CHEMICAL REVIEWS

Reactivity of Organic Compounds in Superheated Water: General Background

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I. Introduction

The present article is the first of a pair which describes an emerging area of chemistry: the transformations of organic compounds in pure superheated water and elevated pressure. The present article addresses the background to, the historical development of, and more practical examples on the subject. The general background is covered, and the effects of various minerals as solid catalysts is described in some detail. Then the following article documents systematically the knowledge base built up for the reactions of various classes of organic compounds with superheated water, the products that are formed, and the mechanisms thus deduced.

Although conventional wisdom holds that most organic compounds do not react with water under normal conditions, this overview demonstrates that

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Photograph and biography for Alan Katritzky can be found on p 838.

water frequently participates as catalyst and/or reactant as well as solvent. Specifically, the behavior of compounds with functional groups and linkages corresponding to those found in coals and shale kerogens, and their precursors, implies that water has important effects on the conversion of plant and animal material into organic fuels under geologic conditions of time, heat, and pressure. These results are of broad significance to geologists and chemists and may provide a means for reducing pollution by

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organic wastes. The implications are beginning to be explored with respect to energy sources and the development of environmentally clean and safe chemistries for chemical synthesis and recycling.

Many classes of organic molecules that were previously considered to be unreactive in liquid water undergo diverse chemical reactions when the temperature is increased to the range from 250 to 350 °C, including reactions that were previously expected only in the presence of strong acid or base. For example, ethers and esters, which are unreactive to heat alone, undergo facile hydrolysis in water at 250–350 °C.[1] Similarly, poly(ethylene terephthalate) polymers (exemplified by plastic soft drink bottles) can be hydrolyzed quantitatively back to their starting materials in 300 °C water in less than 1 h.[2] Other polyesters and also polyamides[2] (such as nylon), polycarbonates,[2] polyethers,[3] polyurethanes,[4] and phenol resins[5] are equally susceptible to hydrolysis. A major analogy to such reactions in nature is catagenesis: the process by which solid petroleum kerogens, which are cross-linked macromolecular structures, in source rocks are converted into liquid petroleum. Natural catagenesis takes place at temperatures below 200 °C over millions of years in aqueous environments at pressures of about 61 MPa. Because of the relatively low temperatures, it has been hypothesized that some of the chemistry by which petroleum is formed is catalyzed by clay minerals in the sediments.[6] Two additional factors can affect and catalyze kerogen conversion and thus are important to petroleum formation. One is that simple aqueous chemistry generates water-soluble products that are acidic or basic or have redox properties. The other is the effect of salts present in seawater or other aqueous environments.[7,8]

Should one expect organic chemical reactions to take place in superheated water? Dramatic changes in the physical and chemical properties of water underline the opportunity: as temperature increases, water becomes more compatible as a medium for reaction of organics. For example, as temperature rises from 25 to 300 °C, the density of water decreases from 0.997 to 0.713 g/cm^3,[9] its dielectric constant (hydrogen bonding structure) decreases from 78.85 to 19.66,[10] and its solubility parameter decreases from 23.4 to 14.5 (cal/cm^3)$^{1/2}$.[11] Over the same temperature range, the ionic product (dissociation constant) of water increases by 3 orders of magnitude, from $10^{-13.99}$ to $10^{-11.30}$,[12] even though the dielectric constant falls with rising temperature. Note also that for deuterium oxide the increment is similar: 10^{-15} to 10^{-12}. The change in dielectric constant makes the solvent properties of water at 300 °C roughly equivalent to those of acetone at 25 °C. Therefore, ionic reactions of organics should be favored by increased solubility in water. The increase in the dissociation constant will increase the rate of both acid- and base-catalyzed reactions in liquid water far beyond the natural acceleration due to increased temperature. Above the critical temperature ($T_c = 374$ °C), the dissociation constant of water decreases greatly (10^{-23} at 600 °C) and, therefore,

even high-density supercritical water is a poor medium for ionic chemistry.[13]

The reactivity of organics in water in the temperature range from 200 to 350 °C[14] has been systematically studied with the use of reactants that include aliphatic and aromatic species containing oxygen, sulfur, and nitrogen functional groups. Many of these are representative of structures found in kerogenous resources such as coals and oil shales. In many cases, salt (brine) and minerals were added to the model organic compound–water systems to simulate the chemistry of diverse natural environments. These reactions were carried out in closed reactors, such as an autoclave, in which a liquid water phase is maintained.[8] Pressures range from ~4 MPa at 250 °C to ~17 MPa at 350 °C. The reactors were never filled to more than 65% of the total volume to allow for maintaining a liquid water phase under autogenous pressure below T_c and for expansion of water in the closed vessel. From these studies, new understandings of aqueous organic chemistry have emerged and several key concepts governing these reactions have been recognized. (i) Water can act as a highly effective acidic or basic catalyst and, indeed, as a powerful acid–base bicatalyst. Such catalyzed reactions are often further accelerated by acidic and basic minerals such as clays and carbonates. (ii) Ionic chemistry predominates as high-temperature water opens reaction pathways that are alternative to and preferred over thermal (free-radical) routes. This ionic chemistry is often facilitated in brine. (iii) Reactions can be autocatalyzed by water-soluble reaction products.

On the basis of these fundamental concepts, this article presents an overview of the reactivity of a broad range of organic molecules in pure hot water, including in the presence of minerals and brine. Other media, e.g., acids and bases, are referred to for comparison on a selective basis. These advances have increased confidence in the ability both to understand organic geochemical processes and to promote new desired reactions under environmentally clean and safe conditions.

