here is not to be exhaustive but rather to show that some research contributions are consistently demanded today, as opposed to the occasional, ad hoc efforts of the past. Thus, no mention is made of some notable research contributions to judicial decision-making, because the process is still sporadic rather than routine, as in certain decision-making processes of the legislative and executive branches.

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14. P. Rossi, G. A. Fisher, G. Willis, *The Condition of the Homeless of Chicago* (Social and Demographic Research Institute, University of Massachusetts, Amherst, and National Opinion Research Center, Chicago, 1986).
15. U.S. General Accounting Office, *The Future Flow of Legal Immigration to the United States* (GAO/PEMD-88-7, January 1988); *Projected Immigration Under S. 448 and Recent Trends in Legal Immigration* (GAO/PEMD-89-12, April 1989); *Immigration Reform: Major Changes Likely Under S. 358* (GAO/PEMD-90-5, November 1989).
16. See the series of evaluations of chemical warfare by the U.S. General Accounting Office: *Chemical Warfare: Many Unanswered Questions* (GAO/IPE-83-6, April 1983); *Progress and Problems in Defensive Capability* (GAO/PEMD-86-11, July 1986); *Bigeye Bomb: An Evaluation of DOD's Chemical and Developmental Tests* (GAO/PEMD-86-12BR, May 1986); *Bigeye Bomb: Unresolved Developmental Issues* (GAO/PEMD-89-27, August 1989); *Bigeye Bomb: Evaluation of Operational Tests* (GAO/PEMD-89-29, August 1989).
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18. J. S. Coleman, T. Hoffer, S. Kilgore, S. S. Peng, *Public and Private Schools* (National Center for Education Statistics, Washington, DC, 1982); T. Hoffer, A. M. Greeley, J. S. Coleman, *Achievement Growth in Public and Catholic Schools*, vol. 58, no. 2 of *Sociology of Education* (American Sociological Association, Washington, DC, April 1985); J. S. Coleman and T. Hoffer, *Public and Private Schools: The Impact of Communities* (Basic Books, New York, 1987).
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21. F. Braudel, in the preface to Alexis de Tocqueville, *Souvenirs* (Gallimard, Paris, 1978), p. 12.
22. P. Sulkunen, *Health Policy* **7**, 325 (1987).
23. P. S. J. Cafferty, B. R. Chiswick, A. M. Greeley, T. A. Sullivan, *The Dilemma of American Immigration* (Transaction Books, New Brunswick, NJ, 1983), p. 47.
24. The General Accounting Office has in fact proposed this initiative to the Office of Management and Budget's director [see *Transition Series: Program Evaluation Issues* (GAO/OCG-89-8TR, November 1988) and *Improving Program Evaluation in the Executive Branch* (GAO/PEMD-90-19, May 1990)]; indeed, the latest federal budget (fiscal year 1992) shows some renewed emphasis being accorded to evaluation after a long period during which executive branch evaluation offices steadily lost both personnel and funds.
25. The views and opinions expressed by the author are her own and should not be construed to be the policy or position of the General Accounting Office.

Reactivity of Organic Compounds in Hot Water: Geochemical and Technological Implications

MICHAEL SISKIN AND ALAN R. KATRITZKY

Understanding of the reactivity of organic molecules in hot water is developing from studies aimed at explaining how organic matter (kerogen) forms in natural environments and then breaks down into energy source materials. In natural systems where kerogens are depolymerized, hot water is ubiquitous and usually contains salt and minerals. Reactions such as ionic condensation, cleavage, and hydrolysis are facilitated by changes in the chemical and physical properties of water as temperature increases. These changes make the solvent properties of water at high temperature similar to those of polar organic solvents at room temperature, thus facilitating reactions with organic compounds. An understanding of aqueous organic chemistry may lead to potential applications in areas as diverse as the recycling of plastics, the synthesis of chemicals, and coal liquefaction.

THIS ARTICLE DESCRIBES AN EMERGING AREA OF CHEMISTRY: the transformations of organic compounds in hot water at elevated pressure. Although conventional wisdom holds that most organic compounds do not react with water under normal conditions, our overview demonstrates that water frequently participates as catalyst 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 interest to geologists and chemists and may provide a means for reducing pollution by 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.

