# **Reactions in High-Temperature Aqueous Media**

Alan R. Katritzky,\*," Daniel A. Nichols," Michael Siskin,<sup>‡</sup> Ramiah Murugan,<sup>§</sup> and Marudai Balasubramanian<sup>§</sup>

Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, ExxonMobil Research and Engineering Company, Corporate Strategic Research Laboratory, 1545 Route 22 East, Clinton Township, Annandale, New Jersey 08801-3059, and Reilly Industries, Inc., 1500 South Tibbs Avenue, P.O. Box 42912, Indianapolis, Indiana 46242

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*	To	whom	corres	pondence	should	be	addressed.
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- University of Florida.
- <sup>‡</sup> Exxon Research and Engineering Co. <sup>§</sup> Reilly Industries, Inc.

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### I. Introduction to Model Compound Studies

The present article is the second of a pair describing the transformations of organic compounds in superheated water at elevated pressures. The first article<sup>1a</sup> addressed the background to this subject and its historical development. The first article also covers the geochemical background and describes the effects of various salts and minerals as catalysts (cf also ref 1b).



Alan Katritzky is the Director of the Florida Center for Heterocyclic Compounds at the University of Florida, where he has been Kenan Professor of Chemistry since 1980. His research encompasses heterocyclic chemistry, synthetic methodology, quantitative structure—property relationships, and many areas of mechanistic and applied organic chemistry. The Katritzky Research Group enjoys close relationships with the chemical and allied industries as documented in detail on his homepage at ark.chem.ufl.edu.



Daniel A. Nichols, born in 1972, received his Ph.D. degree in Organic Chemistry in 1999 at the University of Florida. He subsequently enlisted in the U.S. Army and received training as a Test, Maintenance, and Diagnostic Equipment Support Specialist. He recently received a direct commission to Captain and will be working as a biochemist.

Photograph and biography for Michael Siskin can be found on p 825.



Ramiah Murugan is a Senior Research Associate in the Chemistry Center of Excellence of Reilly Industries Inc. His expertise is in the area of heterocyclic chemistry. He holds a B.S. degree from American College, Madurai, and a M.S. degree from Madurai University. He received his Ph.D. degree from the University of Florida working with Professor Katritzky.



Marudai Balasubramanian, often known as Balu, grew up in Trichy, South India. He received his M.S. degree at Vivekananda College/Madras University, Chennai, India, and his Ph.D. degree in Organic Chemistry from the Indian Institute of Technology, Chennai, India, in 1987. He was a Research Associate briefly at ICI India Ltd., Chennai, India. He did postdoctoral work (1988–1992) with Dr. Alan R. Katritzky, Department of Chemistry, University of Florida, Gainesville. His main research was on reactions in hot water, and also in this period he acquired in-depth knowledge in various aspects of heterocyclic chemistry, especially pyridine chemistry. Since 1993 he has been a Research Chemist at Reilly Industries, Inc., Indianapolis. His expertise is in the synthesis of pyridine intermediates for agrow and Pharma products. Recently, he has been focusing on pyridine-based water-soluble polymers in household cleaning products. He is currently working in a team to identify new products and new business opportunities.

The present article is intended to cover systematically the knowledge base that has been built up for the reactions of various classes of organic compounds with superheated water, detailing the products that are formed and describing the mechanisms that were deduced for their formation.

# A. Scope

Most of the work carried out in the laboratories of the present authors was concerned with the establishment of this knowledge base to assist the interpretation of the study of fuel stock transformations induced by high-temperature aqueous treatments. This bias is reflected in the content of this review, although we have attempted to include all available relevant work. We attempted to assemble all relevant references for the period 1950-1999 which cover reactions of organic compounds in aqueous media at high temperatures (generally  $\gg 100$  °C). We have included reactions in water containing (usually small quantities of) a number of common simple additives including bases, acids, salts, CO, SO<sub>2</sub>, etc., to clarify mechanistic interpretations. We have not included, for the most part, reactions between two organic molecules or the influence of water on such reactions (see, e.g., ref 2a). We have, for space and time reasons, treated only briefly or not at all highly halogenated compounds, high-energy (polynitro) substances, and polymeric derivatives. The treatment within these limits is more extensive than, for example, in the review by Savage,<sup>2b</sup> as indicated by the fact that his review quotes less than 1 in 5 of the references in the present review; but our treatment is much less extensive than that of Savage regarding engineering aspects, decomposition of complex materials, and oxidation (SCWO). Thus, the present review can be considered to be complementary to that of Savage.2b

#### **B.** Organization

The present article is intended to cover systematically the knowledge base that has been built up for the reactions of various classes of organic compounds with superheated water, detailing the products that are formed and describing the mechanisms that were deduced for their formation.

The content of the present article is organized according to the structure of the starting material. We first consider hydrocarbons and heterocycles without functional groups. In general, the model compounds investigated are those which are most relevant to studies of natural fuel stocks. Therefore, the hydrocarbons considered include mono- and polycyclic benzenoids. We also describe in some detail pyridines and pyrroles and their derivatives. In rather less detail, the available work on thiophenes and furans and their benzo derivatives is described. Heterocycles with two or more heteroatoms are covered only briefly because they occur only in very low concentration in fuel stocks.

We then consider compounds containing the most relevant different types of functional groups. These are classified according to the elements that they contain. Thus, oxygen-containing groups are first considered, then nitrogen-containing, followed by sulfur-containing functional groups, and finally there is a short section on compounds containing other elements.

#### C. Role of Additives

We have examined not only reactions in water alone, but also in the presence of a number of additives. Because it rapidly became evident that many of the reactions in hot water were heterolytic (ionic) rather than free radical in nature, it was natural to examine acid and base catalysis by using acids and bases as additives. Our standard acid additive has been phosphoric acid, a reasonably strong and very stable acid which (unlike sulfuric acid) does not normally act as an oxidizing agent even at high temperatures. As base, we chose sodium carbonate rather than sodium hydroxide, which we believe would be difficult to avoid conversion at least in part to carbonate either inadvertently or by  $CO_2$ formed in the reactions.

Sodium sulfate and sodium chloride were used as additives in view of their occurrence in many natural waters and because of their geological importance. Sodium sulfite was originally chosen as an additive to test for the Bucherer interconversion of naphthylamines and naphthols. Later it was studied for its own sake and as a cheap and very readily available additive for large-scale processes.

Finally, as indicated in the first article in this pair of papers,<sup>1a</sup> because water/CO chemistry has been widely applied to the conversion of resources ranging from leaves to coals<sup>3</sup> into liquids, we have included the use of aqueous formic acid and sodium formate in our studies. It is generally hypothesized that CO reacts with alkali in the presence of water to generate formate intermediates which are the active hydride transfer reducing agents (eq 1).<sup>4,5</sup> The mechanism of the reaction of the formate intermediate with, e.g., coal was the subject of further speculation (eqs 2 and 3).<sup>6–8</sup>

$$M + OH^{-} + CO \rightarrow HCOO^{-}M^{+}$$
(1)

 $coal + HCOO^{-}M^{+} \rightarrow coal(H)^{-}M^{+} + CO_{2}$  (2)

$$\operatorname{coal}(\mathrm{H})^{-}\mathrm{M}^{+} + \mathrm{H}_{2}\mathrm{O} \rightarrow \operatorname{coal}(\mathrm{H}_{2}) + \mathrm{M}^{+}\mathrm{OH}^{-} \quad (3)$$

Using NMR to investigate reacting systems under high pressures, Horvath<sup>9</sup> presented evidence for the formation of formate ions during the reactions of lowrank coals with carbon monoxide and water via cation exchange of metal carboxylates in the coals with formic acid formed by reaction of carbon monoxide with water.

Unlike most hydroconversion systems, which are based on thermal/free radical chemistry, the aqueous chemistry is generally believed to operate through an ionic mechanism. Dual independent reaction pathways take place in the treatment of coal with  $H_2O/CO$ : (1) a hydrogenation pathway which results in an increased H/C (hydrogen to carbon) ratio and (2) an acid-catalyzed bond-breaking (depolymerization) pathway that generates a soluble extractable product.

Thus, hydroaromatic hydrogen is incorporated into the coal in pathway 1. The role of the aqueous carbon monoxide treatment in depolymerizing coal has been variously attributed to bond-breaking activity or to the removal of potential cross-link sources which cause repolymerization to higher molecular weight products following thermal bond rupture. The major depolymerization reactions are thought to be acid catalyzed, wherein water is believed to act as an acid catalyst, and in the presence of CO, formic acid also acts as an acid catalyst as well as an hydride transfer reducing agent. The acidic functionalities and acidic minerals in the coal as well as soluble acidic products which are generated during the treatment are believed to act synergistically to enhance conversion.

# II. Hydrocarbons and Heterocycles without Functional Groups

### A. Aliphatic and Alicyclic Hydrocarbons

#### 1. Alkanes

In the absence of water, alkanes react only at relatively high temperatures: at 450 °C, anhydrous pyrolysis of hexadecane, 2-methyloctadecane, and tridecylcyclohexane each give substantial amounts of alkanes and alkenes (Scheme 1).<sup>10</sup> However, alkanes



react at lower temperatures in the presence of water and a catalyst. Thus, bentonite, an acidic clay, catalyzes the conversion (90%) of octacosane in water at 375 °C into an insoluble black carbonaceous material and small amounts of alkenes and aromatics; in the absence of water, only 1% of the octacosane is converted.<sup>11a</sup> For analogous work on hexadecane, see ref 11b.

Heating the saturated hydrocarbon docosane  $(C_{22}H_{46})$  at 330 °C with solvent-extracted (bitumen removed from the pores) shale in an excess of D<sub>2</sub>O shows only minor deuteration of the re-isolated docosane (80%),<sup>12</sup> suggesting that simple hydrogen exchange does not occur on saturated molecules.

The kinetics and mechanism of methane oxidation by  $O_2$  in supercritical water has been studied. At temperatures between 525 and 587 °C, the conversion ranges from 3% to 70% with CO being the primary product at low conversions and  $CO_2$  at higher conversions.<sup>13</sup> The extensive work on  $O_2$ oxidation of hydrocarbons in the presence of supercritical water has been thoroughly reviewed by  $Savage^{2b}$  and therefore will not be covered in the current review.

#### 2. Alkenes

The direct addition of water to olefins to give alcohols has been studied for many years.<sup>14</sup> Thermodynamically, hydration is favored by low temperatures and high pressures or a large excess of water; acceptable rates require catalysis. Early investigations focused on the hydration of ethene, propene, and butene with nitrogen bases (pyridine or quinoline), acids in solution, acidic salts, and various oxides as catalysts. Such catalytic hydrations are equilibrium controlled and sensitive to variations in pressure and temperature. Ethers and ketones are produced in low yields in addition to the expected alcohols. Branched alkenes hydrate under milder conditions than their straight chain analogues; isobutene hydrates at 35 °C with dilute nitric acid, whereas 1-butene hydrates at 225 °C and 200 atm pressure in a dilute sulfuric acid solution of zinc chloride.

Hydration-dehydration and hydrogenation-dehydrogenation interconversions of cyclohexane, cyclohexene, cyclohexanol, cyclohexanone, benzene, and phenol have been studied using varying catalysts and pH in water at 375 °C (Scheme 2).<sup>15</sup> Dehydrogena-

# Scheme 2. Interconversions of Six-Carbon Species (375 °C, $H_2O$ with additives)<sup>15</sup>



tions of cyclohexanone, cyclohexanol, cyclohexene, and cyclohexane occur in the presence of Pt catalysts. Dehydration of cyclohexanol is acid or base catalyzed without additional catalyst, while the acid- or basecatalyzed hydration of cyclohexene requires PtO<sub>2</sub>. These reactions do not occur in pure water up to 375 °C. However, the thermal chemistry of alkenes is significantly altered in aqueous media from predominantly free radical to ionic processes. At 250 °C, 1-decene undergoes double-bond migration to give 2-, 3-, 4-, and 5-decene, showing similar reactivity in cyclohexane (6% conversion), water (8% conversion), and brine (10% NaCl) (11% conversion). Additionally, appreciable amounts of (E)-10-, cis-9-, and trans-9icosene are also formed from 1-decene via dimerization. Conversion and the extent of double-bond isomerization increases with the ionic strength and acidity of the system.<sup>16</sup> For similar work on hexadecene, see ref 11b. Sen<sup>11c</sup> summarized work in aqueous media on transition-metal-catalyzed functionalization of alkanes. 1-Octadecene is reduced to octa decane (60%) by heating at 330  $^\circ C$  for 3 days in  $D_2O$  with simultaneous significant deuterium incorporation.  $^{12}$ 

Cesium dodecatungstophosphate ( $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ), an insoluble solid acid, efficiently catalyzes hydration of 2,3-dimethyl-but-2-ene in excess water at 343 °C; typical oxide-based catalysts such as silica and alumina are almost inactive.<sup>17</sup> In refluxing hexane for 1 day, 1-hexene, 1-octene, and 1-decene react in the presence of hydrated cation-exchanged ( $Al^{3+}$ ,  $Cr^{3+}$ ) layered clays to give the corresponding bis(1methylalkyl)ethers (Scheme 3). Hydrated metal cat-

# Scheme 3. Hydration of 1-Alkenes Over Clays (1 day, reflux, hexanes)<sup>18</sup>



ions alone, not on a clay, fail to give the ethers.<sup>18</sup> Recall that 1-decene in heated cyclohexane or water only gives double-bond isomerization or dimerization products.<sup>16</sup>

#### 3. Alkynes

At 250 °C for 2.5 days, 1-decyne thermolyzes much faster in cyclohexane (72% conversion) than in water (7% conversion) to yield several alkenes as well as 1,4-dioctylbenzene and 2,4-dioctyltoluene. The last two products probably arise from trimerization reactions involving acetylene and propyne, elimination products of 1-decyne.<sup>16</sup> Catalysis by CpCo(CO)<sub>2</sub> induces quantitative cyclotrimerization of 1-hexyne into substituted benzenes at 374 °C for 2 h in water.<sup>19</sup>

Aquathermolysis of 1-decyne at 250 °C for 2.5 days gives 1- and 2-decene together with some 2-decanone, the production of which is facilitated by acidic clays.<sup>16</sup> 1-Heptyne is converted to heptan-2-one in 78% yield when treated for 1 h at 280 °C in 0.5 M H<sub>2</sub>SO<sub>4</sub>.<sup>20</sup> Acidic metal salts, like CuCl<sub>2</sub> and SnCl<sub>2</sub>, catalyze the aqueous hydration of alkynes to ketones at 374 °C after 2 h.<sup>19</sup>

#### 4. Terpenes

Hydration of some terpene olefins occurs readily. For example, addition of water to the 8,9-double bond of carvone proceeds at a lower temperature than did aromatization; this addition is regioselective and in accord with Markovnikov's rule,<sup>20</sup> indicating an ionic mechanism, and is consistent with general conclusions reached for other reactions in superheated water.<sup>21</sup> Carvone is not racemized in the hydration step, corresponding with results for the acid-catalyzed hydration at ambient temperature.<sup>22</sup> In hightemperature water, the conversion of carvone to 8-hydroxy-*p*-6-menthen-2-one (hydroxydihydrocarvone) was lower than that obtained in concentrated acid at ambient temperature but the reaction time is far shorter (see also section III.B.1).

In the presence of montmorillonites (acidic clays) at temperatures between 140 and 175 °C, limonene is converted mainly into aromatic *p*-cymene and *p*-menthene (Scheme 4).<sup>23</sup>

#### 5. Steroids

Tannenbaum and co-workers showed that isomerization ratios of steranes and triterpanes, from kerogen that is pyrolyzed at 300 °C for 2 h, which are widely used as maturation indicators, are affected by the presence of minerals.<sup>24</sup> Not only do different clays vary the overall rates of isomerizations (montmorillonite > illite), but different clays also affect particular isomerizations differently. These authors<sup>24</sup> realized that such use of biomarkers must take into account mineral matrix effects, which had previously been largely ignored.

