	Time	
Aryl nitriles, amides and amines:			
benzonitrile	250	5d	hydrolysis, benzoic acid, benzamide
benzamide	250	5d	benzoic acid, benzene
benzyl amine	250	5d	toluene, benzaldehyde, benzyl alcohol
dibenzyl amine	250	5d	toluene, 1-phenyl- <i>iso</i> -indole, benzyl amine
2-cyanopyridine	250	5d	pyridine
pyridine-2-carboxamide	250	5d	pyridine
2-pyridylmethylamine	250	5d	2-methylpyridine, pyridine
3-cyanopyridine	250	5d	nicotinic acid, pyridine, pyridine-3-carboxamide
pyridine-3-carboxamide	250	5d	pyridine, nicotinic acid
3-pyridylmethylamine	250	5d	3-methylpyridine, pyridine
4-cyanopyridine	250	5d	pyridine-4-carboxylic acid, pyridine, pyridine-4-carboxamide
pyridine-4-carboxamide	250	5d	pyridine-4-carboxylic acid, pyridine, pyridine-4-carboxamide
4-pyridylmethylamine	250	5d	4-methylpyridine, dimers
Sulfides and disulfides:			
phenyl methyl sulfide	250	5d	biphenyl, diphenyl sulfide
diphenyl sulfide	250	5d	dibenzothiophene, thiophenol
benzyl phenyl sulfide	250	5d	diphenyl disulfide, benzaldehyde, thiophenol
phenyl β -phenylethyl sulfide	250	5d	ethylbenzene, thiophenol, diphenyl sulfide
dibenzyl sulfide	250	5d	benzaldehyde, toluene, dimethyl disulfide
diphenyl disulfide	250	5d	toluene, bibenzyl, benzoic acid, stilbene
dibenzyl disulfide	250	5d	diphenyl sulfide, thiophenol
di-2-pyridyl disulfide	250	5d	toluene, benzoic acid, bibenzyl, tetraphenylthiophene
di-4-pyridyl disulfide	250	5d	4-pyridone, 2-pyridinethione
dibenzothiophene	550*	3 h	4-pyridone, 4-pyridone, di-4-pyridyl sulfide N.R.

Table 2. continued

Reactant	Conditions ²		Major Reactions and Products
	Temperature (°C)	Time	
Mercaptans and sulfonic acids:			
phenylmethanethiol	250	5 d	desulfurization, toluene
phenylethanethiol	250	5 d	desulfurization, ethylbenzene, toluene
phenylpropanethiol	250	5 d	3-phenylpropanol, <i>n</i> -propylbenzene
2-phenylethanesulfonic acid	250	5 d	N.R.
2-(2-pyridyl)ethanesulfonic acid	250	5 d	2-methylpyridine, pyridine
naphthalene-2-thiol	250	26 h	di-2-naphthyl sulfide, di-2-naphthyl disulfide
thiophenol	250	70 h	diphenyl sulfide, thianthrene, diphenyl disulfide
diphenyl sulfide + NaHSO ₃	250	22 h	trace thiophenol
thioanisole + NaHSO ₃	250	60 h	thiophenol, diphenyl sulfide
benzothioephene + NaHSO ₃	250	82 h	N.R.
4-methylthiophenol + NaHSO ₃	250	82 h	di-4-methylphenyl disulfide, di-4-methylphenyl sulfide

¹Major examples from the open series of papers by Katritzky *et al.* (1990a-o, 1991) and Siskin *et al.* (1990a-c, 1991), and * = data from Townsend *et al.* (1988).

²Higher temperatures were used to increase reactivity. Solvents were water and simulated brine with addition of NaHSO₃ or H₃PO₄ for the aqueous tests and nonane, hexane, cyclohexane or decalin for non-aqueous thermal tests.

N.R. = no reaction.

3.3. REDUCTIVE REACTIONS

All hydrothermal systems examined to date yield organic products derived primarily from reductive alteration reactions. Dry pyrolysis generates equal amounts of alkenes (olefins) as alkanes from organic matter (e.g. van de Meent *et al.*, 1980). Alkenes are not detectable in the hydrothermal products because the precursor intermediates are hydrogenated yielding alkanes. The same is the case for other labile organic compounds as for example biomarkers such as sterols which are converted primarily to steranes (IX).