Reactions of organic compounds with pure water at high temperatures, both sub- and supercritical, have been much studied, with especially significant contributions made by the groups of Klein,[15–20] Strauss,[21] Houser,[22–25] Penninger,[26,27] and Clark.[28–32] Our own group collaborated in a major joint Exxon–UF investigation over the period 1985–1993. Recent reviews of this field have appeared by Savage,[33,34] Lubineau,[35,36] Li,[37] and Breslow.[38] Supercritical water in the presence of oxygen has been studied extensively for the disposal of hazardous waste.[39,40]

Recent interest in this area has led to reviews of supercritical water as a medium for chemistry,[41] books on aquatic chemistry,[42,43] a review on water oxidation catalysts,[44] accounts of molecular recognition in aqueous solution,[45] and aquathermolysis.[46]

II. Objectives

An important initial objective was to uncover the general pattern of reactivity toward high-tempera-

ture water of the common, naturally occurring ring systems and functional groups. Structural types, e.g., acid anhydrides, acid halides, etc., expected to be reactive in water at low temperatures are not covered in this review. As a whole, the work provides an organic chemistry base to aid understanding of the geological formation (diagenesis) of the oxygen-rich ($\sim$10−20 wt %) insoluble organic material (kerogen) in fossil fuel resources (coal and oil shale), which takes place in anoxic (oxygen-free) aqueous environments, and the subsequent depolymerization, or breakdown, of these kerogens. These processes have been used to generate fuels from coals by human processing and occur naturally to generate petroleum over geologic time periods from oil shale kerogens and some coals (catagenesis) in superheated liquid water in a marine or lacustrine environment.[47,48] Kerogen-forming reactions involve condensation and other dehydration reactions and addition and alkylation reactions, whereas the depolymerization chemistry includes a broad range of hydrolytic cleavage reactions. Such a chemistry base should also allow experiments designed to modify fuel feedstocks to be carried out more efficiently. Attention has been focused on relatively small groups of related compounds, wherein information obtained from one compound would be of general value in interpreting reactions of other members of the group. Mechanistically, bond cleavage reactions of model compounds, which dissolve in water under reaction conditions and which take place in neutral liquid superheated water below the critical temperature (T_c) of 374 °C would be expected to involve largely oxygen-containing bridges/cross-links (e.g., esters and ethers, not pendant carboxylic acids or phenols) and to proceed via ionic pathways. Above T_c, a competition between ionic and thermal free-radical pathways would be expected, with radical pathways catching up and finally predominating as temperature increases. In complex systems such as kerogens, depolymerization reactions leading to petroleum formation in nature take place at high pressure ($\sim$61 MPa [8845 psi]) over millions of years below 200 °C and would be expected to involve parallel ionic and radical pathways. In natural systems, the ionic pathways could be catalyzed by acidic and basic minerals and dissolved salts.

A. Overview of Experimental Approaches

Various experimental details have been described[8] and controls run to rule out catalysis by contaminants.[49−51] Hoering[49] and Klein and co-workers[50] observed no significant effects by the metal surfaces on a variety of reactions studied in liquid water. Analysis by inductively coupled plasma emission spectroscopy (ICPES) of deuterium oxide after a 10-day exposure at 300 °C and of the reactor contents following reactions failed to indicate any significant amounts of metallic components.[51] Controls in sealed quartz tubes and sapphire NMR tubes were run.[51] Reactions reported were usually carried out, in the absence of air, in both sub- and supercritical water. Only differences in rate, not in pathway, were observed in going from sub- to supercritical water, except in a few cases involving elimination of organic
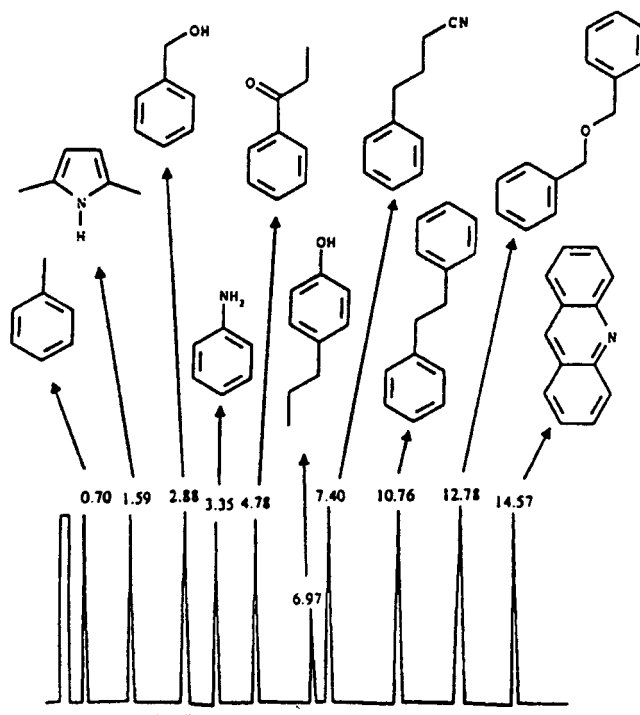

Figure 1. GC trace of a mixture of ten compounds. (Reprinted with permission from ref 54. Copyright 1995 The Royal Society of Chemistry.)

sulfur and hydrogenation of aromatic N-containing heterocycles when carbon monoxide was present.[52,53] This indicates that ionic pathways persist in functionalities less susceptible to cleavage by neutral free-radical processes in water.

Complex mixtures containing up to 30 different compounds derived from a single precursor at high temperature can be analyzed satisfactorily by GC/MS methods. The peaks were resolved, and from their fragmentation patterns, knowledge of the precursor, and some idea of the mechanism, chemical structures can be assigned to all products. Detailed interpretations of the MS fragmentation patterns of compounds not available, or whose spectrum was not available in a database or from an alternative source, are included in the Supporting Information in many publications.