# B. Benzenoid Hydrocarbons, Including Alkyl-, Alkenyl-, and Alkynyl-Substituted

Benzenoid hydrocarbons without any aliphatic side chains are ubiquitous in all fossil fuel resources. Such compounds are largely unreactive under the aquathermolysis conditions up to 460 °C, see section II.B.2. However, the presence of an alkyl substituent significantly increases the reactivity.

#### 1. Monocyclic

Pyrolysis of pentadecylbenzene (PDB) at 375–450 °C gives as major products toluene, 1-tetradecene, tridecane, and styrene (Scheme 5). Hydrogen abstraction at the α-carbon forms a free radical of PDB which undergoes β-scission to produce precursors for toluene **1** and 1-tetradecene **2**. Abstraction of a hydrogen atom at the α-carbon gives another free radical, which then forms styrene **3** plus a tridecane precursor **4**. Minor products are formed by initial hydrogen abstraction at other positions.<sup>25</sup> Similar free-radical chain processes are quite familiar and were, e.g., proposed for the thermolysis of 1,3-diphenylpropane to toluene and styrene at 350 °C.<sup>26</sup>

Examination of hydrogen exchange in C–H acids revealed fluorene (100% D incorporation at C9) to be a stronger acid in deuterium oxide than triphenylmethane (no D incorporation under equal reaction conditions of 1 h at 300 °C).<sup>27</sup> This order in acidity corresponds to that established in DMSO. It also





#### Scheme 5. Pyrolysis of Pentadecylbenzene (PDB) at 375-450 °C<sup>25</sup>



Scheme 6. Products from 1-Cyclohexylbenzene (460 °C, 1 h, 15% NaCO<sub>2</sub>H<sub>(aq)</sub>)<sup>36</sup>



Scheme 7. Products from 1-Cyclohexylnaphthalene (460 °C, 1 h, 15% NaCO<sub>2</sub>H<sub>(au)</sub>)<sup>36</sup>



agrees with reported p*K* values of 22.6 and 23.0 in methanolic sodium methoxide for fluorene<sup>28,29</sup> and 31.5 for triphenylmethane.<sup>30</sup> This work indicates that compounds with p*K*'s up to 40 will undergo H/D exchange in pure D<sub>2</sub>O at 200–300 °C. The basicity of D<sub>2</sub>O at 300 °C proved insufficient to abstract methyl hydrogens of toluene, which has a reported p*K* of 40.9.<sup>31</sup>

The deuteration of alkylbenzenes in sub- and supercritical  $D_2O$  solutions has been studied. Depending upon conditions, toluene is either deuterated completely or only the aromatic protons are replaced.<sup>32</sup> 1,3,5-Trimethylbenzene and butylbenzene show hydrogen/deuterium exchange at both the aromatic and  $\alpha$ -methyl protons.<sup>33</sup>

Scheme 8. Products from hexylbenzene (460 °C, 1 h, 15%  $NaCO_2H_{(aq)})^{36}$ 



Scheme 9. Products from Decylnaphthalene (460 °C, 1 h, 15% H<sub>2</sub>O)<sup>36</sup>



Toluene is converted to benzoic acid (41%) by aqueous KMnO<sub>4</sub>/KOH at 180 °C in just 1.3 min [caution: highly exothermic reaction].<sup>34</sup> Houser has shown that ethylbenzene undergoes minor conversion to benzene and toluene after 2 days in water at 450 °C.<sup>35</sup> Cyclohexylbenzene (Scheme 6), 1-cyclohexylnaphthalene (Scheme 7), hexylbenzene (Scheme 8), and 1-decylnaphthalene (Scheme 9) show similar reactivity at 460 °C in cyclohexane, water, 15% aqueous formic acid, and 15% aqueous sodium formate, indicating that radical rather than ionic reactions predominate.<sup>36</sup> The conversion rates for the *n*-alkyl-substituted aromatics are noticeably higher than those for the cyclohexyl-substituted aromatics.<sup>36</sup>

Styrene at 250 °C for 5 days gives polystyrene in water, but dimers, trimers, and tetramers form in cyclohexane.<sup>37</sup> The Willgerodt conversion (using sulfur and aqueous ammonia) of styrene into phenylacetamide can be significantly improved by the use of a microwave batch reactor at 200 °C with time reduced from several hours to 15 min and yield increased.<sup>38,39</sup>

In cyclohexane, phenylacetylene undergoes complete conversion in 5 days at 250 °C to phenylnaphthalenes and triphenylbenzenes, while in water, acetophenone is the major product.<sup>37</sup> Strauss and coworkers converted phenylacetylene and 1-phenylprop-1-yne to acetophenone and phenylpropanone, respectively, in high yields at 280 °C in dilute sulfuric acid.<sup>20</sup> The quantitative, CpCo(CO)<sub>2</sub>-catalyzed synthesis of triphenylbenzenes from phenylacetylene in water at 374 °C is also reported.<sup>19</sup>

#### 2. Polycyclic

**a. Fused Polycyclic.** Naphthalene,<sup>36</sup> fluorene, and phenanthrene<sup>40</sup> are unreactive in water at 460 °C.

Anthracene is reactive in 15% aqueous formic acid, undergoing 80% conversion after 1 h at 460 °C to give mainly products of reduction, such as di- (53%) and tetrahydro derivatives (24%) (Scheme 10).<sup>40</sup> After 2

Scheme 10. Products from Anthracene (460 °C, 1 h, 15%  $HCO_2H_{(aq)}$ )<sup>40</sup>



h with hydrogen gas in water at 425 °C, anthracene is converted to the extent of 76% mainly to the di-(9%) and tetra hydro derivatives (53%) along with methylbenzohydrindene (8.3%).<sup>41</sup>

Hydrocarbons such as methylnaphthalene and methylphenanthrenes undergo complete hydrogen/deuterium exchange in alkaline  $D_2O$  media at temperatures above 230 °C.<sup>33,42</sup>

**b.** Aryl–Aryl. Biaryl and heteroaryl–aryl linkages represent the most refractory of the cross-links in fossil fuel resources. They are essentially unreactive thermally at 460 °C in both the absence and presence of supercritical water.<sup>43</sup> Many biaryls do, however, undergo bond cleavage and heteroatom removal under reducing conditions in supercritical water, including aryl–pyridines, –quinolines, –indoles, –thiophenes and, –benzothiophenes (see sections II.C.1.c, II.C.2, II.D.2, and II.E for more information).



Binaphthyl is essentially unreactive at 315 °C, giving only traces of reduction and cleavage products, but at 460 °C in 15% aqueous sodium formate, it gives a 13% conversion to naphthalene and products of reduction (Scheme 11).

**c. Aryl**–(**CH**<sub>2</sub>)<sub>*n*</sub>–**Aryl**. Diphenylmethanes are unreactive in water at 430 °C after 1 h.<sup>44</sup> In 15% aqueous formic acid at 460 °C, 1-benzylnaphthalene (Scheme 12) undergoes slow conversion (8% in 1 h)

# Scheme 12. Products from 1-Benzylnaphthalene (460 °C, 1 h, 15% $HCO_2H$ )<sup>36</sup>



into naphthalene and toluene whereas 1-benzyltetralin (Scheme 13) undergoes rapid conversion (99% in 7 min) mainly to tetralin and toluene; both probably react via radical pathways.<sup>36</sup>

In water at 400 °C, bibenzyl is cleaved and dehydrogenated by normal thermal chemistry to give toluene and stilbene.<sup>45</sup> 4,4'-Substituted bibenzyls have also been studied with synthesis gas in super-critical water.<sup>46</sup>

# C. Pyridines, Benzopyridines, and Alkyl and Aryl Derivatives

#### 1. Pyridine, Alkylpyridines, and Arylpyridines

a. Pyridine, Piperidine, and Alkyl Derivatives. Pyridine is essentially unaffected by aquathermolysis at 350 °C (3 days) even in the presence of 10% sulfuric acid. Of the many clays tested, only calcium montmorillonite increases the conversion to 5% with most of the product being a mixture of bipyridyls; there is no denitrogenation. Ten percent phosphoric acid gives 10% conversion of pyridine after 3 days at 350 °C to a long slate of products, most retaining the nitrogen (Scheme 14).47 On heating at 400 °C in D<sub>2</sub>O containing 0.016 M NaOD, pyridine is pentadeuterated.<sup>32</sup> At 460 °C in supercritical water, pyridine is almost unreacted after 1 h under both thermolysis and aquathermolysis conditions. However, in 15% aqueous formic acid at 460 °C for 7 min, small quantities of *N*-alkylpiperidines are observed, and on extending the time to 1 h, small amounts of *C*-alkylpyridines are observed.<sup>48</sup>

Aquathermolysis of 2-picoline at 350 °C for 3 days shows a 6% conversion to a mixture of products which

Scheme 13. Products from 1-Benzyl-1,2,3,4-tetrahydronaphthalene (460 °C, 1 h, 15% HCO<sub>2</sub>H)<sup>36</sup>



Scheme 14. Aquathermolysis of Pyridine (350 °C, 3 days, 10% H<sub>3</sub>PO4<sub>(aq)</sub>)<sup>47</sup>



Scheme 15. Aquathermolysis of 2-Methylpyridine (350 °C, 3 days, 10% H<sub>2</sub>O)<sup>47</sup>



include phenol and minor amounts of other denitrogenated compounds (Scheme 15).47 Addition of phosphoric acid gives a higher conversion (25%) with over one-half of the product mixture being phenols and other nitrogen-free compounds. 3-Methylpyridine is essentially unchanged by aquathermolysis (3 days at 350 °C), and the addition of 10% formic or sulfuric acid makes little difference. 2,4,6-Trimethylpyridine is only slightly affected at 460 °C for 1 h in cyclohexane, water, or 15% sodium formate. A 12% conversion is observed with 15% aqueous formic acid to give 2,4-dimethylpyridine (10%) and *m*-xylene (2%). Under the above conditions, 4-propylpyridine shows minor conversion into 4-methyl-, 4-ethyl-, and 4-isopropylpyridine.<sup>49</sup> Anhydrous pyrolysis of 2-npentadecylpyridine for 1 h at 450 °C gives alkanes and alkenes.<sup>10</sup>

Phenylpiperidine, after 6 h at 400 °C in water, is partially denitrogenated and partially converted into pyridines.<sup>50</sup> Six hours at 450 °C in pure water induced no reaction with 3-phenylpyridine, but with added ZnCl<sub>2</sub>, after a slow reaction, ammonia is detected in molar quantities equivalent to that of the reacted starting material.<sup>50</sup>

Reactions of pyridines and piperidines with aqueous formic acid at high temperatures have revealed a fascinating reaction pattern. With piperidines and pyridines at 350 °C for 2 h, 49% formic acid behaves as a formylating, methylating, reducing, and oxidizing agent to produce the N-substituted piperidine derivatives highlighted in Scheme 16. Pyridine and piperidine are both converted into 1-methyl-, 1-ethyl-, and 1-propylpiperidines. Of the N-alkyl groups, isotopic labeling shows that only the N-methyl product is derived from the formic acid, while the N-ethyl and *N*-propyl groups arise from heterocyclic ring C-Cbond fission by retro-vinylogous-bis-aza-Aldol reactions. Detailed analysis of the products from pyridine, piperidine, and their 4-methyl derivatives, reacted separately and mixed, supports mechanisms in which a piperidine adds 1,2 to a dihydropyridine to initiate reaction sequences leading to the product slates found.51,52

**b. Arylpyridines.** 2-Phenyl- and 2-(1-naphthyl)pyridines are significantly degraded (57% and 67%, respectively) in 15% aqueous formic acid at 460 °C

Scheme 16. Products from 4-Methylpyridine (350 °C, 2 h, 49%  $HCO_2H_{(aq)})^{51}$ 



after 1 h. The major reactions observed are the reduction and fragmentation of the pyridine ring (Scheme 17) to give hydrocarbon products such as benzene or naphthalene and their C<sub>1</sub>–C<sub>4</sub> alkylated derivatives via heteroatom removal.<sup>43</sup> *N*-Phenylpiperidine gives near quantitative conversion to alkylbenzenes and tar via heteroatom removal at 400 to 450 °C for up to 6 h. In the presence of ZnCl<sub>2</sub>, 3-phenylpyridine in water at 450 °C undergoes 71% conversion to alkylbenzenes, naphthalene, and heavier products by nitrogen extrusion.<sup>50</sup>

#### 2. Quinolines, Isoquinolines, and 2-Methylquinolines

In aqueous acids, quinoline, isoquinoline, and related polycyclic ring systems are much more reactive than monocyclic pyridines. After 48 h at 400 °C in water, quinoline is converted to the extent of 68%.<sup>53</sup> Of the reaction products, 48% do not retain the nitrogen and 31% are alkylbenzeneamines. Under the same conditions without water, quinoline only undergoes 23% conversion, with only 19% of the products being denitrogenated and another 10% having undergone ring opening.<sup>53</sup> The kinetics of the ZnCl<sub>2</sub>-catalyzed supercritical water–quinoline reaction have been studied; the reaction is first order with

respect to both quinoline and ZnCl<sub>2</sub> and inversely proportional to water concentration.<sup>54</sup> At 350 °C for 3 days in 10% aqueous formic acid, quinoline is 41% converted into a complex array of products, including some resulting from denitrogenation, as shown in Scheme 18.<sup>47</sup> The main product, formed through reduction, was tetrahydroquinoline.<sup>47</sup> After 7 min at 460 °C in 15% aqueous formic acid, quinoline is converted in 97% yield into 1,2,3,4-tetrahydroquinoline; traces of ring-opened products were formed from tetrahydroquinoline upon extending the reaction time to 1 h.<sup>48</sup> After 2 h under hydrogen gas (5.3 MPa, 750 psig) in water at 425 °C, quinoline is converted to the extent of 63%, mainly (43%) to 1,2,3,4-tetrahydroquinoline.<sup>41</sup>

Isoquinoline, with or without water, undergoes 15% thermal conversion into denitrogenated products after 2 days at 400 °C.<sup>53</sup> Isoquinoline also reacts rapidly (70% after 1 h) in 15% aqueous formic acid at 460 °C.<sup>48</sup> A wide range of alkylaromatic products results from reduction and denitrogenation (Scheme 19).<sup>48</sup> In the presence of Fe<sub>2</sub>O<sub>3</sub>, quinoline reacts in water at 400 °C over 2 days to produce *o*-xylene and anilines while isoquinoline produces various dialkylbenzenes.<sup>53</sup>

2-Phenyl- and 2-(1-naphthyl)quinolines in 15% aqueous formic acid at 460 °C rapidly (7 min) undergo substantial conversion to 1,2,3,4-tetrahydroquinoline derivatives; a longer reaction time (1 h) gives hydrocarbon products such as benzene or naphthalene and their  $C_1-C_4$  alkylated derivatives via heteroatom removal.<sup>43</sup>

Benzo[*f*]quinoline- $d_9$  is prepared from the hydrogen analogue by reaction in supercritical alkaline D<sub>2</sub>O.<sup>33</sup>

5,6,7,8-Tetrahydroquinoline undergoes dehydrogenation to quinoline at 460 °C in 15% aqueous formic acid followed by the typical ring opening/denitrogenation pathways for this heterocycle.<sup>49</sup> A range of simpler heterocycles is believed to arise via retro-Diels–Alder-type ring opening (Scheme 20).