Deuterium labeling has shown that the hydrogen for the reductive reactions derives from the water medium (Hoering, 1984; Simoneit *et al.*, unpublished data). Hydrous pyrolysis of samples of an organic-matter-rich shale (Messel shale, Eocene age, Germany, extracted previously with organic solvents) in D₂O at 330°C for 3 days, generated a series of extensively deuterated, saturated hydrocarbons resembling petroleum (Hoering, 1984). A portion of the product was a series of *n*-alkanes in the range of C₁₄ to C₃₀, with each alkane containing distributions of isomers having 0 to more than 14 deuterium atoms. The maximum deuterium substitution was in the D₄ to D₆ range and was very broad. This indicates extensive deuterium scrambling but confirms the D source from the water. However, further experiments are needed because these are enigmatic results. Furthermore, when *n*-octadec-1-ene, a terminal olefin, was subjected to these conditions, 60% of it was recovered as the corresponding deuterated alkane. This result confirms the presence of reducing chemistry, but the product contained significantly lower levels of deuterium than did the alkanes produced from the shale (Hoering, 1984). The deuterium distribution peaked at D₂ rather than at D₄₋₆, indicating possible matrix or catalytic effects and less scrambling. Nevertheless, such experiments carried out over a temperature/time series will permit the elucidation of the reaction pathways for hydrothermal alterations of organic species.

4. Examples of Industrial Applications

4.1. SUPERCRITICAL WATER

Supercritical fluid technology has been successfully applied in the processing industry in three major areas: 1) extraction, 2) coal liquefaction (hydrogenation), and 3) waste oxidation (Josephson, 1982). Some of the basic chemistry will have implications for hydrothermal systems and thus these chemical engineering research areas should be examined. There are numerous symposium volumes, reports, and reviews summarizing the state of the art in supercritical fluid technology (e.g. Franck *et al.*, 1983; Franck, 1987; Johnston and Penninger, 1989; Jones and Radding, 1980; Paulaitis *et al.*, 1983; Penninger *et al.*, 1985; Shaw *et al.*, 1991; Siskin and Katritzky, 1991; Squires and Paulaitis, 1987; Townsend *et al.*, 1988; Wu *et al.*, 1991). Additional information can be found in the chapter by Ferris (this volume). Reductive reactions with supercritical water have been applied primarily for upgrading shale oil and liquefying waste, biomass and coals (e.g. Antal *et al.*, 1985; Funazukuri *et al.*, 1987; Hong *et al.*, 1987, 1988; Köll *et al.*, 1983;

Paspek and Klein, 1990; Ross, 1984; Ross *et al.*, 1986). Oxidative reactions with supercritical water are utilized primarily for waste disposal and include the patented MODAR process (e.g. Hong *et al.*, 1987, 1988; Modell *et al.*, 1982; Staszak *et al.*, 1987). Various chemical reactions using organic compounds have been studied with both static and flow reactors using supercritical water (e.g. Helling and Tester, 1988; Houser *et al.*, 1986, 1989; Metzger *et al.*, 1983; Ramayya *et al.*, 1987; Shaw *et al.*, 1991). A more detailed perusal of the literature should uncover additional reports on specific organic reactions.

4.2. OTHER SUPERCRITICAL FLUIDS

Non-aqueous and aqueous/organic fluid mixtures have been applied in the supercritical state for various extraction processes (cf. reviews by Eckert *et al.*, 1986; Paulaitis *et al.*, 1982). Supercritical carbon dioxide is used extensively for extraction of polar organic compounds, e.g. for decaffeination and for extraction of oils from foods and seeds (Paulaitis *et al.*, 1982; Polak *et al.*, 1989). Supercritical hydrocarbon mixtures are utilized to extract thermally generated coal liquefaction products (Finn *et al.*, 1983). Phenols and carbohydrates can be extracted essentially quantitatively from wood by supercritical acetone or methanol (McDonald *et al.*, 1983). The phase behavior and critical properties of various fluid mixtures have been determined and reviewed (Franck *et al.*, 1983; Johnston *et al.*, 1982; Paulaitis *et al.*, 1982). These systems operate at lower temperatures and pressures, especially CO₂, and are generally excellent solvents for organic matter.

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