However, before a quantitative analysis could be made, it was necessary to know the response factors (RF) for all of the compounds, i.e., the relationship between the integrated area under the GC curve for the individual peaks and the compound structure. Response factors vary considerably. Many of the compounds formed as products were unavailable or, in some cases, even unknown; it was quite impractical to measure the response factors experimentally. This was resolved by an investigation of QSPR (quantitative structure property relationship) relationships (for a review, see ref 54) between GC analytical response factors and chemical structures.

An illustration of the problem is demonstrated by the analysis of the GC trace of the mixture shown in Figure 1. Partial least-squares analysis was used to search for a reliable dependence of the RF on structural descriptors which could be derived solely
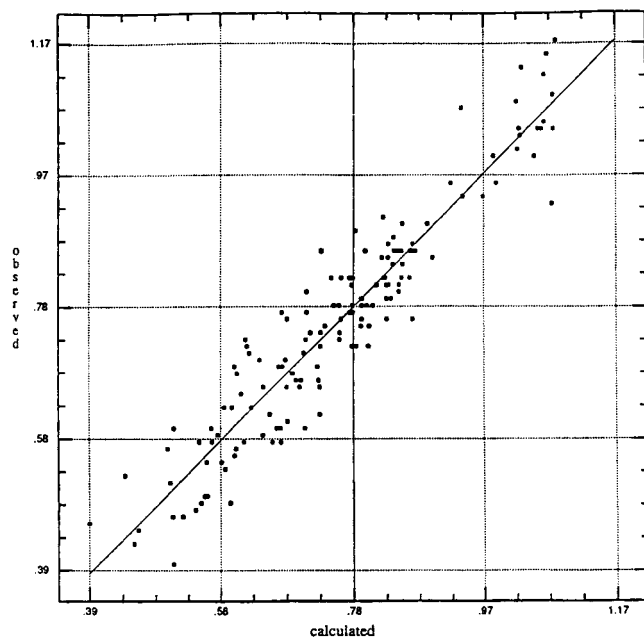
Figure 2. Correlation between the observed and predicted response factors (RF) using the best six-parameter equation obtained with the combined set of 37 descriptors. (Reprinted with permission from ref 56. Copyright 1994 American Chemical Society.)

from the structure formed.[54-56] The response factors were measured for a set of 120 different compounds under standard conditions. An initial treatment[55] utilized the PLS (partial least squares) method in terms of atomic groupings. Later the CODESSA program (for a review, see ref 57) was applied[56] to the measured response factors of 152 individual structures incorporating a wide cross-section of organic compounds. It provided a six-parameter equation ($R^2CV = 0.88$ for RF Dietz) which reveals the relative weight of the "effective carbon atoms" and the total one-carbon, one-electron repulsion energy as the most important descriptors[56] to enable the prediction of response factors for hypothetical compounds. The success of the method is shown graphically in Figure 2. Although the correlation is not perfect, it is certainly much better than the alternative, which was to have set all of the RF values as equal to unity. Recently this correlation was re-examined with state-of-the-art methods, and minor improvements were made.[58]

B. Aqueous Systems

In addition to carrying out the reactions in pure water, comparisons were also made under other conditions. In almost all cases, this included heating for the same time period in cyclohexane or other unreactive hydrocarbon solvent in order to differentiate aqueous from purely thermal reactions. Cyclohexane was chosen for most of the studies because of its nonpolar character and because it seemed likely to give rise itself to a fairly small number of side products for which the structures should be easy to deduce. Reactions in aqueous formic acid provide a convenient means to consider the technically important result of heating under reducing conditions with water and carbon monoxide. The use of sodium
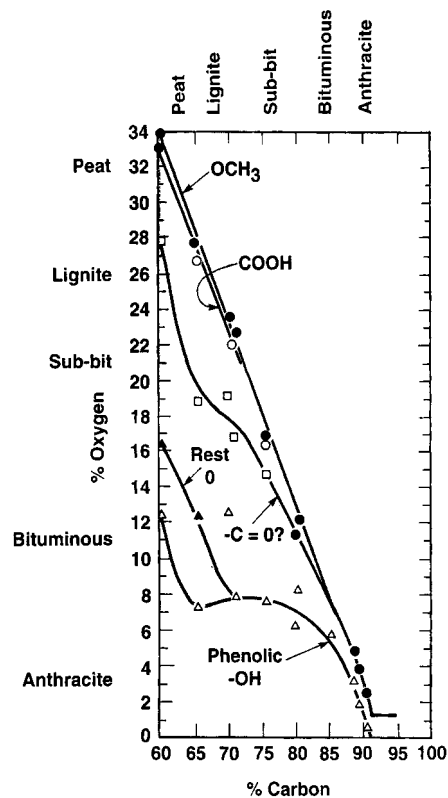

Figure 3. Oxygen functional groups in coals vary according to rank.

formate has allowed the probable effects of ion exchange of alkalis in the form of metal carboxylates, as found in fuel sources, to be studied in combination with an aqueous carbon monoxide treatment. Sodium bisulfite (because of the common occurrence of sulfur) and phosphoric acid (to study the effects on rate and mechanism using a thermally stable acid) were also used together with pyridine, calcium carbonate, or sodium carbonate to study the effects of base.