#### 3. Acridine and Phenanthridine

Both phenanthridine (Scheme 21) and acridine (Scheme 22) have been heated at 350 °C for 3 days in cyclohexane, water, and water with various additives.<sup>47</sup> Hydrogenation and/or oxidation products





Scheme 18. Products from Quinoline (350 °C, 3 days, 10% HCO<sub>2</sub>H<sub>(aq)</sub>)<sup>47</sup>



Scheme 19. Products from Isoquinoline (460 °C, 1 h, 15% HCO<sub>2</sub>H<sub>(aq)</sub>)<sup>48</sup>



were produced, depending upon the additive, but no nitrogen removal was observed. Acridine is converted to the extent of 91% into di-(46%), tetra-(44%), and octahydro (1%) derivatives in 10% formic acid. The use of acidic clays gives a lower conversion (74% for calcium montmorillonite) but produces significant amounts of 9(10H)-acridone (35%) in addition to the

products of reduction.<sup>47</sup> When heated for 7 min at 460 °C in 15% formic acid, acridine gives 100% conversion into 9,10-dihydroacridine.<sup>55</sup> In 10% formic acid, phenanthridine undergoes 40% conversion into di-(27%) and tetrahydro (13%) derivatives, while in 10% sulfuric acid it is converted to the extent of 51% to 6(5H)-phenanthridinone.<sup>47</sup>



Scheme 21. Products from Phenanthridine (350 °C, 3 days, aqueous 10% H<sub>2</sub>SO<sub>4</sub> and 10% HCO<sub>2</sub>H)<sup>47</sup>



Phenanthridine- $d_9$  is prepared by supercritical heating of phenanthridine in alkaline D<sub>2</sub>O.<sup>33</sup>

### 4. Pyridine and Benzopyridine N-Oxides

Aryl *N*-oxides were subjected to thermolysis at 460 °C in water alone, in 15% aqueous formic acid, in 15% aqueous sodium formate, and for comparison of purely thermal reactions in cyclohexane. In all cases, deoxygenation is the major transformation.<sup>40</sup> For example, pyridine-1-oxide quantitatively gives pyridine in 15% aqueous formic acid after only 7 min. Thermolysis of pyridine-1-oxide in cyclohexane also leads to deoxygenation with small amounts of cyclohexylpyridines formed via deoxygenative alkylation on the pyridine-1-oxide (Scheme 23).

The 2-oxide of isoquinoline undergoes virtually complete deoxygenation to isoquinoline after 7 min in cyclohexane or water at 460 °C.<sup>40</sup> When the same reaction was run in 15% aqueous formic acid, deoxygenation was followed by ring opening in the acid-catalyzed fashion observed for the parent heterocycle.<sup>48</sup>

# D. Pyrroles, Benzopyrroles, and Alkyl Derivatives

#### 1. Monocyclic Pyrroles

After 5 days at 250 °C, pyrrole is unchanged in cyclohexane, and in water there is less than 1% conversion to indole. In aqueous phosphoric acid,

Scheme 22. Aquathermolysis of Acridine (conditions as indicated)<sup>47,48</sup>



Scheme 23. Thermolysis of Pyridine-1-oxide (460  $^{\circ}$ C, 7 min, cyclohexane or 15% HCO<sub>2</sub>OH, as indicated)<sup>40</sup>



pyrrole undergoes complete polymerization at 250 °C after 1.5 h. At 200 °C for 1 day, 18% conversion of pyrrole to indole by stepwise cycloaddition is noted (Scheme 24). The observation that indole is not

Scheme 24. Mechanism of the Formation of Indole from Pyrrole



formed under purely thermal conditions may suggest that the cycloaddition proceeds via an ionic route rather than a concerted [4+2] cycloaddition mechanism,<sup>56</sup> although it is known that water accelerates certain cycloadditions.<sup>57</sup> Pyrrole shows 17% conversion when reacted in 15% aqueous formic acid at 460 °C for 1 h to give mainly products of formylation and reduction; very little denitrogenation or ring opening is observed (Scheme 25).<sup>49</sup>

2,5-Dimethylpyrrole is unreactive under purely thermal conditions (5 days at 250 °C in cyclohexane)

but is more reactive than pyrrole in water at 250 °C, where conversion is 28% in 1 day and 65% after 5 days. The main product is 3-methylcyclopent-2-en-1-one (46%), which results from ring opening and loss of ammonia followed by intramolecular aldol condensation (Scheme 26). Again, the reaction is catalyzed by phosphoric acid, and under these conditions, different denitrogenated products are formed: during 2 h at 150 °C, the main products formed from a 33% conversion are the two trimethylindanones of Scheme 26. After 5 days at 250 °C, all three indanones of Scheme 26 appear; the tetramethyl derivative is in the highest amount along with a considerable amount of polymer.<sup>56</sup> 2,5-Dimethylpyrrole is moderately reactive in 15% aqueous formic acid, giving products arising mainly from cycloaddition reactions, demethylation, and methyl-group transfer; little ring opening is observed.<sup>49</sup>

#### 2. Indoles

In cyclohexane, indole shows very little change at 350 °C after 5 days; in water, the same conditions give traces of aniline and *o*-toluidine (1% each).<sup>56</sup> Aqueous phosphoric acid hardly affects indole at 250 °C, but there is 61% conversion in 1 h at 350 °C into aniline (32%), 2-methyl indole (21%), and 2,3-dimethylindole (5%) as major products (Scheme 27).<sup>56</sup> In 15% aqueous formic acid,  $^{48}$  indole undergoes Cand *N*-methylation at 460 °C, presumably by formylation and subsequent reduction. Reduction to the corresponding indolines also occurs as expected in this medium; after 7 min, the conversion is 47% (46% to indolines). The indoles then undergo ring opening (13% after 1 h) and methylation.<sup>48</sup> Indole, Me<sub>2</sub>NH, in aqueous HCHO undergo nearly quantitative conversion to gramine at 160 °C in 1.2 min.<sup>34</sup>

In 15% aqueous formic acid at 460 °C, 1-methylindole is 61% converted after 7 min, predominantly by hydrogenation to 1-methylindoline (Scheme 28).<sup>49</sup> 2-Methylindole is unchanged after 5 days at 350 °C in either cyclohexane or water. At 250 °C in aqueous phosphoric acid, 2-methylindole undergoes 30% conversion after 5 days to 2,3-dimethylindole and 1,2,3and 2,3,5-trimethylindole (Scheme 29); only 1% of the

Scheme 25. Products from Pyrrole (460 °C, 1 h, 15% HCO<sub>2</sub>H)<sup>49</sup>



Scheme 26. Formation of Various Products from 2,5-Dimethylpyrrole (2 h, 150 °C, 10% H<sub>3</sub>PO<sub>4</sub>)<sup>56</sup>



other products of transmethylation of indole are detected, probably due to polymerization.  $^{56}$ 

3-Methylindole shows 2% polymerization after 5 days at 350 °C in cyclohexane. In water at 350 °C over 5 days, 3-methylindole is 29% converted into a mixture of indole (14%) and 2,3-dimethylindole (14%). In phosphoric acid at 250 °C for 5 days, 3-methylindole is 24% converted into 2,3-dimethylindole; very little indole is detected presumably due to polymerization (Scheme 30).<sup>56</sup>

2,3-Dimethylindole experiences 2% of 3-demethylation during 5 days at 350 °C in cyclohexane. In water, under the same conditions, conversion of 2,3dimethylindole is over 40% (Scheme 31) into indole, 2-methylindole, and various di- and trimethylindoles. Aqueous phosphoric acid at 250 °C gives a clean Scheme 27. Formation of Anilines and Phenols from Indole (350 °C, 1 h, 10%  $H_3PO_{4(aq)})^{56}$ 







Scheme 29. Products from 2-Methylindole (250 °C, 5 days, 10% H<sub>3</sub>PO<sub>4(aq)</sub>)<sup>56</sup>



Scheme 30. Products from 3-Methylindole (250 °C, 5 days, 10%  $H_3PO_{4(aq)})^{56}$ 



conversion (40% in 5 days) into 2-methylindole (15%) and 1,2,3-trimethylindole (25%).<sup>56</sup>

2-Arylindoles in 15% aqueous formic acid at 460 °C are gradually converted (e.g., 2-phenylindole to the extent of 5% after 1 h) into hydrocarbon products including benzene or naphthalene and their  $C_1-C_4$  alkylated derivatives via heteroatom removal.<sup>43</sup>

#### 3. Other Fused Indoles

1,2,3,4-Tetrahydrocarbazole at 460 °C in 15% aqueous formic acid is mostly reacted (94%) after 60 min. Ring opening to form mainly indoles (69%) is the

Scheme 31. Products from 2,3-dimethylindole (350  $^\circ C,~5~days,~H_2O)^{56}$ 



major route observed.<sup>49</sup> Interestingly, retro-Diels– Alder-type reactions appear to be responsible for the ring opening of 1,2,3,4-tetrahydrocarbazole in aqueous formic acid at 460 °C (Scheme 32).

Carbazole is unaffected by supercritical water at 460  $^\circ C$  after 1  $h.^{48}$ 

# E. Thiophenes, Benzothiophenes, and Aryl Derivatives

Thiophene, 2-methylthiophene, 2,5-dimethylthiophene, and benzo[b]thiophene are unaffected under both thermolysis and aquathermolysis conditions up to 350 °C.<sup>57</sup> However, after 5 days in 10% aqueous phosphoric acid at 350 °C, thiophene undergoes 72% conversion mainly to tetrahydrothiophene (23%) (Scheme 33) and 2-methyltetrahydrothiophene (18%) (Scheme 34) along with other alkylthiophenes.<sup>57</sup> Earlier studies on the catalyzed aquathermolysis of thiophene at 250 °C for several days showed only minor amounts of desulfurization, with polymerization being the major reaction pathway.<sup>58-60</sup> 2-Methylthiophene affords dimethylbenzothiophenes (52%), alkylthiophenes (10%), and 2-methyltetrahydrothiophene (10%) after 5 days at 350 °C in 10% aqueous phosphoric acid (Scheme 35).<sup>57</sup> Under the same conditions, 2,5-dimethylthiophene was more reactive (62% conversion) and furnished several mono- and disubstituted alkylthiophenes.57



Scheme 33. Products from Thiophene (350  $^\circ C,$  5 days, 10%  $H_3PO_{4(aq)})^{57b}$ 



Scheme 34. Fredel–Craft Methylation and Acid-Catalyzed Intramolecular Methyl Scrambling of Alkylthiophenes<sup>57b</sup>



Scheme 35. Products from 2-Methylthiophene (5 days, 350  $^\circ C,$  10%  $H_3PO_4)^{57b}$ 



Benzothiophene in 350 °C water gives several higher molecular weight products via processes such as Diels–Alder additions and dimerization; desulfurization also occurs (Schemes 36 and 37).<sup>57</sup> The use of platinum-group metal ions gave similar results but with slightly more desulfurization.<sup>61</sup> 2-Arylthiophene and benzothiophene derivatives gradually react in 15% aqueous sodium formate at 460 °C to give hydrocarbon products such as benzene or naphthalene and their  $C_1-C_4$  alkylated derivatives via heteroatom removal. For example, 2-phenylthiophene gives 8% of hydrocarbon products after 1 h.<sup>43</sup>

Hydrodesulfurization of benzothiophene at 370 °C in water with ruthenium, palladium, and platinum metal species forms 2,3-dihydrobenzo[*b*]thiophene (8–10%) and ethylbenzene (10–24%) after 3 h.<sup>62</sup> Catalytic desulfurization (up to 95 mol % sulfur removal) of benzothiophene in water–toluene emulsion has been achieved at 340 °C using phosphomolybdic acid through activation of H<sub>2</sub>O to generate H<sub>2</sub> via the water gas shift reaction.<sup>63</sup>

Benzothiophene is thermally unreactive after 3 h at 400 °C, but in water and Fe<sub>2</sub>O<sub>3</sub>, it undergoes a 6% conversion into butanediol (3%) and naphthalene (1%).<sup>53</sup>

Scheme 36. Products from Benzothiophene (350 °C, 5 days, 10% H<sub>3</sub>PO<sub>4(aq)</sub>)<sup>57b</sup>



Scheme 37. Products from Benzothiophene (350  $^\circ C,$  5 days, 10%  $H_3PO_4)^{57b}$ 



Dibenzothiophene undergoes rapid deuterium exchange of all protons in supercritical alkaline  $D_2O$ .<sup>33,32</sup>

#### F. Furans and Benzofurans

2-Methylfuran is converted to 5-methylfurfuryldimethylamine in 48% yield by treatment with Me<sub>2</sub>-NH/aqueous HCHO at 165 °C for 1.4 min.<sup>34</sup> 2,5-Dimethylfuran yields 2,5-hexanedione quantitatively in 30 min at 250 °C in  $D_2O.^{27}$ 

2,3-Dihydrobenzofuran shows 4% conversion both in cyclohexane and water at 250 °C after 3 days. In an aqueous sulfite mixture or in 10% aqueous phosphoric acid, it is converted to the extent of 87% and 60%, respectively. The main product in both cases is phenol; in water or the aqueous sulfite mixture, 2and 4-ethylphenols are also observed. In phosphoric acid, both the ethylphenols and ethyldihydrobenzofurans are formed (Scheme 38).<sup>64</sup>

Dibenzofuran is unreactive when heated to 460  $^\circ\text{C}$  in water for 1  $h.^{36}$ 

#### G. Heterocycles with Two or More Heteroatoms

Fully deuterated pyrazoles (410 °C for 8 h) and quinoxalines (290 °C for 2 h) are prepared in syn-

thetically useful quantities in superheated, dilute aqueous NaOD.<sup>65</sup> Many heterocycles, e.g., phenothiazine and pyrazine, readily undergo complete hydrogen/deuterium exchange in D<sub>2</sub>O/NaOD at temperatures between 230 and 430 °C.<sup>32,33</sup> Further examples are given in a review of hydrogen isotope exchange reactions.<sup>42</sup>

# III. Compounds with Oxygen-Containing Functional Groups

# A. Phenols and Ethers

### 1. Monocyclic Phenols

*p*-Cresol is essentially unreactive at 250 °C, having less than 2% conversion, after 3 days in water, 10% aqueous Na<sub>2</sub>CO<sub>3</sub>, 10% aqueous NaHCO<sub>3</sub> or 80% aqueous H<sub>3</sub>PO<sub>4</sub>.<sup>66</sup> On treatment with aqueous ammonium sulfite and ammonia for 27 h at 250 °C, *p*-cresol gives only 2% of the expected Bucherer reaction product *p*-toluidine together with aniline (1%) and phenol (5%).<sup>66</sup>

4-Alkylphenols are largely dealkylated at 250 °C for 56 h in aqueous sulfite mixtures via an oxidative pathway accompanied by minor products of alkylation and ring closure.<sup>66</sup> Thus, aqueous sulfite mixtures (3 days) or 0.1 M aqueous sulfuric acid at 250 °C converts *p*-cresol primarily into phenol to the extent of 39% and 46%, respectively.<sup>66</sup> In aqueous sulfite mixtures at 250 °C for 82 h, 5,6,7,8-terahydro-2-naphthol is 35% converted into 2-naphthol.<sup>66</sup> 4-Benzylphenol at 250 °C for 57 h undergoes 34% conversion into phenol (22%), benzene (5%), and 2-benzylphenol (6%) in 10% phosphoric acid, while in aqueous sulfite mixtures, it is converted to the extent of 62% into phenol (36%), toluene (4%), benzoic acid (6%), and 4-hydroxybenzophenone (12%).<sup>66</sup>