Organic molecules that were previously considered to be unreactive in liquid water undergo many chemical reactions when the temperature is increased to 250° to 350°C; these reactions were previously expected only in the presence of strong acid or base. For example, ethers and esters, which are unreactive to heat alone,

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undergo facile cleavage and hydrolysis, respectively, in water at 250° to 350°C (*1*). Similarly, polyethylene terephthalate polymers (found in plastic soft drink bottles) can be hydrolyzed quantitatively back to their starting materials in hot water in less than an hour (*2*). Other polyesters and also polyamides (such as nylon) 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, are converted in source rocks 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 (*3*). Two additional factors can affect and catalyze kerogen 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 aqueous environments (*4, 5*).

Should one expect organic chemical reactions to take place in hot water? Dramatic changes in the physical and chemical properties of water suggest the possibility: as temperature increases, water becomes more compatible to reaction with 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 (*6*), its dielectric constant decreases from 78.85 to 19.66 (*7*), and its solubility parameter decreases from 23.4 to 14.5 (cal/cm^3)$^{1/2}$ (*8*). Over the same temperature range, the ionic product (dissociation constant) of water increases by three orders of magnitude, from $10^{13.99}$ to $10^{11.30}$ (*9*), even though the dielectric constant falls with rising temperature. These changes in physical properties make 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 water far beyond the natural acceleration due to increased temperature.

The reactivity of organics in water in the temperature range 200° to 350°C (*10*) 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 are carried out in closed reactors, such as an autoclave, in which a liquid water phase is maintained (*5*). Pressures range from ~4 MPa at 250°C to ~17 MPa at 350°C. 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, we present in this article an overview of the reactivity of a broad range of organic molecules in hot water, including in the presence of minerals and brine. These advances have increased our confidence in our ability both to understand organic geochemical processes and to promote new desired reactions under environmentally clean and safe conditions.

Geochemical Background

Plant substances are transformed in the relatively quiescent waters of swamps to peat. The subsequent burial of the peat in an aqueous anoxic 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 aromaticity increases by a series of condensations that include dehydration, dehydrogenation, alkylation, and elimination reactions. The concept is further illustrated by comparison (Fig. 1) (*11*) 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 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 (*12*) and a medium-rank bituminous coal (*13*) (type III kerogens) are illustrated in Fig. 2. 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 shale kerogens, which

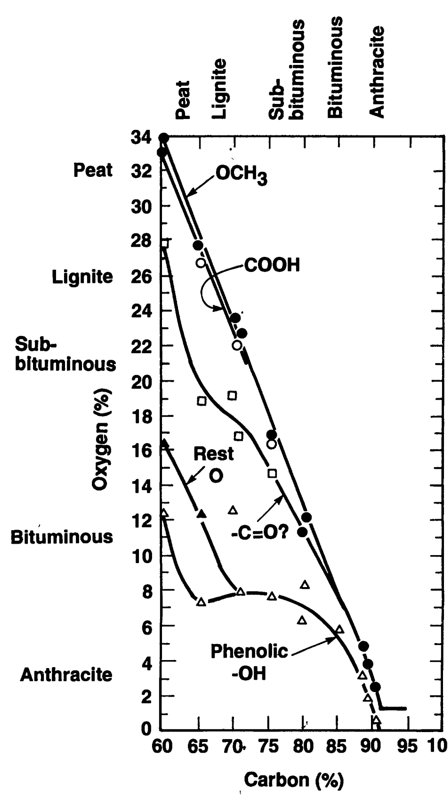


Fig. 1. Oxygen functional groups in coals vary according to rank. [Adapted from van Krevelen (*11*) with permission]

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 (*3*) suggested that the clay minerals in shale and sediments concentrate organic substituents by absorption and then act as acid catalysts in converting kerogens into petroleum.

Typical coals and kerogens (*14*) in oil shales consist of two- to three-ring aromatic clusters connected largely by cross-links, or bridges (Fig. 2), of carbon as diaryl methanes 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 Fig. 2 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 diaryl ethane bridges, but diaryl methanes 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° to 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 compound studies, the aliphatic derivatives typify the structures found in oil shale kerogens and the aromatic structures found in coals.