III. General Background

Plant substances are transformed into peat in the relatively quiescent waters of swamps. The subsequent burial of the peat in an aqueous anoxic (oxygen-free) environment causes further chemical and physical changes, and the peat is converted into lignite during the first stage of coalification. From a chemical point of view, coalification can be grossly viewed as a progression of molecular changes, some microbiological, that converts lignocellulosic plant material to coal, over millions of years and with increasing severity of geological conditions (especially temperature and pressure). Coalification is largely a deoxygenation–aromatization process; as the rank (degree of metamorphosis) of the coal progressively increases during heating, the organic oxygen content decreases and the proportion of aromatic rings increases by a series of condensations that include dehydration, dehydrogenation, alkylation, and elimination reactions. The concept is further illustrated by comparison (Figure 3)[59] of two parameters of rank in the principal reactive component of coal (vitrain): percent oxygen and percent carbon. During formation of bituminous coal, which lies about halfway along
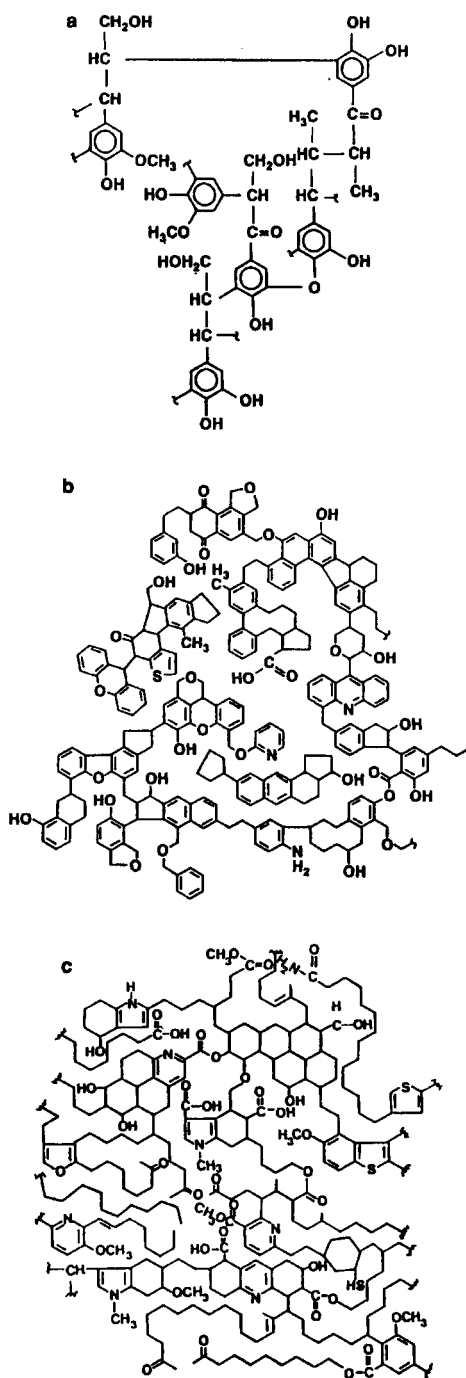
Figure 4. Portions of structural models of the representative organic material in resources: (a) lignite coal (Reprinted with permission from ref 60. Copyright 1990 Elsevier Science.), (b) bituminous coal (Reprinted with permission from ref 61. Copyright 1984 Elsevier Science.), (c) oil shale kerogen (Reprinted with permission from ref 62. Copyright 1989 Amercian Chemical Society.).

the metamorphic pathway between peat and high-ranked anthracite coal, the initial organic material becomes largely an insoluble, cross-linked macromolecular network. Parts of two-dimensional structural models believed to be representative of a low-rank lignite[60] and a medium-rank bituminous coal[61] (type III kerogens) are illustrated in Figure 4. To be solubilized or converted into liquid products, these structures must be chemically or thermally broken down or depolymerized. Most current technologies convert solid coal to synthetic fuel liquids by thermal free-radical depolymerization.

The organic material in oil shale is derived largely from algal material deposited in the mineral sediments of a lacustrine or marine environment. This process, called diagenesis, consists of condensation and aromatization pathways similar to those for coals and forms insoluble cross-linked macromolecular structures (types I and II kerogens). These kerogens typically have a higher aliphatic carbon content than coals. It is generally believed that the shale kerogens, which in an aqueous environment were exposed to increasing temperature and pressure, are the immediate precursors for most of the naturally occurring gaseous (natural gas) and liquid (petroleum) hydrocarbons. Because the temperature remains below 200 °C during oil generation, many researchers have postulated that catalysis would have been required to sufficiently lower the activation energies of the decomposition reactions. The most obvious natural catalysts are the clay minerals of the matrix in which the kerogen is dispersed. Grim[6] suggested that the clay minerals in shale and sediments concentrate organic substituents by absorption and then act as acidic catalysts in converting kerogens into petroleum.

Typical coals, and kerogens[62] in oil shales, consist of two- to three-ring aromatic clusters connected largely by cross-links, or bridges (Figure 4), of carbon as diarylmethanes and -ethanes, oxygen as diaryl and alkyl aryl ethers and some esters, and sulfur as diaryl and alkyl aryl sulfides. Hydroxyaromatics are abundant in coals, whereas carboxylic acids, ammonium carboxylates, primary amides, and smaller amounts of esters predominate in oil shales as pendant groups on aliphatic chains. In both coals and oil shales, most of the sulfur and nitrogen is present in heterocyclic rings.

The models in Figure 4 also suggest that carbon and oxygen cross-links need to be broken if solid coals and oil shale kerogens are to be converted into liquids usable as synthetic fuels. Thermal conversion at 400 °C easily cleaves 1,2-diarylethane bridges, but diarylmethanes are less susceptible and biphenyl-type linkages are thermally unreactive. Methylene-bridged cross-links are not reactive in hot water at 350 °C except in the presence of strong acids. In contrast, ether and ester cross-links are only slowly cleaved thermally at 350 °C, but in water they can be readily broken by hydrolysis at much lower temperatures (250–300 °C). Moreover, some of the water-soluble products generated (for example, acids and bases formed by hydrolysis of pendant ester, amide, and nitrile groups and by decarboxylation of acids and carboxylate salts) can be expected to autocatalyze these and other reactions both in commercial processes and in nature.