4-Phenoxyphenol undergoes a 2% conversion to phenol after 2 h at 343 °C in decalin.<sup>67</sup> Under the same conditions in water, the extent of its conversion is 90% with phenol (78%) being the major product detected (Scheme 39). 4-(Benzyloxy)phenol undergoes complete conversion in decalin and water at 343 °C





Scheme 39. Products from 4-Phenoxyphenol (343 °C, 2 h, H<sub>2</sub>O)<sup>67</sup>



during 2 days to give toluene (63% and 44%), hydroquinone (32% and 35%), and 2-benzylhydroquinone (4% and 12%) (Scheme 40).<sup>67</sup> *o*-Methoxyphenol on

Scheme 40. Products from 4-(Benzyloxy)phenol (343 °C, 2 h,  $H_2O$ )<sup>67</sup>



pyrolysis for 90 min at 383 °C gives mainly char and some *o*-hydroxyphenol (18%), without any methanol, comprising an 84% conversion.<sup>68</sup> Reaction under the same conditions in water at a reduced density of 1.6 gives an 88% conversion with catechol (58%) and methanol (48%) as primary products.<sup>68</sup> Reaction characteristics in aqueous salt solutions at 383 °C indicate that the hydrolysis of *o*-methoxyphenol into *o*-hydroxyphenol and methanol proceeds through a polar transition state.<sup>69</sup>

Aqueous sulfite mixture for 6 h at 250 °C causes phenols to lose 4-( $\alpha$ -oxygenated, carbon-linked) substituents (as in, e.g., 4-(hydroxymethyl)phenol, 4-hydroxybenzaldehyde, and 4-hydroxybenzoic acid) to give phenol virtually quantitatively.<sup>66</sup>

Aquathermolysis of *o*-alkylphenols in pure water at 250 °C gives small quantities of oxidatively coupled products, e.g., 3,4,5-trimethylphenol gives 4% of 2,2',4,4',6,6'-hexamethyl-4,4'-bicyclohexadienone after 2 days.<sup>69</sup> In aqueous sulfite at 250 °C, 2-alkylphenols, except *o*-cresol, give benzofurans after short reaction times; these benzofurans are then transformed into phenols and shorter chained 2-alkylphenols after longer times. For example, 2-isopropylphenol after 14 h is 58% converted into 3-methyl-2hydroxybenzofuran, 3,5-dimethylbenzofuran, and 3-methylbenzofuran (43%), *o*-ethylphenol (3%), *o*cresol (4%), and phenol (9%).<sup>69</sup> After 72 h, 2-isopropylphenol is 98% converted into *o*-ethylphenol (3%), *o*-cresol (37%), and phenol (57%) (Scheme 41).<sup>69b</sup> 2-Phenylphenol is 40% transformed after 1 h at 460 °C in cyclohexane, almost entirely into benzene (Scheme 42),<sup>40</sup> but it is little changed in water or 15% aqueous formic acid. However, 15% aqueous sodium formate under the same conditions converts 17% of 2-phenylphenol into 2-methylnaphthalene (8%), benzene (3%), biphenyl (2%), toluene (2%), and naphthalene (2%).<sup>40</sup>

Unlike their *ortho*- and *para*-analogues, *meta*-alkylphenols resist aquathermolysis at 250 °C even after 264 h. $^{69}$ 

A kinetic study of the decomposition of cresols, hydroxybenzaldehydes, nitrophenols, and benzenediols in anoxic water at 460 °C for 10 s, which primarily produces phenol,<sup>70</sup> shows that phenols with an *ortho*-substituent react faster than *meta-* or *para*substituted compounds. Nitrophenols react more rapidly than hydroxybenzaldehydes, which in turn react more rapidly than cresols.<sup>70</sup>

### 2. Naphthols and Other Fused Aromatic Alcohols

1-Naphthol shows significant reactivity in a variety of solvents after 1 h at 460 °C (Scheme 43).<sup>36</sup> In pure water, it gives 16% of 1,1'-binaphthyl ether. In 15% aqueous formic acid, 1-naphthol is converted to the extent of 37% into 1-tetralone (16%) and naphthalene (21%). In 15% aqueous sodium carbonate, conversion is nearly quantitative to 1,1'-binaphthyl ether (51%), naphthalene (3%), and alkylbenzenes (44%).<sup>36</sup> 2-Naphthol is inert both in water and in cyclohexane at 315 °C after 3 days.<sup>71</sup> In 15% aqueous sodium formate, it converts under the same conditions to the extent of 64% into naphthalene (33%) and tetralin (28%).<sup>71</sup>

Dihydroxynaphthalenes are reactive after 2 h at 315 °C in cyclohexane, water, 15% formic acid, and 15% sodium formate.<sup>71</sup> Nearly complete conversion is reached in aqueous sodium formate, with the major products being 1- and/or 2-naphthol and naphthalene. Thus, after 2 h in water at 315 °C, 1,2-dihydroxynaphthalene is converted to the extent of

OH CH<sub>3</sub>

OH

9%

CH<sub>3</sub>

42%

#### Scheme 41. Products from 2-Isopropylphenol (14 h, 250 °C, 10% sulfite)<sup>69b</sup>



31%

7%

Scheme 42. Products from 2-Phenylphenol (460 °C, 1 h, C<sub>6</sub>H<sub>12</sub>)<sup>40</sup>



3%

19% with 2-naphthol as the major product (15%). In 15% sodium formate under the same conditions, it undergoes 96% conversion into 2-naphthol (43%), 1-naphthol (8%), naphthalene (11%), and tetralin (19%) (Scheme 44). 1,3-Dihydroxynaphthalene, as a resorcinol derivative, not unexpectedly gives a product slate different than the 1,2-, 1,4-, or 2,3-analogues. In 15% aqueous sodium formate at 315 °C for 2 h, 1,3-dihydroxynaphthalene is completely converted into 1-hydroxy-4-methylnaphthalene (21%), 1-naphthol (12%), and 1-phenylpropan-2-one (54%) (Scheme 45).<sup>71</sup>

1,5-, 1,6-, 1,7-, and 2,6-Dihydroxynaphthalenes were also heated at 315 °C for 2 h in cyclohexane, water, 15% aqueous formic acid, and 15% aqueous sodium formate.<sup>55</sup> 1,7-Dihydroxynaphthalene is resistant to aquathermolysis, while the other isomers reacted in 15% aqueous sodium formate. 1,5-Dihydroxynaphthalene gives a 6% conversion into 1-naphthol, the 1,6- isomer gives a 47% conversion into

3-methylphenol (36%) and 9,10-octalin-1,6-dione, and the 2,6-isomer gives 12% conversion into 1-methyl-5-hydroxyindane (1%) and 2-hydroxy-5,6,7,8-tetrahydronaphthalene (11%).<sup>55</sup>

2-Hydroxydibenzofuran and 2-hydroxycarbazole are unreactive to aquathermolysis after 3 days at 315 °C or 7 min at 460 °C.<sup>55</sup> 4-Hydroxyacridine undergoes 100% conversion after 3 days at 315 °C, with the products in cyclohexane being 9,10-dihydro-4-hydroxyacridine (94%) and 9-cyclohexyl-4-hydroxy-9,10-dihydroxyacridine (6%) and those in water being acridine (31%), 1,2,3,4-tetrahydroacridine (19%), and 9,10-dihydroacridine (50%).<sup>55</sup>

#### 3. Diaryl Ethers

In apparently divergent reports, diphenyl ether was stated (a) to undergo decomposition via radical reaction to phenol and phenyltetralin in tetralin at 400 °C<sup>72</sup> and (b) to be unreactive thermally and in the presence of coal minerals after 1 h at 450 °C.<sup>73</sup>

Scheme 43. Products from 1-Naphthol (460 °C, 1 h, 15% Na<sub>2</sub>CO<sub>3(aq)</sub>)<sup>36</sup>



Scheme 44. Products from 1,2-Dihydroxynaphthalene (315 °C, 2 h, 15% NaCO<sub>2</sub>H<sub>(aq)</sub>)<sup>71</sup>



The last paper stated that 1-phenoxynaphthalene under these conditions undergoes 13% conversion into phenol and that 9-phenoxyphenanthrene is even more reactive with 45% conversion into phenol (48%), benzene (2%), and phenanthrene (13%). The addition of  $SiO_2-Al_2O_3$  increased the extent of conversion of 9-phenoxyphenanthrene to 100% into phenol (43%), benzene (23%), and phenanthrene (49%).<sup>73</sup> Further study of the decomposition of diaryl ethers in tetralin under hydrogen gas at 430 °C for 5 h confirms that increasing the number of rings in the aromatic structure increases the rate of conversion.<sup>74</sup>

Diphenyl ether is virtually unreactive (i) after 1 h in water at 405 °C,<sup>75</sup> (ii) after 3 days in cyclohexane, water, or 15% aqueous formic acid at 315 °C,<sup>64</sup> and (iii) in an aqueous sulfite mixture or 10% aqueous phosphoric acid at 350 °C.<sup>64</sup> Fifteen percent aqueous phosphoric acid at 315 °C converts diphenyl ether to

the extent of 92% in 3 days into phenol (Scheme 46). A 33% conversion into phenol is also observed when diphenyl ether is treated with 15% aqueous sodium carbonate at 460 °C for 1 h.<sup>36</sup> Studies in water at 415–480 °C indicate that the reaction depends on the water density: acid-catalyzed hydrolysis to phenol dominates at the high range; at low water densities, benzyne may be an intermediate.<sup>76b</sup> In supercritical water, increasing the concentration of NaCl first decreases and then increases the hydrolysis rate, behavior that is rationalized<sup>76c</sup> in terms of the Lewis acid/ base behavior of Na<sup>+</sup> and Cl<sup>-</sup> ions in SCW.

1-Naphthyl phenyl ether undergoes virtually complete scission in water during 3 days at 315 °C into 1-naphthol and phenol (Scheme 47). In 15% aqueous  $H_3PO_4$  at 315 °C, 1-naphthyl phenyl ether undergoes 92% of such scission in only 30 min.<sup>76</sup>

Scheme 45. Products from 1,3-Dihydroxynaphthalene (315 °C, 2 h, 15% NaCO<sub>2</sub>H<sub>(aq)</sub>)<sup>71</sup>



Scheme 46. Formation of Phenol from Diphenyl Ether: (a) 3 days, 315 °C, 15%  $H_3PO_4$  and  $HCO_2$ <sup>-</sup>Na<sup>+</sup>;<sup>76a,78</sup> (b) 1 h, 460 °C, 15% Na<sub>2</sub>CO<sub>3</sub>)<sup>36</sup>

3%



Interestingly, the rate of hydrolysis of diaryl ethers is affected dramatically by the addition of salts such as NaCl, LiCl, KBr, and Na<sub>2</sub>SO<sub>4</sub>.<sup>77</sup> The conversion of 1-naphthyl phenyl ether in water alone at 315 °C after 72 h was 95%; on treatment of this substrate with 1% aqueous solutions of the above four salts, the conversion was reduced to 7%, 5%, 4%, and 0%, respectively. These results demonstrate that at high temperatures, alkali-metal halides and disodium sulfate behave as the salts of strong bases and weak acids.<sup>77</sup> CaCO<sub>3</sub>, KCl, MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, and Na<sub>2</sub>CO<sub>3</sub> also inhibit conversions of 1-phenoxynaphthalene and 9-phenoxyphenanthrene into the corresponding phenols in water at 315 °C.<sup>78</sup>

#### 4. Aryl Alkyl and Aryl Benzyl Ethers

After 3 h at 400 °C, benzyl phenyl ether is converted to an unspecifed extent into phenol, toluene, benzaldehyde, benzyl alcohol, and *o*-benzylphenol while hydroquinone monobenzyl ether gives hydroquinone, toluene, benzaldehyde, benzyl alcohol, and catechol monobenzyl ether.<sup>46</sup>

Thermal reactions of benzyl phenyl ether and dibenzyl ether at 300 and 400 °C in tetralin under hydrogen have been studied with and without the addition of coal ash.<sup>73</sup> The free-radical chain decomposition of dibenzyl ether into toluene and benzal-dehyde and phenethyl phenyl ether into phenol and styrene at 350 °C have been studied kinetically.<sup>26</sup> Pyrolysis of benzyl phenyl ether in supercritical tetralin and toluene has also been carried out.<sup>79</sup> Decomposition of dibenzyl ether to benzyl alcohol, or toluene and benzaldehyde, and finally into polymers at 374, 401, and 412 °C in water has been performed.<sup>80</sup>

Scheme 47. Products from Naphthyl Phenyl Ether (315 °C, 3 days, H<sub>2</sub>O or 315 °C, 30 min, 15%  $\rm H_3PO_{4(aq)})^{76a,78}$ 



Heating allyl phenyl ether in water for 1 h above 180 °C gives a product distribution which is sensitive to temperature.<sup>81</sup> At 200 °C, 2-allylphenol comprised 56% of the product, while at 250 °C, 72% of the product is 2-methyl-2,3-dihydrobenzofuran. Less than 1% of 2-(2-hydroxyprop-1-yl)phenol formed at both 180 and 260 °C, but it accounted for 37% of the product at 230 °C.<sup>81</sup> Solvent (including 28.5% aqueous ethanol at 159–170 °C) effects on the *o*-Claisen rearrangement of allyl-*p*-tolyl ether have been studied.<sup>82</sup>

2-Naphthyl methyl ether in dilute aqueous HCl undergoes 92% conversion after 90 min into 2-naphthol and methanol via proton-catalyzed hydrolysis at 390 °C. The rate of hydrolysis is also enhanced by NaCl, presumably by base catalysis (see section III.A.3). In subcritical conditions, decomposition to cracking products and polycondensates, typical of radical thermolysis, occurs.<sup>83</sup>

Anisole is unreactive in cyclohexane or water after 3 days at 250 °C; in aqueous sulfite, it undergoes 27% conversion into phenol.<sup>64</sup> Kinetics of the thermolytic hydrolysis at 380 °C for up to 8 h have been studied for anisole, *p*-methylanisole, *p*-hydroxyanisole, *m*-trifluromethylanisole, and *m*- and *p*-anisaldehyde. *m*-Anisaldehyde underwent the lowest conversion (17%) and *p*-methylanisole the greatest (94%).<sup>84</sup>

*n*-Butyl phenyl ether is unreactive in cyclohexane or water, but it is converted to the extent of 19% after 3 days into phenol by aqueous sulfite at 250 °C.<sup>64</sup> After 3 days at 250 °C in 10% aqueous  $H_3PO_4$ , butyl phenyl ether is completely converted into diverse products including phenol (33%), 2-(1-methylpropyl)phenol (23%), 4-(1-methylpropyl)phenol (19%), and 2,6-di(1-methylpropyl)phenol (13%). All these products are readily rationalized as being due to hydrolysis followed by subsequent isomerization of the initially formed primary  $C_4H_9^+$  carbenium ion (Scheme 48).<sup>64</sup>

After 7 min at 460 °C, cyclohexyl phenyl ether is converted in hexane to the extent of 97% into cyclohexene (49%) and phenol (47%); in water, 100% ionic conversion occurs into phenol (44%), cyclohexanol (2%), and 1-methylcyclopentene (54%) (Scheme 49).<sup>36</sup> At 343 °C in water, the product slate was similar but the conversions were lower.<sup>67</sup>

After 3 days at 250 °C, 2,3-dihydrobenzofuran is thermally converted both in cyclohexane and in water to the extent of 4% into phenol. In 10% aqueous  $H_3$ -PO<sub>4</sub>, conversion increases to 60% with the major product being phenol (48%) along with a variety of alkylphenols, alkyl-2,3-dihydrobenzofurans, and dimers. In aqueous sulfite under the same conditions, 2,3dihydrobenzofuran gives a similar product slate with an 87% conversion into phenol (77%) and other products.<sup>64</sup>