Condensation Reactions

A wide variety of organic compounds has been found to undergo condensation reactions in the presence of hot water. Alkenes and alcohols react alone, or together, in the presence of hydrated, cation-exchanged (Al^{3+}, Cr^{3+}) layered clays at 100° to 200°C to give the corresponding ethers (*15*). The aldehyde 1-decanal reacts readily in water at 250°C to form large amounts of the aldol condensation product (*4*). The cyclic dehydration of butane-1,2,4-triol to 3-hydroxytetrahydrofuran takes place in the presence of water and a hydrated montmorillonite (*16*).

In water and 10% aqueous brine, 1-decylamine is converted in low yield (~8%) into *N,N'*-di- and *N,N',N''*-tridecylamine. In the presence of calcium montmorillonite, the condensation reaction is much accelerated (*4*). Primary and secondary amines can be converted, also in the presence of hydrated cation-exchanged (Al^{3+}, Cr^{3+}) layered clays, into secondary and tertiary amines, respectively (*15*).

Several types of condensation reactions and synergisms would be expected to take place if three 3-pyridyl derivatives (Scheme 1) were present in a diagenetic environment, where solid kerogens are

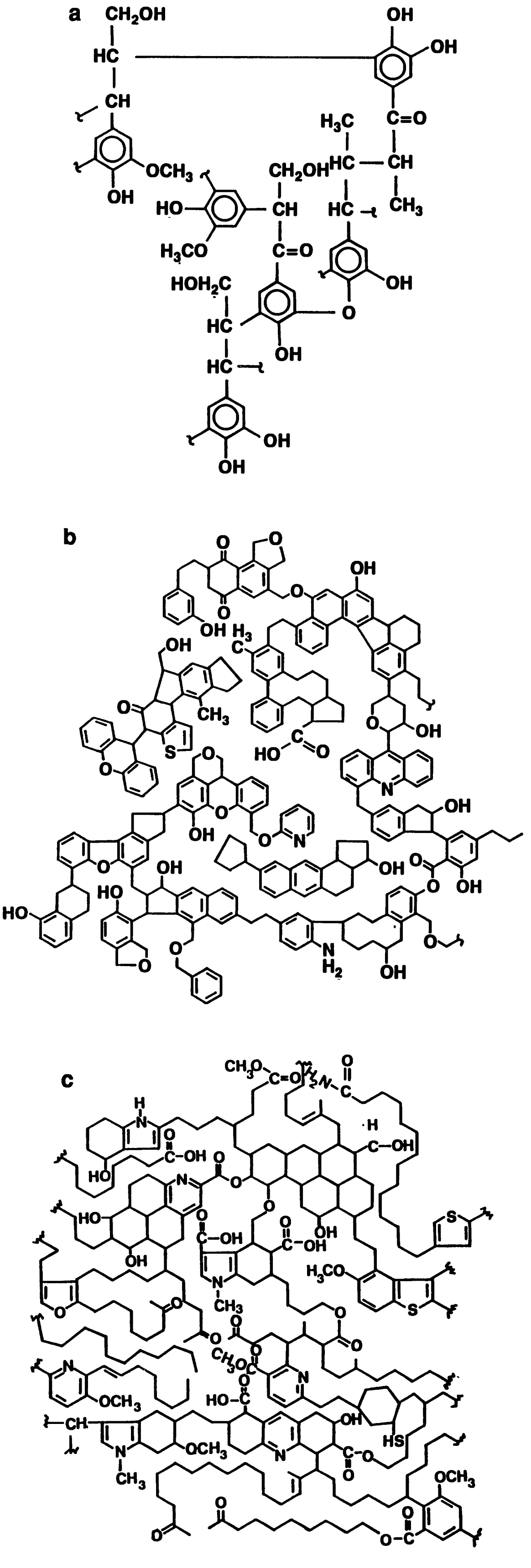
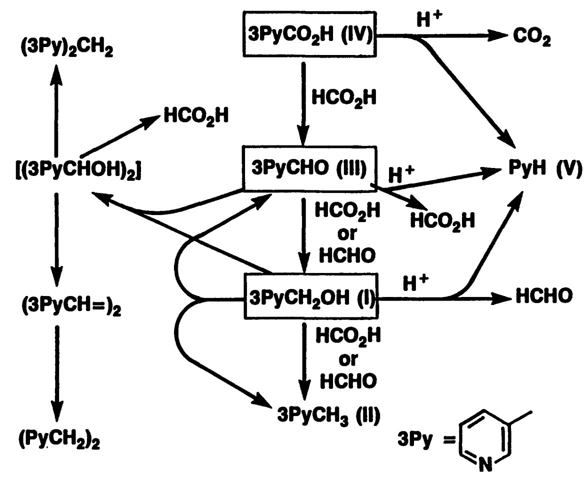