During diagenesis, condensation reactions predominate in the conversion of the initial plant and algal materials into the macromolecular network structures characteristic of kerogen. During catagenesis (the macromolecular depolymerization that generates petroleum) cross-link cleavage and hydrolysis reactions become dominant. Generally, in many model

Scheme 1[8] Condensation Reactions of Three 3-Pyridyl Derivatives in a Diagenetic Environment (Reprinted with permission from ref 8. Copyright 1990 American Chemical Society.)
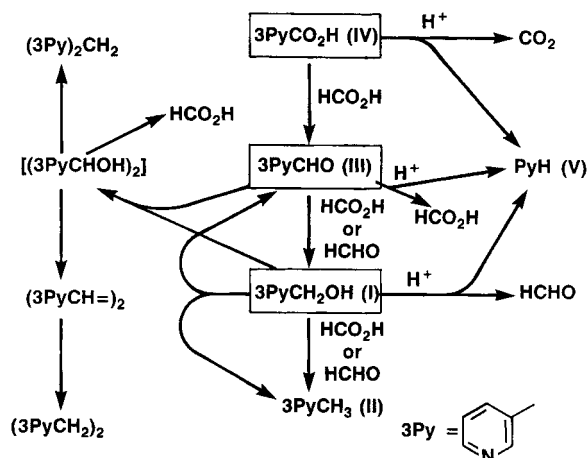
compound studies, the aliphatic derivatives typify the structures found in oil shale kerogens and the aromatic structures found in coals.

A. Autocatalysis

In the formation and depolymerization of resource materials, autocatalysis appears to be a major mechanistic pathway. During the diagenesis of kerogens, oxygen functionalities such as carboxylic acids, aldehydes, and alcohols are lost directly by cleavage and indirectly by condensation reactions that form methylene-bridged, ether and ester cross-links. The cleavage reactions release water-soluble products such as carbon dioxide, formic acid, and formaldehyde (Scheme 1). In the water-filled pore systems of oil-bearing rocks, the acids and formaldehyde can autocatalyze diagenesis and subsequent catagenesis chemistry. In addition to acid catalysis by carbon dioxide and formic acid, the formaldehyde and formic acid act as transfer agents for hydride ions and thereby reduce oxygen functionalities to alkyl groups and polycyclic aromatics to their partially hydrogenated hydroaromatic derivatives. When the three oxygenated pyridine derivatives (acid, aldehyde, and hydroxymethyl) are allowed to react in added formic acid or in formaldehyde generated in the forward reactions (Scheme 1), the course of the reaction changes such that methylated reduction product (**II**) is favored over pyridine (**V**).[8]

The effect on reaction rates of benzyl alcohol emphasizes the significance of autocatalysis. Benzyl alcohol undergoes ∼30% conversion to toluene, benzaldehyde, and dibenzyl ether in water after 1 day at 250 °C. Under these conditions, benzyl acetate is rapidly hydrolyzed to benzyl alcohol and 1 equiv of acetic acid; in the presence of acetic acid, conversion of the benzyl alcohol is three times as fast and not only are more toluene, benzaldehyde, and dibenzyl ether produced but also a series of alkylated products (benzylated benzyl alcohols and benzylated toluenes) not observed with the pure benzyl alcohol.[63] Many aqueous reactions are facilitated by increasing the ionic strength of the medium and catalyzed by acidic

and basic minerals in the geological formation, as well as by generation of organic acids (from aqueous hydrolysis of, for example, esters) and bases such as ammonia (by hydrolysis of nitriles and amides). For example, benzonitriles, pyridinecarbonitriles, benzamides, and pyridinecarboxamides are almost unaffected by thermolysis but are rapidly hydrolyzed in water at 250 °C to the corresponding ammonium carboxylates (the nitriles via the amides). The ammonia formed autocatalyzes these hydrolyses and the subsequent decarboxylations.[64]

Cycloalkyl-X-aryl (X = O, S, N) structures are representative of the major cross-links in a sample of a Kimmeridge shale, which is a source rock for petroleum found in the North Sea.[65] Studies of cyclohexyl phenyl compounds with oxygen, sulfur, and nitrogen links showed that they were relatively unreactive thermally but readily cleaved in water at 250 °C to form methylcyclopentene together with phenol, thiophenol, or aniline, respectively (eq 1).[66] The latter three products can autocatalyze other reactions in a mixture.
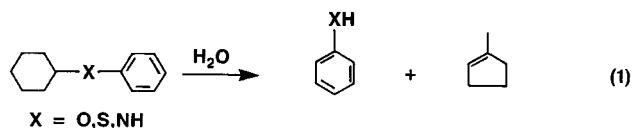
These ionic reactions are enhanced in brine (10% aqueous NaCl) and in the presence of an acidic clay, but are depressed by basic calcium carbonate. This evidence supports the notion that an acid-catalyzed carbocation mechanism operates in water at high temperature for this system. Other aryl ethers, especially diaryl ethers, are more representative of the structures found in coals. Additional more practical examples of autocatalysis are discussed next.

In other studies[7] modeling kerogen reactivity, decyl decanoate was readily hydrolyzed in water at 250 °C in an ionic reaction catalyzed by brine and calcium montmorillonite. Norton[67] described a hydrolytic process for making aromatic carboxylic acids from nitriles at 200−300 °C. In this approach no catalyst is added directly, but the aqueous solution from earlier hydrolyses is reused in order to take advantage of autocatalysis by ammonia formed during the hydrolysis of the amide intermediate. Analogous autocatalytic approaches have been used to form glycols by hydrolysis of the corresponding acetic acid diesters,[68] in order to produce formic acid from methyl formate,[69] and glycerine by hydrolysis of glycerol triacetate with water at 180−245 °C.[70] Evstratova et al.[71] hydrated 2,6-dicyanopyridine stepwise to the diamide in boiling water in a reaction that is acid- and base-catalyzed.