3-Hydroxy-2-methyl-4-pyrone in aqueous ammonia is converted in 69% yield into the corresponding pyridone after 30 min at 130 °C.<sup>39</sup> Reaction of the same starting material with 25% aqueous methylamine for 1.3 min at 161 °C also gives the corresponding pyridone in 65% yield.<sup>34</sup>

**Dialkyl Ethers.** Decyl methyl ether is unreactive under both aqueous and purely thermal conditions at 250 °C for 13.5 days.<sup>16</sup> A process for converting ethers and polyethers into their corresponding alcohols after 2 h of reaction in water at elevated temperatures (250–450 °C) is patented.<sup>85</sup>

### B. Aliphatic Alcohols and Carbonyl Compounds

### 1. Alcohols

Galwey<sup>86,87a</sup> studied the thermal desorption of alcohols from montmorillonite and ferric oxide at 230 °C and concluded surface reactions in the presence of reaction products yielded *n*-alkanes, isoalkanes, and cycloalkanes, all hydrocarbons which are abundant in petroleum. By contact, mainly olefins formed when the products were rapidly swept away. Rates were sufficiently great to suggest that such processes could significantly participate in the formation of natural hydrocarbons. The acid-catalyzed dehydration rate of *n*-propane in supercritical water increases with pressure in line with the dielectric constant.<sup>87b</sup> The kinetics and mechanism of the dehydration of *tert*-butyl alcohol in hot compressed water has been extensively discussed.<sup>87c,87d</sup>

Alcohols react with alkenes in the presence of hydrated cation-exchanged (Al<sup>3+</sup>, Cr<sup>3+</sup>) bentonite clay at 150 °C via protonation of the alkene, isomerization to the most stable carbocation, and subsequent nucleophilic attack by the alcohol to give the corresponding ethers.<sup>88</sup>

Decanol undergoes <5% conversion after 13 days at 250 °C in water into nonane, 1-decene, decanal,

Scheme 48. Products from Butyl Phenyl Ether (250 °C, 3 days, 10% H<sub>3</sub>PO<sub>4(ag)</sub>)<sup>64</sup>



Scheme 49. Products from Cyclohexyl Phenyl Ether (460 °C, 7 min, H<sub>2</sub>O)<sup>36</sup>



and decane.<sup>16</sup> However, at higher temperatures, alcohols readily dehydrate to give alkenes. For example, traces of protic acids in water at 400 °C give high yields of dehydration products (ethene from ethanol, propene from propanol, acetaldehyde from ethylene glycol, and acrolein from glycerol) in less than 1 min.<sup>89</sup> 1-Propanol at 375 °C in water undergoes a specific acid-catalyzed  $E_2$  dehydration that is

first order in alcohol;<sup>90</sup> a similar study has been performed with ethanol.<sup>91</sup> Cyclohexanol undergoes nearly complete dehydration in 0.05 wt % aqueous sulfuric acid after 30 min at 250 °C.<sup>27</sup> In water at 300 °C, *cis*- and *trans*-2-methylcyclohexanol undergo elimination to 1-methylcyclohexene in low yield after 1 h, but after 18 h, a mixture of methylcyclohexenes, the products of dehydration/hydration equilibria, were produced with a 70% conversion.<sup>27</sup> Ethylene glycol, 2-chloroethanol, ethanol, 1-propanol, and 2-propanol were used as alkene synthon equivalents in Heck coupling reactions at 400 °C in water with iodobenzene.<sup>92</sup> Since 1-propanol only afforded 1-phenylpropane while 2-propanol afforded a mixture of 1-and 2-phenylpropane, the mechanism is not a simple dehydration—Heck reaction sequence.

Quantitative rearrangement of pinacol, 1,1'-dihydroxy-1,1'-dicyclopentyl, and 1,1'-dihydroxycyclohexyl to the corresponding ketones occurs in 60 min at 275  $^{\circ}C$  in  $D_2O.^{27}$ 

Geraniol, in 220 °C water for 10 min, gives a 91% yield of a 1:1:3 mixture of linalool,  $\alpha$ -terpineol, and monoterpene hydrocarbons.<sup>20</sup> Linalool gives  $\alpha$ -terpineol and monoterpene hydrocarbons (1:30) in 89% yield under the same conditions<sup>20</sup> (see also section 4).

At 290 °C in water for 1 h, 1-ethynyl-1-cyclohexanol gives 1-acetyl-1-cyclohexene in 45% yield. However, after 1 h at 200 °C in 0.1 M aqueous NaOH, 1-ethynyl-1-cyclohexanol gives 76% of cyclohexanone.<sup>20</sup>

#### 2. Aldehydes and Ketones

Only 2% of aldol condensation into the corresponding  $\alpha,\beta$ -unsaturated aldehyde and ketone, respectively, is observed for 1-decanal and 2-decanone in water at 250 °C after 5.5 days.<sup>16</sup>

3-Methylcyclopent-2-en-1-one is prepared in 80% yield, using nonextractive isolation, by reaction of 2,5-hexanedione in only 0.01 M NaOH at 200 °C.<sup>93,20</sup> The reaction of phenylhydrazine with butanone in water at 222 °C for 30 min yields 67% of 2,3-dimethylindole; the use of 1 M aqueous sulfuric acid instead of water gave a comparable yield after only 1 min.<sup>20</sup> The kinetics of the H/D exchange of pinacolone with deuterium oxide at 225 °C was studied.<sup>94</sup>

Ionone and carvone are converted into ionene (30%) and carvacrol (95%), respectively, by heating in water for 20 min or less at 250 °C.<sup>20</sup> The (*S*)-(+)-isomer of carvone is converted into (*S*)-(+)-8-hydroxy-*p*-6-menthen-2-one in 21% yield by heating for 10 min in water at 210 °C.<sup>20</sup> 8-Hydroxy-*p*-6-menthen-2-one is converted into a 1:1 mixture (66%) of carvone and carvacrol after 10 min in water at 230 °C.<sup>20</sup>

The Beckmann rearrangement of cyclohexanone oxime into  $\epsilon$ -caprolactam has been performed in pure water at around 374 °C.<sup>94</sup>

#### 3. Carboxylic Acids

Formic acid decomposes primarily to CO and  $H_2O$ in the gas phase but to  $CO_2$  and  $H_2$  in the aqueous phase.<sup>95</sup> Acetic acid is readily converted to carbon dioxide and methane in water at 300 °C, with<sup>96a,b</sup> and without<sup>97</sup> a catalyst. Formation of acrylic acid from lactic acid in both sub-<sup>98</sup> and supercritical<sup>99</sup> water has been studied. Three reaction pathways are available to lactic acid under these conditions, and the optimum conditions for acrylic acid production (58% based on reacted lactic acid) are 0.4 M reactant with traces of Na<sub>2</sub>HPO<sub>4</sub> at 360 °C.<sup>98</sup> Decarboxylation kinetics of malonic acid and monosodium malonate in water at 120–30 °C were studued by IR spectroscopy.<sup>100</sup> Heck coupling between iodobenzene and alkenes, prepared in situ from amino acids, gives less than 10% product in water at 400  $^{\circ}C.^{92}$ 

Jurg and Eisma reacted samples of behenic acid (n-C<sub>21</sub>H<sub>43</sub>COOH) with bentonite clay in sealed tubes in the presence and absence of water at 200 °C for 89 and 760 h.<sup>101</sup> They found significant hydrocarbon formation only in the presence of the clay catalyst.

Some related work of interest, although nonaqueous conditions were used, is briefly reported below. Shimoyama and Johns reacted behenic acid with calcium montmorillonite under anhydrous conditions at 200 and 250 °C for 50–500 h and obtained results similar to those of Jurg and Eisma.<sup>101,102</sup> Anhydrous calcium carbonate also promoted the degradation of the C<sub>21</sub> and C<sub>22</sub> fatty acids to alkanes at 250 °C.<sup>103</sup>

#### 4. Olefinic Carboxylic Acids

The dimerization of monounsaturated fatty acids has been 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.<sup>104-106</sup>

#### 5. Esters

Methyl acrylate is converted in 30% yield by aqueous formaldehyde/DABCO into methyl 2-(hy-droxymethyl)acrylate after 1.5 min at 161 °C.<sup>34</sup> In water, ethyl cinnamate is converted to the acid in 51% yield after 60 min at 250 °C and to styrene in 69% yield after 360 min at 290 °C.<sup>20</sup> The uncatalyzed manufacture of glycerol by continuous countercurrent hydrolysis of glycerol triacetate with water at 180–245 °C is patented.<sup>107</sup>

Hexyl acetate is hydrolyzed to acetic acid and hexanol in 94% yield after 3 h at 295 °C.<sup>20</sup> Decyl decanoate is four times more reactive in water than thermally at 250 °C: after 1.5 days in water, 81% is converted into decanoic acid (47%), decanol (8%), didecyl ether (2%), and decenes (24% total). Although the last two products are probably formed by dehydration of decanol, no decarboxylation of decanoic acid is observed.<sup>16</sup> The relative activities of acid sediments as catalysts have been screened by following the rate of isobutylene evolution from the decomposition of *tert*-butyl acetate.<sup>108</sup>

# C. Oxygen Functionality $\alpha$ to Benzenoid or Heterocyclic Rings

#### 1. Introduction

An early objective of our studies was to define the behavior of the common single-carbon functional groups attached to benzenoid or heteroaromatic rings. Analysis of the 3-pyridyl family, the interpretation of which is simpler than either that for the phenyl compounds (where the ring is much more susceptible to electrophilic substitution) or for 2- and 4-pyridyl derivatives (where the  $\alpha$ -CH of the functional group is more activated toward proton loss) aided in understanding the behavior of other families. As an introduction, we briefly consider successively the principles of interconversions between  $-CO_2H$ , -CHO, and  $-CH_2OH$ , their loss by ring-C scission, C-C bond formation by aldol-type reactions, the

formation of ethers and esters by C–O bond formation, and the formation of ring C–C bonds.

In water, a series of oxidation-reduction reactions is set up between  $-CO_2H$ , -CHO, and  $-CH_2OH$ when they are directly attached to a benzene<sup>109</sup> or pyridine ring.<sup>110–112</sup> Thus, –CH<sub>2</sub>OH substituents can disproportionate to -CHO and -CH<sub>3</sub> and similarly -CHO substituents to -CO<sub>2</sub>H and -CH<sub>2</sub>OH. For example, in water at 200 °C, 4-pyridinecarboxaldehyde is converted primarily into 4-methylpyridine (22%), 4-pyridinecarboxylic acid (59%), and pyridine (3%) after 6 h, while after 24 h, the percentage of products changed to 19%, 42%, and 34%, respectively, due to decarboxylation.<sup>112</sup> Hydride-ion transfer from  $RCH_2O^-$  or  $RCH(OH)O^-$  is probably involved. In such sequences, the methyl derivative behaves as a thermodynamic sink. Added oxidizing agents, or reducing agents such as formaldehyde and formic acid, shift the oxidation-reduction reactions in the expected direction.

In water, carboxylic acids lose  $CO_2$  quite readily from the 2- or 4-positions of a pyridine ring,<sup>111,112</sup> less easily from the pyridine 3-position,<sup>110</sup> with difficulty when directly attached to benzene,<sup>109</sup> but more easily from PhCH<sub>2</sub>CO<sub>2</sub>H.<sup>113</sup> This pattern is readily understandable as it follows the stability of the carbanion left after loss of  $CO_2$  from the acid anion. The substituents  $-CH_2OH$  and -CHO can also be lost from pyridine rings as HCHO and HCO<sub>2</sub>H, respectively; again, the mechanism probably involves the expulsion of Ar<sup>-</sup> from ArCH<sub>2</sub>O<sup>-</sup> or ArCH(OH)O<sup>-</sup> anions.

Aldol-type reactions in water are generally ionic, rely on the formation of a carbanionic center  $\alpha$  to the ring, and usually need base catalysis. The phenyl group does not afford much activation, and reactions of this type are not observed in benzenes containing CH<sub>3</sub>, CH<sub>2</sub>OH, CHO, or CO<sub>2</sub>H substituents.<sup>109</sup> The corresponding 3-substituted pyridines are more reactive and form various products containing two pyridine rings. The initial step is probably reaction of the aldehyde with the alcohol and/or methyl derivative.<sup>110</sup> Such C–C bond-forming reactions become very favorable in the 2- and 4-pyridine series. A whole host of products arise from elaboration of the initial aldoltype products, as illustrated for the 4-series.<sup>112</sup> The product slate for 2-substituted pyridines is still more complex.<sup>111</sup>

Unexpectedly, in addition to C–O bond cleavages, C–O bond formations occur quite readily in aqueous solution as well as in cyclohexane. Thus, 2-phenylethanol and benzyl alcohol both form equilibria in which considerable proportions of the corresponding ethers formed by dehydration are present.<sup>109,113</sup> Esters are also formed, as well as hydrolyzed, quite readily in aqueous solution. Thus, heating benzyl and phenethyl alcohol in aqueous acetic acid gives significant amounts of benzyl acetate (PhCH2OCOCH3) and phenethyl acetate (PhCH<sub>2</sub>CH<sub>2</sub>OCOCH<sub>3</sub>), respectively.<sup>109</sup> Heating PhCHO with HCHO gives some PhCO<sub>2</sub>CH<sub>3</sub> by intermediate hydride transfer to PhCO<sub>2</sub>H and CH<sub>3</sub>OH.<sup>109</sup> 4-PyCH<sub>2</sub>OH gives some 4-PyCO<sub>2</sub>CH<sub>3</sub>: here some HCHO is liberated and hydride transfer provides the required 4-PyCO<sub>2</sub>H and

#### Scheme 50. Products from Pyridines with Oxygen-Substituted Carbon-Linked Groups in the 3-Position



CH<sub>3</sub>OH.<sup>113</sup> Water-insoluble polyethers<sup>113</sup> and polyesters,<sup>85</sup> including polycarbonates, are depolymerized in superheated water.