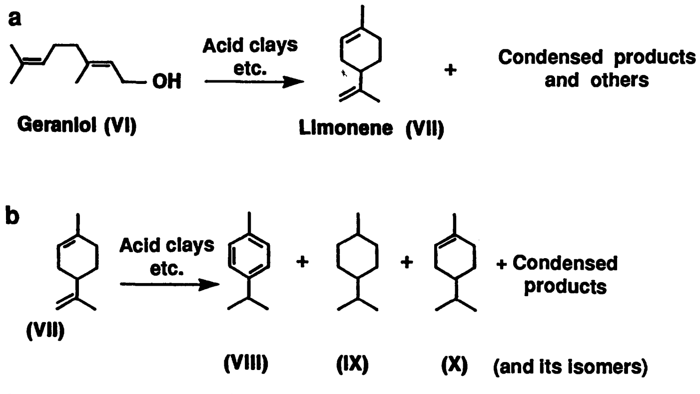
Fig. 2. Portions of structural models of the representative organic material in resources: (**a**) lignite coal [from (*12*) reprinted with permission from Pergamon Press PLC]; (**b**) bituminous coal [from (*13*), reprinted with permission from Butterworth-Heinemann Ltd. and the author]; (**c**) oil shale kerogen (*14*).



Scheme 1. Condensation reactions of three 3-pyridyl derivatives in a diagenetic environment. [Adapted from (*5*) with permission from the American Chemical Society]

formed from plant and algal material in water (*4*). The 3-pyridyl methanol (I) disproportionates into 3-picoline (II) (which does not react further) and pyridine-3-carboxaldehyde (III). The aldehyde and alcohol then condense to the bridged methylene, ethane, and ethylene structures (left side of Scheme 1). Parallel decomposition reactions of the acid (IV), alcohol (I), and aldehyde (III) in water generate molecules of carbon dioxide, formic acid, and formaldehyde, respectively, which are water-soluble and potential reagents in acid catalysis and hydride transfer reductions.

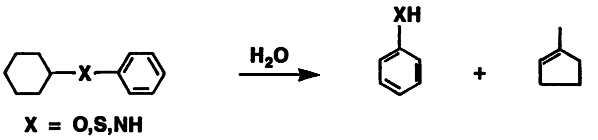
Frenkel and Heller-Kalai (*17*) demonstrated that the main reaction of the low-molecular-weight terpene limonene (VII), in the presence of montmorillonite, is converted to the aromatic hydrocarbon *p*-cymene (VIII) and to *p*-menthane (IX) and *p*-menthene (X). This sequence demonstrates that such structures 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 (*18*) 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 to 9.7).



Scheme 2. Reactions of geraniol (**a**) and limonene (**b**) in the presence of clay. [Adapted from (*17*) with permission from Pergamon Press PLC]

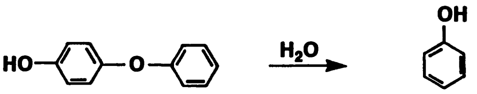
Bond Cleavage Reactions

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 (*19*):



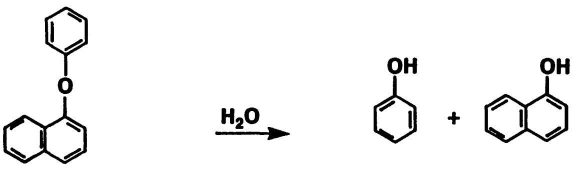
(1)