B. Related Reactions

Henderson et al.[72] showed that montmorillonite, in water at 375 °C, catalyzes the conversion (90%) of octacosane ($C_{18}H_{38}$) into an insoluble black carbonaceous material and small amounts of alkenes and aromatics. Without water, only 1% of the octacosane was converted to other alkanes and aromatics.

Jurg and Eisma[73] reacted samples of behenic acid (n-$C_{21}H_{43}COOH$) with montmorillonite in sealed tubes in the presence and absence of water at 200 °C for 89 and 760 h. They found that hydrocarbon formation was significant only in the presence of the clay catalyst. The ratios of iso- to normal-butane (1:40) and iso- to normal-pentane (1:40) were raised significantly in the absence of water (1:1) in both cases; the data indicate that the water did not induce carbocation chemistry. The increase in the proportion of saturated hydrocarbons with time at the expense of unsaturated hydrocarbons suggests that alkylation or hydrogenation reactions were occurring. Among the higher molecular weight hydrocarbons (C_{14}–C_{34}), there was a strong predominance (55–60%) of $C_{21}H_{44}$, the direct decarboxylation product of behenic acid. On the other hand, the aromatic carboxylic acid 1-naphthoic acid was decarboxylated slowly in pure water at 250 °C but reacted quantitatively in <2 h at 343 °C. Decarboxylation reactions are both acid and base catalyzed. Under anhydrous conditions, 1-naphthoic acid did not react at 250 °C; reaction at 343 °C was slow.[1] Seewald[74] and Lewan[75,76] alluded to the effect of water on carbon dioxide formation from kerogens during hydrous pyrolysis experiments (see section III.C).

Johns[77] studied the kinetics of the decarboxylation of behenic acid (n-$C_{21}H_{43}COOH$) using a series of clays under anhydrous conditions at 200–250 °C for 50–500 h. Arrhenius plots of the data show large decreases in activation energy (from 58.4 to 24.7 kcal/mol) for decarboxylation in the clay-catalyzed reactions compared to the reaction without clay catalysis. The time required for 90% decarboxylation at 60 °C is estimated to be from 2.9×10^{20} years for the thermal conversion to only 0.03 year when nontronite, an iron-containing clay, was present. Johns pointed out that the catalytic activity measured in these laboratory studies surpasses that of the natural shale kerogen systems, a finding consistent with the sharp decrease in clay acidity with increasing water content. Anhydrous calcium carbonate was also shown to promote the decarboxylation of C_{21} and C_{22} carboxylic acids to alkanes at 250 °C. The most prominent product formed with $CaCO_3$ from the C_{22} acid contained two less carbon atoms and was the C_{20} normal alkane (icosane). Much of the consumed fatty acid was converted to a brown, insoluble, kerogen-like material. The detailed kinetics of the thermal decarboxylation of aqueous solutions of acetic acid and sodium acetate with various clays and other minerals has been reported by Bell and co-workers.[78]

Frenkel and Heller-Kalai[79] demonstrated that the main reaction of the low molecular weight terpene limonene (**VII**), in the presence of montmorillonite, is conversion into the aromatic hydrocarbon p-cymene (**VIII**) and to p-menthane (**IX**) and p-menthene (**X**). This sequence demonstrates that such structures in kerogens could be converted by surface-active materials in sediments to low molecular weight aromatic compounds of the type found in petroleum (Scheme 2). A subsequent study by Goldstein[80]

Scheme 2. Reactions of Geraniol (a) and Limonene (b) in the Presence of Clay. (Adapted with permission from ref 79. Copyright 1977 Elsevier Science.)
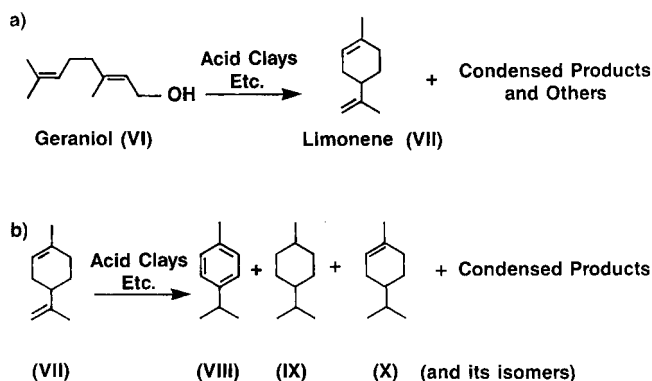
showed that geraniol (**VI**), a biologically synthesized unsaturated alcohol, undergoes a similar stepwise catalytic conversion in the presence of water, clays, and other sediments at <100 °C initially to form polymeric materials. These polymeric materials were converted into the thermodynamically stable phenyl, naphthyl, and higher condensed aromatic products. This model system study demonstrates that clay, limestone, and other sediments catalyze a wide variety of reactions in closed, water-containing systems of varying pH (3.9–9.7). Rates over clays and silica alumina decreased only by 40–50% versus the anhydrous systems.

The dimerization at the alkene bond in mono-unsaturated fatty acids was carried out at 200–260 °C in the presence of 2–5% of an acid-activated clay and 1–5% water in a pressure vessel or under reflux.[81,82] In this case, polymerization reactions were minimized in the presence of small amounts of clay. The yield of dimerization products was about 60% for oleic acid. It was hypothesized that the presence of steam prevents anhydride formation and decarboxylation.

Clark and co-workers studied the reactions of thiophene and tetrahydrothiophene in water at 240 °C: these compounds were converted slowly in water[28] but more rapidly in acidic media[29] and in the presence of metal cations.[30,31] A small quantity of H_2S was produced, as well as CO_2 and low molecular weight hydrocarbons as gaseous products, and a complex array of liquid sulfur-containing products. Tetrahydrothiophene was more reactive than thiophene and showed some reactivity at high pH. More recently, Clark and co-workers[32] studied the reactions of benzothiophene with water and in the presence of metal cations and identified several higher molecular weight products.