Reactions forming C–C bonds at ring carbon atoms generally involve the ring carbon as a nucleophile which is attacked by a C-electrophile. The ring carbon atoms of pyridine are strongly deactivated toward electrophilic attack and do not show such reactions in aquathermolysis. By contrast, they are very common for benzenes and the aquathermolysis of benzyl alcohol results in a highly complex set of products<sup>109</sup> based on the fundamental carbocation reaction type PhCH<sub>2</sub>OH<sub>2</sub><sup>+</sup> + ArH  $\rightarrow$  ArCH<sub>2</sub>Ph. Substitution generally occurs *ortho* or *para* to the existing substituent, and multiple reactions are common. Alkylations, acylations, and condensation reactions in pure near critical water have been carried out recently by other research groups.<sup>114–116</sup>

# 2. 3-Pyridyl Systems

Pyridine-3-carboxylic acid, -3-carboxaldehyde, and -3-carbinol each undergo aquathermolytic cleavage to pyridine with the release of carbon dioxide, formic acid, and formaldehyde, respectively.<sup>110</sup> These 3-substituted pyridines also undergo reduction by formic acid and/or formaldehyde to give 3-methylpyridine, pyridine-3-carboxaldehyde, and 3-pyridylcarbinol. The latter two compounds subsequently undergo aldoltype condensations to afford, after further transformations, di(3-pyridyl)methane and 1,2-di(3-pyridyl)ethane. Bimolecular products are probably formed by reaction sequences of the type shown in Scheme 50, in which the diol as a common intermediate undergoes Wagner-Meerwein rearrangement to yield an aldehyde (immediately cleaved to formic acid) or eliminates water to give a ketone, which is reduced to give 1,2-di(3-pyridyl)ethane. The following evidence supports this mechanism: (i) bimolecular products are produced from 3-PyCH<sub>2</sub>OH only in the presence of 3-PyCHO or HCHO (which can act as an oxidizing reagent) and (ii) bimolecular products are obtained from 3-PyCHO under all aqueous conditions but in larger amounts in the presence of HCO<sub>2</sub>H, which is an active reducing agent.<sup>110</sup>

Scheme 51. Products from  $\alpha$ -pyridoin (1 day, cyclohexane, 150 °C)<sup>111</sup>



Specifically, after 120 h at 250 °C, pyridine-3carboxylic acid undergoes 2% conversion into pyridine in cyclohexane, 52% conversion into pyridine in water, and 100% conversion into pryidine in aqueous H<sub>3</sub>PO<sub>4</sub> and gives 97% pyridine and 3% 3-methylpyridine in aqueous formic acid.<sup>110</sup> After 120 h at 250 °C, pyridine-3-carboxaldehyde is (i) unreactive in cyclohexane, (ii) 100% converted into pyridine (87%) and 3-methylpyridine (13%) in  $H_3PO_4$ , and (iii) 98% converted into pyridine (56%), 3-methylpyridine (26%), 3-pyridylcarbinol (5%), di(3-pyridyl)methane (5%), and 1,2-di(3-pyridyl)ethane (7%) in aqueous formic acid. 3-Pyridylcarbinol undergoes (i) only 5% and 7% conversions in cyclohexane and water, respectively, into pyridine, 3-methylpyridine, and pyridine-3-carboxaldehyde, (ii) 42% conversion into 3-methylpyridine in aqueous formic acid, and (iii) 100% conversion in H<sub>3</sub>PO<sub>4</sub> into 3-methylpyridine (94%) and pyridine (6%).110

The autocatalytic reductions of pyridine-3-carboxaldehyde and 3-pyridylcarbinol, by hydride transfer from formic acid and formaldehyde generated during aquathermolysis, illustrate how autocatalysis can affect reaction pathways and activate relatively unreactive molecules.<sup>110</sup> We believe that such types of autocatalyzed procedures provide vital pathways, which occur in parallel with thermal reactions, in the formation of petroleum from kerogens.<sup>109</sup>

### 3. 2-Pyridyl Systems

Pyridine-2-carboxylic acid, -2-carboxaldehyde, and -2-carbinol are all more reactive than the corresponding 3-isomers. The acid is readily decarboxylated. The aldehyde thermolyzes in cyclohexane via its dimer 2-pyridoin (cf Scheme 51) and in water by loss of HCHO).<sup>111</sup> A feature of the reactions of the aldehyde and alcohol under more forcing conditions is the production of complex slates of products containing two or even three pyridine rings. Scheme 52 shows how the various products form from 2-Py-CO<sub>2</sub>H, 2-Py-CHO, and 2-Py-CH<sub>2</sub>OH are linked with each other. Pyridine-2-carboxylic acid is 100% converted into pyridine after 6 h at 150 °C in either cyclohexane or water.<sup>111</sup> After 120 h at 250 °C, pyridine-2-carboxaldehyde is (i) 40% converted in cyclohexane into pyridine (22%), 2-methylpyridine (9%), 2-pyridylcarbinol (3%), and di(2-pyridinyl)methanone (4%) and (ii) 100% converted in water into pyridine (72%), 2-methylpyridine (16%), and a variety of other minor products. Under the same conditions, 2-pyridylcarbinol is less than 5% converted in cyclohexane but to the extent of 97% in water primarily into pyridine (32%) and 2-methylpyridine (57%).<sup>111</sup>

### 4. 4-Pyridyl Systems

In aquathermolysis, pyridine-4-carboxylic acid, -4carboxaldehyde, and -4-carbinnol are also all more reactive than the corresponding 3-isomers. Pyridine-4-carboxylic acid is less reactive than picolinic acid, being only partially decarboxylated. The 4-aldehyde yields pyridine, 4-picoline, 1,2-di(4-pyridyl)ethane, and, for reactions carried out in cyclohexane, 1,2-di-(4-pyridyl)ethene. The alcohol forms in water similar products to those from the aldehyde; in cyclohexane they are again accompanied by more complex molecules containing two or three pyridine rings (Scheme 53).<sup>112</sup>

Specifically, after 5 days at 250 °C, pyridine-4carboxylic acid is converted into pyridine to the extent of 3% in cyclohexane and 46% in water.<sup>112</sup> Under these conditions, pyridine 4-carboxaldehyde is completely converted in both cyclohexane and

Scheme 52. Products from Pyridines (5 days, 250 °C, H<sub>2</sub>O)<sup>111</sup>



Scheme 53. Products from 4-Substituted Pyridines (5 days, 250 °C,  $H_2O$ )<sup>112</sup>



water. The products from the aqueous reaction include pyridine (46%), 4-methylpyridine (11%), pyridine-4-carboxylic acid (35%), and 1,2-di(4-pyridyl)ethane (7%). In cyclohexane, although the product slate is more complex, the same major products are 2-Py(C<sub>6</sub>H<sub>11</sub>)CHCH<sub>2</sub>Py-2

formed in 15%, 7%, 24%, and 39% yields, respectively. At 250 °C for 5 days, 4-pyridylmethanol also is completely converted in both cyclohexane and water. In water, the products are primarily pyridine (14%), 4-methylpyridine (27%), pyridine-4-carboxylic acid (14%), and 1,2-di(4-pyridyl)ethane (45%). In cyclohexane, the product slate is more complex with 4-methylpyridine (69%) the only product given in over 8% yield.<sup>112</sup>

From the experiments described above, it can be concluded that in anoxic aqueous environments, pyridine, methylpyridines, and 1,2-di(pyridyl)ethanes are unreactive. Previous characterization studies on oil shale kerogens identified bridges containing two methyene units  $[-(CH_2)_2-]$  between aromatic and heteroaromatic moieties as the major cross-links cleaved during thermal treatments to generate oil.<sup>117</sup>

#### 5. Monosubstituted Benzenes

Compared to pyridine, benzene rings are much more susceptible to electrophilic substitution reactions, but conversely as summarized above,  $CH_2$  groups next to a pyridyl group are more reactive than those  $\alpha$  to phenyl.<sup>109</sup>

Benzyl alcohol is 98% converted after 5 days at 250 °C in cyclohexane and 67% of the product mixture is dibenzyl ether.<sup>109</sup> This provides water, and the consequent polar environment allows a slate of minor products to form by ionic mechanisms which is similar to the product slate for aquathermolysis. Indeed, benzyl alcohol is 82% converted after 5 days

# Scheme 54. Products of Benzyl Alcohol (1 day, 250 °C, H<sub>2</sub>O, 1 equiv HOAc)<sup>109</sup>



in water at 250 °C with benzaldehyde (34%) and toluene (23%) as major products.

Addition of additives, such as pyridine, phenol, acetic acid, benzene, formic acid, and formaldehyde, can have dramatic affects on both the extent of conversion and the product slate (cf Scheme 54). When conversion is by an acid-catalyzed ionic pathway, conversion is dramatically accelerated by added acid.  $^{109}$  For example, aqueous  $CF_3SO_3H$  causes a 90% conversion of benzyl alcohol in 1 h at 250 °C with dibenzyl ether (12%), 4[(2'-benzyl)benzyl]toluene (16%), and 2[(4'-benzyl)benzyl]toluene as major products. Reversible dehydration to dibenzyl ether, disproportionation to benzaldehyde and toluene, and selfbenzylation to 2- and 4-benzylbenzyl alcohols all occur. The benzylbenzyl alcohols can react further, and polyalkylated products are also formed by the mono- and dibenzylation of toluene to give a range

of dibenzyltoluenes and (benzylbenzyl)toluenes. Small amounts of the methylene- and ethylene-bridged cross-linked products including diphenylmethane, dibenzyl, and their benzylated products are also formed. The facile hydrolysis of benzyl acetate to produce benzyl alcohol and acetic acid in water at high temperature and pressure is well-known (see section III.B.5).

After 1 h at 290 °C in 0.1 M NaOH, benzaldehyde has 56% disproportionated into benzoic acid and benzyl alcohol.<sup>20</sup> At 250 °C, benzaldehyde is converted to the extent of 13% and 19% in cyclohexane and water, respectively, mostly into benzoic acid.<sup>109</sup> The conversion is reduced to just 5% by the addition of 1 equiv of pyridine but greatly increased to 74% by formic acid (1 molar equiv, 1 day) with benzyl alcohol (34%), toluene (10%), benzoic acid (10%) and dibenzyl ether (5%) as major products.<sup>109</sup> In aqueous 2 M



Scheme 56. Products from Benzophenone (1 h, 460 °C, HCO<sub>2</sub>-Na<sup>+</sup>)<sup>40</sup>



ammonia, benzaldehyde undergoes 100% conversion after 9 h at 267 °C to give as major products benzene (18%) and toluene (38%). $^{50}$ 

Benzoic acid is unreactive in cyclohexane or water after 5 days at 250 °C; after 1 day at 250 °C with 1 equiv of aqueous formaldehyde, it undergoes 7% conversion to methyl benzoate.<sup>109</sup> After 20 min at 200 °C, a 96% yield of the methyl ester resulted from reaction of benzoic acid with methanol and 2 M aqueous HCl.<sup>39</sup>

Conversion of methyl benzoate into benzoic acid is achieved quantitatively in 5% aqueous NaOH after just 1 min at 167 °C.<sup>34</sup> Acetophenone is converted into phenylacetamide in 72% yield by reacting for 10 min at 185 °C with elemental sulfur, pyridine, and 28% aqueous ammonia.<sup>39</sup> Pentyl benzoate is hydrolyzed to benzoic acid and pentanol after 3 h in water at 298 °C in 84% yield, while benzyl benzoate is converted to the corresponding acid and alcohol in 98% yield after 1 h at 250 °C.<sup>20</sup>

Reaction of di-*n*-butylphthalate in water at 305– 390 °C results in *o*-phthalic acid, butanol, and butenes as primary products, with subsequent conversion of *o*-phthalic acid into benzoic acid and some benzene.<sup>118</sup> Decarboxylation of benzoic acid, formation of char, and polycondensation of phenyl species, which are common in thermolysis, are suppressed in supercritical water.<sup>118</sup>

#### 6. Polycyclic Benzenoids

In supercritical aqueous solutions, aryl carbonyl substrates undergo mainly carbonyl-group reduction. Significant amounts of ring opening were observed for 1,4-naphthoquinone and 3,4-benzocoumarin.<sup>40</sup> Anthraquinone undergoes 98% conversion into 9-anthrone (76%), probably via 9-hydroxyanthrone, in 15% aqueous sodium formate after 7 min at 460 °C; after 1 h, anthracene (43%) and 9,10-dihydroan-thracene (9%) are present in addition to 9-anthrone (Scheme 55).<sup>40</sup>

Benzophenone is unreactive in cyclohexane or water after 7 min at 460 °C.<sup>40</sup> After 1 h at 460 °C in cyclohexane, it is converted to the extent of 22% into benzene (19%) (Scheme 56). Under the same conditions, benzophenone is converted into diphenylmethane (6%) in 15% aqueous formic acid but into diphenylmethanol (25%) in 15% aqueous sodium formate. Benzophenone oxime is readily converted to benzophenone in 460 °C water (94% after 7 min).<sup>40</sup>

Fluorenone, after 1 h at 460 °C, is converted into fluorene (93%) in 15% aqueous formic acid, while in 15% aqueous sodium formate, it is 83% converted into fluorene (62%), biphenyl (17%), and 2-methylbiphenyl (2%) (Scheme 57).<sup>40</sup> Fluorenone oxime in 460 °C water is converted into 9-fluorenone in 98% yield after 7 min; after 1 h, the products are 9-fluorenone (6%), fluorene (62%), and biphenyl (31%) (Scheme 58).<sup>40</sup>

After 60 min at 460 °C, 1-tetralone shows 75% conversion in 15% aqueous sodium formate, mainly into naphthalene (49%) and tetralin (14%).<sup>36</sup>

In water at 343 °C, methyl 1-naphthoate gives naphthalene (60%), 1-naphthoic acid (18%), and 2-naphthoic acid (18%) after 2 h (Scheme 59).<sup>67</sup> The high proportion of 2-naphthoic acid produced presumably reflects the thermodynamically unfavorable epi interaction of the 1-COOH group with the proton at C8. Aquathermolysis of 1-naphthoic acid at 343 °C for 2 h yields only naphthalene.<sup>67</sup> Methyl bibenzyl-4-carboxylate was heated at 400 °C in D<sub>2</sub>O for 3 h;

Scheme 57. Products from Fluorenone (1 h, 460 °C, 15% NaHCO<sub>2</sub>)<sup>40</sup>











demethylation and decarboxylation predominated with a deuterium substitution pattern suggestive of an ionic decarboxylation.  $^{46}$ 

Ethyl indole-2-carboxylate gives a 94% yield of indole-2-carboxylic acid when heated to 200  $^\circ C$  in 0.2

M aqueous NaOH for 10 min or indole when heated under these conditions at 255  $^\circ C$  for 20 min.^119

# D. Oxygen-Functionality in Two-Carbon Side Chains

# 1. Oxygenated at the $\beta$ -Position

In cyclohexane at 250 °C over 5 days, 7% of 2-phenylethanol is converted into the ether PhCH<sub>2</sub>-CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>Ph (4%), styrene (2%), and traces of ethylbenzene and toluene.<sup>120</sup> The reactivity of 2-phenylethanol in water at 250 °C over 5 days is negligible (1%) but is enhanced greatly by acetic acid, as is that of benzyl alcohol. In aqueous acetic acid (1 molar equiv), 2-phenylethanol is converted to the extent of 27% into 2-phenethyl acetate (18%), PhCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>CH<sub>2</sub>Ph (3%), benzene (2%), ethylbenzene (1%), and higher molecular weight products (3%) (Scheme 60).<sup>120</sup>

# Scheme 60. Products from 2-Phenylethanol (5 days, 250 °C, HOAC (1 equiv))<sup>120</sup>



The thermal reaction (250 °C over 5 days) of phenylacetic acid in cyclohexane gives mainly dibenzyl ketone (11%) by a Claisen condensation followed by decarboxylation. In water alone, very little reaction takes place under these conditions (99.8% recovery) (Scheme 61).<sup>120</sup>

# Scheme 61. Products from Phenylacetic Acid (5 days, 250 °C, cyclohexane)<sup>120</sup>



Phenylacetaldehyde is much more reactive than benzaldehyde: 33% conversion occurs in water at 100 °C in 1 day and 80% after 5 days at 250 °C.<sup>120</sup> Under these conditions, the major conversion pathway is via the aldol reaction leading to triphenylbenzene (21%) and higher boiling products (10%) (Scheme 62). Phenylacetaldehyde also undergoes reactions that result in the formation of phenylnaphthalenes and chrysene.<sup>120</sup>

# 2. Oxygenated at the $\alpha$ -Position

1-Phenylethanol reacts completely in 5 days at 250 °C in water, primarily through cationic pathways.<sup>37</sup>

Scheme 62. Products from Phenylacetaldehyde (5 days, 250 °C, H<sub>2</sub>O)<sup>120</sup>



Scheme 63. Products from 1-Phenylethanol (5 days, 250 °C, H<sub>2</sub>O)<sup>37</sup>

16%



Styrene is formed (5%) and trapped in aqueous solution by phenethyl cations to give di- (19%) and trimers (5%) instead of polymerizing. Other products include acetophenone (44%), 3-phenylpropene (7%), and ethylbenzene (8%). The situation shows similarities to the reaction of benzyl alcohol and suggests that the mechanisms are ionic even in cyclohexane, where the rapid production of water again provides a relatively polar environment (Scheme 63).<sup>37</sup>