These ionic reactions are enhanced in brine (10% 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. 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 (*20*). Other aryl ethers, especially diaryl ethers, are more representative of the structures found in coals. Although an acyclic diaryl ether(diphenyl ether) and a cyclic diaryl ether (dibenzofuran) were unreactive under both aqueous and thermal conditions, an activated diaryl ether (4-phenoxyphenol) was preferentially cleaved in water to form large amounts of phenol (*1*):

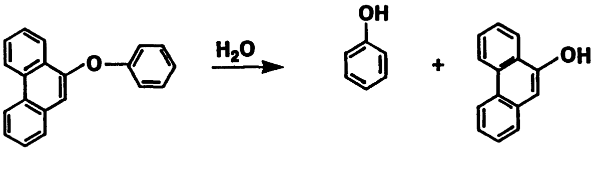


(2)

Similarly, benzyl aryl ethers were much more susceptible to cleavage under aqueous than thermal conditions at 250°C. Significantly, the unactivated diaryl ethers 1-phenoxynaphthalene and 9-phenoxyphenanthrene are cleaved in water at 315°C in 2 hours to phenol and 1-naphthol or 9-phenanthrol, respectively (*21*):



(3)

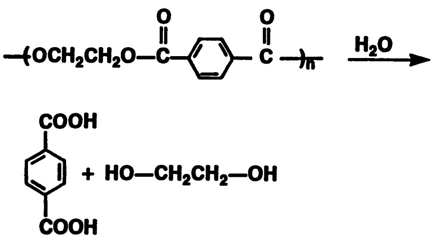


(4)

Ester groups, which are bound into the network of resource structures and serve as cross-links, although thermally unreactive, are easily cleaved in water at 250° to 350°C (*4*).

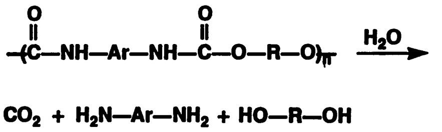
Hydrolysis Reactions

Synthetic polymers can be considered analogous in structure to and contain many of the functional groups found in the macromolecular structure of resource materials. Hydrolysis reactions have been used to effect desired chemical changes in synthetic polymers in a manner similar to natural geochemical reactions (as discussed later). Mandoki (*2*) described a simple approach for the neutral hydrolytic decomposition of condensation polymers such as polyethylene terephthalate (soda bottles), nylon 6 and 66, other synthetic fibers, and polycarbonates in water at 200° to 300°C:



(5)

Similarly, polyurethane foams can be hydrolyzed to reusable diamines and glycols (*22*):



$$-\!\{\overset{\overset{O}{\|}}{C}-NH-Ar-NH-\overset{\overset{O}{\|}}{C}-O-R-O\}_n \xrightarrow{H_2O} CO_2 + H_2N-Ar-NH_2 + HO-R-OH \qquad (6)$$

In other studies (*4*) modeling kerogen reactivity, decyl decanoate was readily hydrolyzed in water at 250°C in an ionic reaction catalyzed by brine and calcium montmorillonite. Norton (*23*) described a hydrolytic process for making aromatic carboxylic acids from nitriles at 200° to 300°C. In this approach, no catalyst is added directly, but the aqueous solution from earlier hydrolyses is used 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 (*24*) in order to produce formic acid from methyl formate (*25*) and glycerine by hydrolysis of glycerol triacetate with water at 180° to 245°C (*26*). Evstratova *et al.* (*27*) hydrated 2,6-dicyanopyridine stepwise to the diamide in boiling water in a reaction that is acid- and base-catalyzed.

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 (*28*).

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 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**) (*5*).

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 one equivalent 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 (*29*). 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). Other more practical examples of autocatalysis were discussed above.

Related Reactions

Henderson *et al.* (*30*) 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 (*31*) 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 hours. 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 presence of water (1:1) in both cases; the data indicate that the water induced 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} to C_{34}), there was a strong predominance (55 to 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 water at 250°C but reacted quantitatively in <2 hours at 343°C. Under anhydrous conditions there was no reaction at 250°C; reaction at 343°C was slow (*1*).