C. Hydrous versus Anhydrous Pyrolysis of Kerogen/H–D Exchange Reactions

In addition, several other studies have considered the reaction of resource materials (kerogens) in superheated water as an alternative to anhydrous pyrolysis at higher temperature. Simulation of petroleum formation requires the presence of hydrous conditions because water is ubiquitous in sediments.

Winters et al.[83] demonstrated that the characteristic low-olefin (high saturates) content of natural petroleum oils could be produced by hydrous pyrolysis of Woodford (Devonian), Phosphoria (Permian), and Kimmeridge (Jurassic) source rock shales at 330 °C. Thus, hydrous pyrolysis in a closed system appeared to be a more realistic reaction system than anhydrous pyrolysis in an open system, which, by contrast, generated large amounts of olefins. This work is complemented by that of Tannenbaum and Kaplan,[84] who carried out a comparative study in which low molecular weight hydrocarbons were generated from Green River oil shale kerogen by both hydrous and anhydrous pyrolysis. At 300 °C, production of initial C_2-C_6 olefins was comparable in both systems, but under aqueous conditions, their concentrations then started to decrease with time (also observed by Jurg and Eisma).[73] This high reactivity of the olefins may explain why olefins were not previously observed under hydrous conditions.

Hydrous pyrolysis[85] of a Messel shale, extracted with benzene-methanol, at 330 °C for 3 days in the presence of D_2O gave saturated hydrocarbon products multiply substituted with 1–14 deuteriums. Heating the saturated hydrocarbon docosane ($C_{22}H_{46}$) with a sample of solvent-extracted shale in an excess of D_2O showed only minor deuteration of the reisolated docosane (80%). This result suggests that simple hydrogen exchange on saturated molecules can be ruled out as a major pathway. However, under similar conditions in the aqueous system, the olefin 1-octadecene was completely reduced to octadecane (60%) with simultaneous significant deuterium incorporation. Hoering[85] applied similar treatment to a kerogen–2-methylheptadecanoic acid mixture and found that the acid decarboxylated to 2-methylheptadecane in 10% yield, whereas facile deuterium exchange took place at hydrogen atoms adjacent to oxygenated functional groups. In other studies, Hoering and Abelson[86] showed that deuterated hydrocarbons are generated from kerogen heated in D_2O at 100 °C and then dried and pyrolyzed in an inert atmosphere. They proposed that olefins, or olefin intermediates generated during pyrolysis, exchanged with the D_2O. Alexander et al.[87] found that there was considerable exchange of isotopic hydrogen between naphthalenes and the acidic clay surfaces at 23 °C or in aqueous slurries at 70 °C. Junk and co-workers observed many types of deuterium isotope exchange with organic compounds in water containing low concentrations of sodium deuterioxide.[88] More recently, Stalker[89] and Koopmans[90] reported that hydrous pyrolysis of Kimmeridge Clay Formation kerogen at ~315 °C for 72 h in D_2O (uncatalyzed) generated hydrocarbons derived from cleavage of the macromolecular structure adjacent to heteroatom (C–O, C–S) linkages in the kerogen. Previous model compounds studies[91] indicated that exchange with ^{18}O-labeled water was less efficient than exchange observed in similar products generated by hydrous pyrolysis of a Kimmeridge clay kerogen under identical conditions.

Ring cleavage reaction of 2,5-dimethylfuran in deuterium oxide[51] led to extensive deuteration of the

Table 1.[51] Hydrogen/Deuterium Exchange in Ketones (Reprinted with permission from ref 51. Copyright 1994 American Chemical Society.)

compound	% D (position)	temp, °C	time, min
pinacolone[a]	100 (α CH$_3$)	277	60
acetone	97 (α,α' CH$_3$)	200	60
cyclopentanone[b]	100 (α,α' CH$_2$)	225	30
1,4-cyclohexanedione	100 (α,α' CH$_2$)	225	30
Acetophenone	>88 (α CH$_3$)	250	60
Deoxybenzoin[c]	99 (α CH$_2$)	250	30

[a] Exchange observed in the rearrangement product of pinacol. [b] Exchange observed in the hydrolysis product of the corresponding ethylene ketal. [c] PhCH$_2$COPh.

methyl and methylene groups of the product, 2,5-hexanedione. The same result was detected by ^1H and ^{13}C NMR when this dione was the initial reagent. Thus, it was reinforced that deuterium oxide without added acid or base was a suitable reactant for $^1H/^2H$ exchange.[51] These exchange reactions afforded a means to study organic transformations in a reaction environment undergoing minimal changes; for example, no products are formed that have significantly different properties or reactivities from those of the initial reagents. Also, no changes occur in reaction mechanisms, volume, vapor pressure, or the dielectric or dissociation constants of deuterium oxide because of the formation of ionic products and potential catalysts or cosolvents. Deuterium isotope effects were not studied. Deuterium oxide treatments of methyl (300 °C, 93 h), isopropyl, and neopentyl alcohol (200 °C, 30 min and 300 °C, 60 min, respectively) did not induce any exchange of C–H hydrogens; the same negative results were obtained in experiments with ethylene glycol (300 °C, 60 min) and pentaerythritol (250 °C, 60 min).[51] However, hydrogen exchange was achieved rapidly and nearly quantitatively in the α and α' (where applicable) positions to ketone carbonyl groups. Table 1 lists the extents and sites of deuteration observed in selected ketones. In all cases, the operating enol–keto tautomerism led exclusively to hydrogen exchange; no aldol products were observed. The ionic mechanism for deuterium exchange is illustrated in eq 2 for pinacolone.[92]
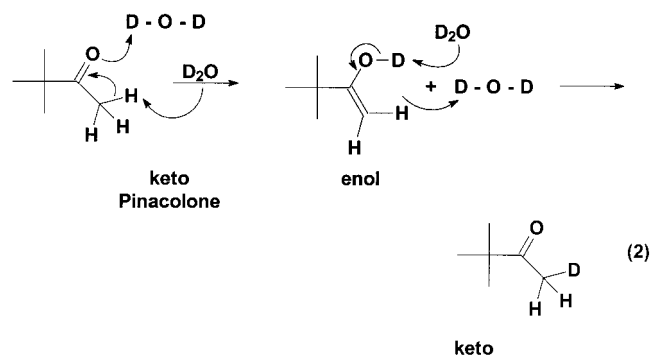
Yonker observed D-exchange via NMR on the aromatic carbons of resorcinol beginning at 200 °C in D_2O.[93] A recent discovery using redox-buffered mineral assemblages (e.g., pyrite–pyrrhotite–magnetite (PPM)) to effect the disproportionation of water into