Acetophenone undergoes acid-catalyzed ionic reactions, but with just 2% conversion after 5 days at 250 °C in both water and in cyclohexane, it is more slowly than those for 1-phenylethanol in either solvent.<sup>37</sup> Moreover, after 14 days at 250 °C in aqueous solution with an equimolar amount of phosphoric acid, only 4% conversion of acetophenone is observed, with triphenylbenzene (2%) as the major product (Scheme 64); this presumably results from a series of aldol condensations. With added aqueous acetic acid, 8% of the acetophenone is converted after 5 days at 250 °C, of which one-half of the product mixture is accounted for by isopropylbenzene. Reaction of ac-

8%





etophenone can result in the formation of phenylnaphthalenes and chrysene.<sup>37</sup> Fully deuterated acetophenone is prepared in D<sub>2</sub>O/NaOD after 12 h at 400 °C.<sup>33</sup> The microwave batch reaction of acetophenones, sulfur, and aqueous ammonia at 185–210 °C formed phenylacetamides (Willgerodt reaction) in 59–72% yields with minimal contamination by sulfur.<sup>38</sup>

2-Phenyl-3-butyn-2-ol is converted in 34% yield into the 3-phenyl-2-butenaldehydes (E:Z = 2:3) after 1 h at 200 °C in water.<sup>20</sup>  $\alpha$ -Ethyl-4-methoxybenzyl alcohol and D,L-4-chloro- $\alpha$ -propylbenzyl alcohol undergo nearly quantitative elimination reactions in water at 277 °C in 75 min.<sup>27</sup>

#### 3. Oxygenated at Both the $\alpha$ - and $\beta$ -Positions

After 30 min at 400 °C in water, ethyl benzilate undergoes complete conversion primarily into diphenylmethane (38%) and benzophenone (40%); after 1 h at 500 °C, benzene (7%) and toluene (13%) are formed at the expense of diphenylmethane (33%) and benzophenone (15%).<sup>50</sup> Added ZnCl<sub>2</sub> facilitates the conversion of ethyl benzilate to monocyclic products; after 2 h at 500 °C, benzene and toluene accounted for 49% and 41% of the product, respectively.<sup>50</sup>

Phenylethyleneglycol (PhCH(OH)CH<sub>2</sub>OH), mandelic acid (PhCH(OH)COOH), benzoylformic acid (Ph-COCOOH), and phenylglyoxal (PhCOCHO) all show high reactivity in both water and cyclohexane.<sup>113</sup> The  $\alpha$ -keto and  $\alpha$ -hydroxy acids undergo mainly decarbonylation and decarboxylation reactions. Disproportionation products are also key intermediates as precursors for condensations and cyclizations. The overall reactions are summarized in Scheme 65, and the individual products given in Scheme 66–69.

Phenylethyleneglycol is 90% converted in water at 200 °C after 6 h versus 14% in cyclohexane under

the same conditions.<sup>113</sup> The major reaction pathways are dehydration to phenylacetaldehyde (24%) and aldol condensations of the phenylacetaldehyde and intermediate benzoylmethanol to give dimeric molecules, especially PhCH=CHCH(CHO)Ph (41%) (Scheme 66).<sup>113</sup>

Mandelic acid shows a slightly higher conversion in cyclohexane (99%) than in water (93%) after 1 day at 250 °C.<sup>113</sup> In cyclohexane, the major observed reaction pathway is the formation of benzaldehyde (74%) via loss of carbon monoxide and water. In water, the major products are benzaldehyde and phenylacetic acid (Scheme 67).<sup>113</sup>

Benzoylformic acid is 6% converted in cyclohexane versus 2% in water when heated at 200 °C for 4 h.<sup>113</sup> Complete conversion is achieved within 24 h at 200 °C in either solvent, demonstrating autocatalysis. Simple decarbonylation to benzoic acid (9%) and decarboxylation to benzaldehyde (87%) forms the main products in water (Scheme 68).<sup>113</sup>

Phenylglyoxal is the most reactive of this group of compounds and shows complete conversion at 200 °C during only 6 h in either water or cyclohexane.<sup>113</sup> In water the major products of phenylglyoxal decomposition are benzaldehyde (10%), benzoic acid (43%), and 2,5-diphenylfuran (27%) (Scheme 69). Some thermal condensation to dimeric compounds occurs in cyclohexane.<sup>113</sup>

Thus, in the monosubstituted benzene series we see a less diverse slate of products formed than in the pyridine series. With more feedback of similarly generated products into the kinetic scheme, the products formed by these pathways reinforce previous conclusions about the significance of autocatalysis, especially reductive autocatalysis by watersoluble formic acid and formaldehyde products in the kerogen maturation process. We see less condensa-

Scheme 65. Products from Benzenes (6 or 24 h as indicated, 200 °C, H<sub>2</sub>O)<sup>113</sup>



tion chemistry to form cross-links than in the pyridine series but more ionic alkylation chemistry.

# IV. Compounds with Nitrogen-Containing Functional Groups

# A. Aliphatic Amines

Reactions and kinetic parameters of aqueous hydroxylammonium nitrate at up to 500 °K were determined with a flow cell and FT Raman spectrometer.  $^{121}$ 

Decylamine on heating in water or 10% aqueous sodium chloride for 5.5 days at 250 °C is 8% converted into give *N*,*N*-didecylamine (5%) and *N*,*N*,*N*-tridecylamine (3%).<sup>16</sup> In the presence of Ca-montmorillonite in water, the coversion under these conditions is 39%. Heating with the clay in 10% aqueous NaCl gave 83% conversion into *N*,*N*-didecylamine (69%) and *N*,*N*,*N*-tridecylamine (14%).<sup>16</sup> Quinuclidine and *N*,*N*,*N*-trihexylamine have been reacted in water at 400 °C; although no quantitative product distribution was defined, nitrogen removal does occur and is facilitated by acidic ZnCl<sub>2</sub>.<sup>50</sup>

Primary and secondary aliphatic amines were converted by hot water in the presence of hydrated cation-exchanged ( $Al_3^+$ ,  $Cr_3^+$ ) bentonite into second-

ary and tertiary amines, respectively.<sup>88</sup> *n*-Butylamine gives 14% of dibutylamine with Al-bentonite after 15 h at 220 °C. *tert*-Butylamine undergoes 6% conversion into 2-methylpropene and its oligomers after 50 h at 210 °C. Cyclohexylamine gives a 57% yield of dicyclohexylamine after 1 day at 220 °C. As shown in Scheme 70, pyrrolidine undergoes intermolecular reactions to give di- and trimeric products in unreported yields under similar conditions. After 18 h at 205 °C with Cr-bentonite, mixtures of benzylamine and cyclohexylamine tend to give low yields of secondary amines; the product distribution is somewhat dependent upon the ratio of starting amines, but the unsymmetrical product *N*-benzylcyclohexylamine always predominates.<sup>88</sup>

On heating with 49% formic acid for varying periods of time, <sup>122</sup> aliphatic primary amines undergo N-formylation at all temperatures studied with subsequent reduction into N-methyl- and N,N-dimethyl-N-alkylamines and also minor amounts of elimination of NH<sub>3</sub> to the corresponding alkenes with partial double-bond isomerization. Tertiary amines undergo reductive cleavage at 350 °C to secondary and primary amines, which subsequently follow the reaction sequences seen for primary amines. For example, after 1 h at 250 °C, n-hexylamine is converted to the





extent of 96% into *N*-hexylformamide (94%) and *N*-methyl-*N*-hexylformamide (2%) (Scheme 71). After 11 h at 250 °C, *N*,*N*-dihexylamine is converted to the extent of 94% into *N*,*N*-dihexylformamide (89%), *N*-methyl-*N*,*N*-dihexylamine (4%), and *N*,*N*,*N*-trihexylamine (1%) (Scheme 73). After 2 h at 350 °C, *N*,*N*-dimethyl-*N*-hexylamine is 74% converted into hexanal (4%), hexanol (7%), *N*-methyl-*N*-hexylformamide (5%), *N*-methyl-*N*,*N*-dihexylamine (45%), *N*,*N*dihexylformamide (1%), *N*,*N*-dihexylamine (7%), and *N*,*N*,*N*-trihexylamine (6%) (Scheme 72).<sup>122</sup>

# **B.** Benzylamines and Pyridylmethylamines

*N*,*N*-Dibenzylamine undergoes only 8% conversion after 5 days at 250 °C in water but is 44% converted into toluene (17%) and 1-phenylisoindole (17%) in cyclohexane.<sup>123</sup> Dry pyrolysis at 400 °C for 1 h completely converts benzylamine into diverse nitrogencontaining compounds along with toluene (27%), bibenzyl (18%), and stilbene (12%).<sup>45</sup> Benzylamine is also completely converted in 5 days by water at 250 °C, mostly into toluene (73%) and benzaldehyde (10%) (Scheme 74).<sup>123</sup> Benzylamine is quantitatively denitrogenated to ammonia with toluene (49%) and benzene (22%) as major products by water in 3 h at 400 °C.<sup>45</sup> Heating benzylamine with water and Albentonite under undisclosed conditions gives a low yield of dibenzylamine, similar to the results of *n*-butylamine (see previous section).<sup>88</sup> The reaction of benzylidenebenzylamine at 400 °C for 9 h in water

primarily produces benzene (34%) and toluene (29%) along with other products including benzaldehyde.<sup>124a</sup> The addition of the hydrogen donor dihydroan-thracene simplifies the product slate by increasing the percentage of formed toluene (54%) at the expense of compounds, including benzene (11%), formed from benzaldehyde.<sup>124a</sup>

All three pyridylmethylamines undergo extensive reaction after 5 days at 250 °C in water, with the conversion decreasing in the order  $4 \rightarrow 3 \rightarrow 2.^{123}$  The product slate for 2-pyridylmethylamine contains 18% starting material, along with 17% pyridine, 35% 2-methylpyridine, 10% 7,8-dihydro-5,7-bis(2-pyridyl)-1,5-naphthyridine, 7% 1,2-di(2-pyridyl)ethane, 9% 1,2,3-tri(2-pyridyl)propane, and other compounds. 3-Pyridylmethylamine undergoes 95% conversion, and the major product is 3-methylpyridine (81%). 4-Pyridylmethylamine is completely converted into 4-methylpyridine (60%), 1,2-di(4-pyridyl)ethane (28%), and 1,2,3-tri(4-pyridyl)propane (11%).<sup>123</sup>

### C. Nitriles

1-Decanenitrile is readily hydrated by hot water to 1-nonanecarboxamide, which is subsequently hydrolyzed into 1-decanoic acid and ammonium hydroxide.<sup>16</sup> The ammonium hydroxide formed autocatalyzes the hydrolysis of 1-decanenitrile and 1-decanamide; added NaCl and Ca-montmorillonite also catalyze this reaction. Specifically, after 2.5 days at 250 °C in water, decanenitrile gives 73% nonanecar-

Scheme 67. Products from Mandelic Acid (24 h, 250 °C, H<sub>2</sub>O)<sup>113</sup>



Scheme 68. Products from Benzoylformic Acid (24 h, 200 °C, H<sub>2</sub>O)<sup>113</sup>



\*These products are found in reaction cyclohexane.

boxamide and 26% decanoic acid.<sup>16</sup> Similarly, octanenitrile at 290 °C in water gives a 29% yield of a 1:1 mixture of acid and amide after 1 h and a 63% yield of a 25:1 mixture after 6 h.<sup>20</sup> Kinetics of the hydrolysis of butyronitrile into the amide and acid at 330  $^{\circ}\text{C}$  have been reported.  $^{124b}$ 

Benzonitrile is readily hydrolyzed to benzoic acid (via benzamide) in superheated water.<sup>20,123</sup> A process

Scheme 69. Products from Phenylglyoxal Hydrate (6 h, 200 °C, H<sub>2</sub>O)<sup>113</sup>



\*Products form in cyclohexane.

# Scheme 70. Products from Pyrroldine<sup>88</sup>



for degrading polyacrylonitrile into water-soluble byproducts without the production of HCN in subcritical water has been patented.<sup>125</sup> Although the cyclization of alkynes into benzenes is facile (see section II.A.3), the mixed cycloaddition of alkynes and acetonitrile to form pyridine derivatives gives poor yields due to the rapid hydrolysis of acetonitrile in supercritical water. $^{92}$ 

The hydrothermolysis chemistry of cyanamide and dicyandiamide have been studied by Brill et al.:<sup>124c</sup> up to 175 °C, cyanamide is converted to dicyandiamide, above this temperature hydrolysis to  $CO_2$  and NH<sub>3</sub> dominates with some conversion to melamine and related compounds.

2-, 3-, and 4-Cyanopyridine are almost unreactive under thermolytic conditions but in water are readily hydrolyzed to the corresponding carboxylic acids (via the amides) at 250 °C.<sup>123</sup> The pyridinecarboxylic acids formed can decarboxylate to give pyridine, which is the only product from 2-cyanopyrdine after 5 days.<sup>123</sup> The hydrolysis of 2,6-dicyanopyridine into the dicarboxylic acid in boiling water is acid and base catalyzed.<sup>126</sup>

#### D. Amides

The kinetics of urea hydrolysis in water at 200-300 °C were measured using IR spectroscopy.<sup>127,128</sup>

#### Scheme 71. Products from 1-Hexylamine (1 h, 250 °C, 49% HCO<sub>2</sub>H)<sup>122</sup>



#### Scheme 72. Products from *N,N*-Dimethyl-1-hexylamine (2 h, 350 °C, 49% HCO<sub>2</sub>H)<sup>122</sup>



Scheme 73. Products from Di-1-hexylamine (11 h, 250 °C, 49%  $HCO_2H)^{122}$ 



Thermolysis partially dehydrates benzamide to the nitrile; the water released hydrolyzes another molecule of the amide to the acid.<sup>123</sup> Thus, after 5 days at 250 °C in cyclohexane, benzamide undergoes 26% conversion into benzonitrile (22%) and benzoic acid (4%). Under the same conditions in water, benzamide is 83% converted into benzoic acid along with traces of benzene.<sup>123</sup>

In cyclohexane at 250 °C, the pyridine carboxamides behave similarly to benzamide but the pyridine acids readily decarboxylate so that the products formed are the pyridine nitriles and pyridine.<sup>123</sup> The extent of reaction is much less in the 2-position (2% conversion) than in the 3- (41%) or 4-positions (17%), probably because it is more difficult to dehydrate pyridine-2-carboxamide to 2-pyridylnitrile. However, after 5 days at 250 °C in water, pyridine-2-carboxamide is quantitatively converted to pyridine while the 3- and 4- analogues each undergo 96% conversions into mixtures of pyridine and the corresponding acid.<sup>123</sup>

After 10 min at 200 °C in 2 M HCl, 4-[(4-*tert*-butyl-1-cyclopenten-1-yl)-carbonyl]morpholine gives 4-*tert*butyl-1-cyclopentene-1-carboxylic acid in 70% yield.<sup>20</sup> Hot water depolymerizes polyamides<sup>37</sup> and polyurethanes.<sup>129</sup> Polyurethane foam waste has been successfully recycled by being fed into a reactor chamber and directly contacted with dry superheated steam at atmospheric pressure and from 232 to 316 °C; the isocyanate is converted to the diamine which is extracted from the condensate.<sup>130</sup>

#### E. Anilines and Aminopyridines

#### 1. C-Monosubstituted Anilines

After 1 h at 380 °C in D<sub>2</sub>O/NaOD, aniline is 78% C-deuterated.  $^{33}$ 