Johns (*32*) studied the kinetics of the decarboxylation of behenic acid using a series of clays under anhydrous conditions. 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 ranged 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.

The dimerization at the alkene bond in monounsaturated fatty acids was carried out at 200° to 260°C in the presence of 2 to 5% of an acid-activated clay and 1 to 5% water in a pressure vessel or under reflux (*33, 34*). The yield of dimerization products was about 60% for oleic acid.

Clark and co-workers studied the reactions of thiophene and tetrahydrothiophene in water at 240°C: these compounds were converted slowly in water (*35*), but more rapidly in acidic media (*36*) and in the presence of metal cations (*37, 38*). 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 (*39*) studied the reactions of benzothiophene with water and in the presence of metal cations and identified several higher molecular weight products.

Hydrous Versus Anhydrous Pyrolysis of Kerogen

The studies of organic compounds discussed above have led to a better understanding of aqueous organic chemistry. In addition, several other studies have considered the reaction of resource materials (kerogens) in hot 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.* (*40*) 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 (*41*), 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 to 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 (*31*)]. This high reactivity of the olefins may explain why olefins were not previously observed under hydrous conditions.

Hydrous pyrolysis (*42*) 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 to 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 (*42*) 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 (*43*) 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.* (*44*) 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.

In later studies, Huizinga *et al.* (*45*) 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° to 300°C in a manner critically dependent on the water concentration. During dry pyrolysis, where only pyrolyzate 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 matrices. 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.* (*46*) carried out the hydrous pyrolysis of a Kimmeridge kerogen (type II) at 280° or 330°C for 72 hours in the presence of clay or carbonate minerals. They found that more organic-soluble pyrolyzate was formed when calcium carbonate was the inorganic phase. This result suggests that base-catalyzed cleavage of cross-links can be significant.

Kawamura *et al.* (*47*) also reported that water present during the 200° to 400°C pyrolysis of Green River kerogen either enhanced the release of long-chain carboxylic acids (C_{10} to 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 (*4*), but not all (*31, 32, 42*) 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.* (*48*) 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 (*49*) 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 hydroxyl groups of the raw coal. This result leads to the conclusion that steam reacts with the ether linkages in coal; this reaction forms hydroxyl groups and thereby substantially decreases an important covalent cross-link in the coal structure (*50*). These conclusions are consistent with model compound studies on ether reactivity in hot water (*1, 19, 21*).

Implications for Technology

Chemical reactions carried out in hot water have the potential to provide a cleaner, safer environment than reactions in hydrocarbon solvent media. In addition, water acting as a catalyst or reagent could minimize, or possibly eliminate, the need for catalyst synthesis, recycle, regeneration, and disposal. Application to the recycle of condensation polymers such as plastics, synthetic fibers, and polycarbonates is attractive (*2, 22*). Another potential application is the use of hot water treatment to upgrade low-value by-products of operating processes. A demonstrated example occurs in the hydration of propylene with sulfuric acid to form isopropyl alcohol and diisopropyl ether as a by-product. Hydrous cleavage of this ether at 315°C for 30 min readily forms essentially equimolar amounts of the desired product, isopropyl alcohol, and recyclable propylene (*51*). Di-*sec*-butyl ether, a by-product in the hydration of butylene to *sec*-butyl alcohol in the methyl ethyl ketone process, similarly can be converted to the alcohol in hot water (*51*).

Kerogens are generated in an aqueous environment largely by condensation reactions followed by depolymerization. Aqueous pretreatment of coals at moderate temperatures could increase the amount of extractable liquids or enhance subsequent liquefaction conversion (*49*). Other potential applications for hot water in by-product upgrading, waste-stream cleanup, recycling of surplus materials, and so forth, are numerous and await innovative ideas.

Conclusions

In this article, we have emphasized the geochemistry of the reactivity of organic molecules in hot water. Apart from biological processes, where aqueous chemistry predominates and is catalyzed by enzymes, kerogen formation and its subsequent depolymerization into petroleum 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 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° to 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.

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