hydrogen and oxygen[94-98] opens up the possibility for free-radical mechanisms for hydrogen exchange (Note: the bond dissociation energy for water is 119.1 kcal/mol). Nearly quantitative exchange by reaction with only 0.016 M sodium deuterioxide solution for 10 min at 400 °C and ~300 bar pressure occurred for molecules having pK_a's up to approximately 40, such as toluene which has a pK_{HB} of 40.9, while longer heating time and more concentrated base solutions allow deuteration of still more weakly acid compounds having pK_a's up to 50.[99-102]

In later studies, Huizinga et al.[103] found that the presence of clay minerals influenced the production of aliphatic hydrocarbons during laboratory thermal maturation studies of immature type I and type II kerogens at 200−300 °C in a manner critically dependent on the water concentration. During dry pyrolysis, where only pyrolysate water is present, normal alkanes of 12 or more carbon atoms and acyclic isoprenoids are almost completely destroyed by montmorillonite but undergo only minor alteration in the presence of illite. The presence of both clay minerals caused significant reduction in alkene formation and preferential retention of large amounts of the polar constituents of the bitumen (soluble, petroleum-like portion) but not alkanes or acyclic isoprenoids. Therefore, in the presence of these clay minerals, especially when dry, the constituents of bitumen fractionate according to their polarity. By this process, alkanes and acyclic isoprenoids are concentrated in the bitumen or petroleum fraction that is not strongly adsorbed on the clay matrixes. The extent of these concentration effects is greatly diminished during hydrous pyrolysis. Under hydrous conditions (a mineral:water ratio of 2:1), the acidity, and therefore the effect of the clay minerals, is substantially reduced.

Eglinton et al.[104] carried out the hydrous pyrolysis of a Kimmeridge kerogen (type II) at 280 or 330 °C for 72 h in the presence of clay or carbonate minerals. They found that more organic-soluble pyrolysate was formed when calcium carbonate was the inorganic component. This result suggests that base-catalyzed cleavage of cross-links can be significant.

Kawamura et al.[105] also reported that water present during the 200−400 °C pyrolysis of Green River kerogen either enhanced the release of long-chain carboxylic acids (C_{10}−C_{32}) or reduced the rate of their thermal destruction. These results suggest that decarboxylation is not an important mechanism for generating aliphatic hydrocarbons during hydrous pyrolysis, a theory that agrees with some[7] but not all[73,78,85] of the studies on reactions of alkyl carboxylic acids in water. However, Kawamura logically suggested that carboxylic acids may be decarboxylated once they are released into bitumen, especially in a clay-rich mineral matrix.

More recently, Eglinton et al.[106] showed that significant quantities of carboxylic acids are generated from bitumen-free (solvent-extracted) kerogen concentrates, especially type II kerogens, and that the presence of minerals significantly influences the amount of acids produced. The major acid product in all cases was acetic acid, suggesting that ester hydrolysis is a key route.

Graff and Brandes[107] found that a steam pretreatment of an Illinois bituminous coal (type III kerogen) between 320 and 360 °C dramatically improved the yield of liquids upon subsequent conversion or solvent extraction. The steam-modified coal contained twice the amount of hydroxyl groups of the raw coal. This result leads to the conclusion that steam cleaves the ether linkages in coal; this reaction forms hydroxyl groups and thereby substantially decreases an important covalent cross-link in the coal structure.[108] These conclusions are consistent with model compound studies on ether reactivity in hot water.[1,66,109]

IV. Conclusions

In this article, we have emphasized the reactivity of organic molecules in superheated water. Apart from biological processes (~37 °C), where aqueous chemistry predominates and is catalyzed by enzymes, kerogen formation and its subsequent depolymerization into petroleum (<200 °C) is the major arena in nature where aqueous chemistry is observed. In this chemistry, water participates as catalyst, reactant, and solvent. Although the geochemical aspects serve as a foundation for understanding the aqueous chemistry, the implications for a wide variety of other organic chemical transformations and technological applications are potentially large and just beginning to emerge. The relevance of the aqueous chemistry to more recent findings of higher temperature petroleum generation (200−300 °C) for hydrogen-rich marine-derived organic matter is even more exciting.[110] The ability of water to carry out condensation, cleavage, and hydrolysis reactions and to effect selective ionic chemistry (not accessible thermally) is largely due to changes in its chemical and physical properties, which become more compatible with the reactions of organics as the temperature is increased. Therefore, the solvent properties of water at 250−350 °C approach those of polar organic solvents at room temperature. Water can act as an acidic or basic catalyst, and its reactivity can often be reinforced by autocatalysis from water-soluble reaction products. Additional positive aspects of the use of aqueous chemistry are its simplicity, low cost, and favorable environmental impact.

V. Acknowledgment

VI. References

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