2-Methyl-, 4-methyl-, 4-ethyl-, and 4-isopropylaniline show no reaction either in cyclohexane or in water after 3 days at 250 °C.<sup>131</sup> In 10% aqueous phosphoric acid, phenolic hydrolysis products are observed along with significant yields of diphenylamines. The mechanism of these hydrolytic reactions presumably involves attack by neutral water at the *ipso* carbon of the immonium cation formed by ring protonation (Scheme 75). The diphenylamines arise from a similar attack of a neutral amine on a C-protonated aniline. For example, 4-ethylaniline undergoes 35% conversion into 4-ethylphenol (14%), 4-ethyldiphenylamine (1%), and 4,4'-diethyldiphenylamine (20%) (Scheme 76).<sup>131</sup>

After 3 days at 250 °C in an aqueous sulfite mixture, the toluidines undergo some oxidative dealkylation to afford anilines but the main products are benzothiazoles.<sup>131</sup> These sulfur heterocycles probably arise from the reaction of sulfur (generated from the sulfite reagent under the reaction conditions) with the arylamines. Dealkylation, with or without realkylation in the ortho position, is common; realkylation can occur with or without partial degradation of the original alkyl group. Specifically, p-toluidine shows 15% conversion into 2-(4-aminophenyl)-6methylbenzothiazole (12%) and aniline (3%). 4-Ethylaniline is converted to the extent of 38% into aniline (26%), o-toluidine (7%), and 4-ethylphenol (3%), while 4-isopropylaniline undergoes 19% conversion into aniline (4%), p-toluidine (2%), and 4-ethylaniline (12%).<sup>131</sup>

After 1 h at 460 °C in cyclohexane, 2-aminobiphenyl is converted to the extent of 42% into benzene (33%) and carbazole (8%), but in water it undergoes only a 15% conversion into carbazole (10%) with only low yields of denitrogenated products (Scheme 77).<sup>40</sup>

#### 2. N-Alkylanilines

Neat pyrolysis of *N*-benzylaniline shows complete conversion in 40 min at 386 °C with molar yields of both aniline and toluene being greater than 50% and that of benzylaniline being 20%; higher molecular weight products are also formed.<sup>132</sup> In both sub- (340 °C) and supercritical (386 °C) water, reaction of

# Scheme 74. Products from Benzylamine:<sup>123</sup> (i) 5 days, 250 °C, H<sub>2</sub>O; (ii) 5 days, 250 °C (cyclohexane)



*N*-benzylaniline is incomplete after 1 h; products include benzyl alcohol, toluene, and aniline.

In cyclohexane and to a greater extent in water at 250 °C after 3 days, *N*-methyl- and *N*-ethylaniline undergo disproportionations.<sup>131</sup> For example, *N*-methylaniline is converted to the extent of 45% into equimolar mounts of aniline and *N*,*N*-dimethylaniline (Scheme 78). The dominant reactions of *N*-methylaniline and *N*-ethylaniline in 10% phosphoric acid at 250 °C after 3 days are dealkylation to aniline and transalkylation to *o*-toluidines, but a significant amount of phenol is also formed by acid-catalyzed hydrolysis. Significant amounts of diphenylamines and carbazoles are formed; the carbazoles

arise from oxidative couplings of diarylamines. The formation of arylamines with either less or more alkyl substituents than the starting materials compares with the aquathermolyses of alkyl-substituted phenols (see section III.A.1). Such products arise from Friedel–Crafts alkylations and dealkylations (in acid media) and from oxidative dealkylations (in aqueous sulfite mixtures). These alkylations and dealkylations can occur either on the starting arylamine or on reactive intermediates such as arylamines, diarylamines, or carbazoles. Specifically, *N*-ethylaniline is 99% converted into 4-ethylaniline (42%) aniline (12%), phenol (10%), 4-ethylphenol (7%), and 2,4diethylaniline (5%) as major products. The product

Scheme 75. Products from C-Alkylanilines (3 days, 250 °C, 10% H<sub>3</sub>PO<sub>4</sub>)<sup>131</sup>







Scheme 77. Products from 2-Aminobiphenyl (1 h, 460 °C, cyclohexane)<sup>40</sup>



\*Products found in H<sub>2</sub>O, see text.

slate from sulfite mixtures is simpler; *N*-ethylaniline is completely converted into aniline (95%), 2-methylbenzothiazole (2%), phenol (2%), and thiophenol (1%).<sup>131</sup>

#### 3. N,N-Dialkylanilines

After 3 days at 250 °C in cyclohexane or water, *N*,*N*-dimethylaniline shows <2% conversion into *N*methylaniline. Under the same conditions, N,Ndiethylaniline is about 6% converted into N-ethylaniline. In 10% aqueous phosphoric acid, both amines are extensively transalkylated, disproportionated, and hydrolyzed; carbazoles and diarylamines are also formed (Scheme 79). For example, the products from the complete conversion of N,N-dimethylaniline include phenol (11%), N-methylaniline (16%), p-cresol (55%), N.N.2-trimethylaniline (6%), and 1-ethylcarbazole (6%). In a sulfite mixture, N,N-dimethylaniline and N,N-diethylaniline both show mainly oxidative dealkylation and some transalkylations. *N*,*N*-Diethylaniline undergoes complete conversion with aniline (41%), 4-ethylaniline (30%), and N,4diethylaniline (6%) as major products.<sup>131</sup>

#### 4. Polysubstituted Anilines

2,4,6-Trimethylaniline shows no reaction at 250 °C over 3 days either in cyclohexane or in water.<sup>133</sup> Under the same conditions with 10% aqueous phosphoric acid, hydrolysis gives 2,4,6-trimethylphenol (4%) together with 2,4-dimethylaniline (1%) (Scheme 80). In an aqueous sulfite mixture, 20% conversion occurs to give a variety of products arising from oxidative dealkylation.

#### 5. Aminopyridines

2-Aminopyridine reacts with acetylene in water at 185 °C over 6 h without a catalyst to form 1-vinyl-2-pyridone in 75% yield. The reaction does not take place through hydrolysis of the amino group followed by vinylation of the 2-pyridone as shown by (i) 2-pyridone not being vinylated under the same conditions without a catalyst and (ii) unreactivity of 2-aminopyridine in the absence of acetylene. The authors believe that the 2-aminopyridine reacts with acetylene to form 1-vinyl-2-iminopyridine, which subsequently hydrolyses to the pyridone.<sup>134a</sup>

#### F. Nitro Compounds

Extensive work on polynitrocompounds is beyond the scope of this review. 1-Nitrobutane degrades some three times faster in SCW than for the neat pyrolysis to give a complex slate of products.<sup>134b</sup>

# V.Compounds with Sulfur-Containing Functional Groups

# A. Aliphatic Thiols

#### 1. Alkylthiols

At 250 °C, decanethiol undergoes more conversion in cyclohexane (67%) than in water (35%) after 13.5 days.<sup>16</sup>

Decanethiol gives a series of desulfurized products at 250 °C in either cyclohexane or water (ca. 50% conversion after 5 days in each case)<sup>135</sup> together with various isomeric didecyl sulfides, disulfides, and trisulfides. The overall sulfur loss from converted

Scheme 78. Products from N-Ethylaniline (3 days, 250 °C, 10% H<sub>3</sub>PO<sub>4</sub>)<sup>131</sup>



material is 34% in cyclohexane but 60% in water, implying an ionic contribution; however, addition of nontronite clay (an iron-containing montmorillonite) has little effect. When the temperature is increased to 300 °C (3 days), the conversion rises to 69% in water but the proportion of converted material which has lost sulfur increases sharply to 93% due to the conversion of the sulfides to nonane and decenes. The formation of the decenes (all of which were detected) and of the 1-, 2-, and 3-decanethiols is depicted in Scheme 81; the suggested mechanism is reminiscent of the Willgerodt reaction.<sup>135</sup>

#### 2. Phenylalkylthiols $[Ph(CH_2)_{1-3}SH]$

Greater conversion in water than in cyclohexane after 1 day at 200 °C is found for benzylthiol (74% versus 12%) and phenethylthiol (30% versus 9%).<sup>136</sup> 3-Phenylpropylthiol is 25% or less converted after 5 days at 250 °C. Thus, the reactivity of these thiols decreases as the number of methylene groups between the phenyl ring and the mercaptan group increases. To different extents, the thiols couple to form both sulfides and disulfides. In addition, desulfurization reactions give toluene, ethylbenzene, and propylbenzene as major products plus some diphenylalkane radical coupling products  $Ph(CH_2)_{2-4}Ph$ . A minor amount of radical cyclization occurs to form benzothiophenes and dithianes. Specifically, benzylthiol is converted to the extent of 74% into toluene (12%), dibenzyl sulfide (13%), dibenzyl disulfide (46%), and trisulfide (2%) at 200 °C and 100% primarily into 1,2-diphenylethane (22%) and toluene (67%) at 250 °C (Scheme 82).<sup>136</sup>

The Co<sub>2</sub>(CO)<sub>8</sub>-catalyzed carbonylation of benzylthiol has been used to synthesize esters in aqueous alcohols at 190 °C over 24 h.<sup>137</sup> 2-(Methylthio)benzothiazole is completely converted after 5 h at 400 °C, thermally mainly into benzothiophene, while in water, aniline and benzothiazole predominate as products.<sup>53</sup>

#### **B.** Arylthiols

Thiophenol is 78% converted after 7 min at 460 °C in water into diphenyl sulfide (74%), dibenzothiophene (3%), and traces of benzene.<sup>138</sup> After 1 h at 460 °C in either 15% aqueous sodium formate or 15% phosphoric acid, conversion is complete into benzene.<sup>138</sup> In an aqueous sulfite mixture, thiophenol is 83% converted after 70 min at 250 °C into diphenyl sulfide (44%), diphenyl disulfide (6%), thianthrene (12%), diphenyl trisulfide (17%), and o-(PhS)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (5%) (Scheme 83).<sup>133</sup> 4-Methylthiophenol undergoes 92% conversion into thianthrene (27%) and di(4-toluyl) disulfide (61%) in an aqueous sulfite mixture (82 h at 250 °C) (Scheme 84).<sup>133</sup>

Scheme 79. Products from N,N-Dimethylaniline (3 days, 250 °C, 10% H<sub>3</sub>PO<sub>4</sub>)<sup>131</sup>



After 26 h at 250 °C, naphthalene-2-thiol undergoes 17% conversion in water and 94% conversion in a sulfite mixture to similar products.<sup>133</sup> Specifically, in aqueous sulfite mixture, the product slate consisted of naphthalene (2%), starting material (6%), 2,2'- (29%) and 1,2'-dinaphthyl sulfide (7%), and 2,2'-(50%) and 1,2'-dinaphthyl disulfide (6%) (Scheme 85).<sup>133</sup> After 5 days at 250 °C in water containing nontronite, naphthalene-1-thiol undergoes complete conversion with 1,1'- (73%) and 1,2'-dinaphthyl sulfide (15%) as major products.<sup>135</sup> Increasing the temperature to 300 °C for only 3 days increases the amount of sulfur loss from 46% to 82% with naphthalene (64%) being the major product from an 87% conversion.<sup>135</sup> Naphthalene-1-thiol is converted to the

extent of 78% after 7 min in water at 460 °C into naphthalene (16%), 1,1'-dinaphthyl sulfide (48%), 1,2'-dinaphthyl sulfide (8%), and 1,1'-dinaphthyl disulfide (6%).<sup>138</sup> Under the same conditions in 15% aqueous formic acid, complete conversion occurs into naphthalene (98%) and tetralin (2%).<sup>138</sup>

# C. Sulfides and Disulfides

Organic sulfides and disulfides are more reactive under thermolysis than under aquathermolysis conditions. The major reactions observed involve homolytic bond cleavages of C-S bonds followed by further reactions of the free radicals generated.





Scheme 81. Aquathermolysis of 1-Decanethiol (300 °C, 3 days, H<sub>2</sub>O)<sup>135</sup>



#### 1. Dialkyl Sulfides

Dibenzyl sulfide undergoes complete conversion in both water and cyclohexane after 5 days at 250  $^{\circ}$ C into toluene (48% and 55%), benzoic acid (10% and

0%), 1,2-diphenylethane (24% and 23%), stilbene (5% and 15%), and other minor products (Scheme 86).<sup>139a</sup> Benzyl methyl sulfide is much less reactive under the same conditions with only 3% conversion in water



Scheme 83. Aquathermolysis of Thiophenol (250 °C, 70 h, aqueous sulfite mixture)<sup>133</sup>



and 17% conversion in cyclohexane, where toluene (10%) is the major product.<sup>139a</sup> Tester and coworkers<sup>139b</sup> documented the complex degradation of thiodiglycol in sub- and supercritical water.

Although dioctyl sulfide undergoes significant (74%) conversion after 5 days at 250 °C in cyclohexane into 1-octene (28%), octanethiol (18%), and dioctyl disulfide (11%), the percent sulfur loss after 3 days at 300 °C in aqueous nontronite is much greater (76% versus 40%), with the major products from an 86% conversion being alkanes (19%), alkenes (43%), and octanethiol (17%) (Scheme 87).<sup>135</sup> Thus, the products from dioctyl sulfide are similar to those from decanethiol (see section V.A.1). Elimination produces 1-octene and octanethiol, which then undergo the Willgerodt sequence to give various isomeric octenes and thiols. Homolysis of the S-C bond leads to octane and a sulfide radical, which would produce the dioctyl disulfide observed. An alternative  $\alpha - \beta$  homolysis gives heptane, some of which is produced under all conditions but is found in up to 14% yield in the nontronite-catalyzed reactions at 300 °C.<sup>139a</sup> Dioctyl sulfide shows almost complete conversion after 7 min in 460 °C water into 1-heptene (38%), 1-octene (55%), and octanethiol (5%).<sup>138</sup>

Scheme 84. Aquathermolysis of Thiophenol (250 °C, 70 h, aqueous sulfite mixture)<sup>133</sup>



#### Scheme 85. Aquathermolysis of Naphthalene-2-thiol (250 °C, 26 h, sulfite mixture)<sup>133</sup>



Aquathermolysis of tetrahydrothiophene at 300 °C for 28 days produced equimolar quantities of  $H_2S$  and  $CO_2$  along with methane and other  $C_2-C_5$  products from an unreported percent conversion.<sup>140</sup> Additional studies on the aquathermolysis of tetrahydrothiophene with added catalysts, including acids and bases,<sup>58</sup> vanadyl sulfate and chloride,<sup>59</sup> and first-row transition-metal cations,<sup>60</sup> indicate that desulfurization of tetrahydrothiophene is readily catalyzed in high-temperature water.

### 2. Aryl Alkyl Sulfides

After 5 days at 250 °C, methyl phenyl sulfide (thioanisole) undergoes <3% conversion in water, cyclohexane,<sup>139a</sup> or 10% aqueous phosphoric acid.<sup>133</sup> In an aqueous sulfite mixture (1 h at 250 °C), thioanisole is 25% converted mainly into thiophenol (19%).<sup>139a</sup> Cyclohexyl phenyl sulfide undergoes extensive conversion after just 7 min at 460 °C in either cyclohexane (radical reactions) or aqueous (significant ionic contribution) media.<sup>138</sup> In cyclohexane, the primary products from an 89% conversion are cyclohexene (26%), thiophenol (21%), cyclohexylbenzene (17%), and biphenyl (15%). There is a 91% conversion of cyclohexyl phenyl sulfide after 7 min at 460 °C in 15% aqueous formic acid into 1-methylcyclopentene (27%), benzene (23%), thiophenol (11%), cyclohexylbenzene (12%), and biphenyl (12%), indicating extensive acid-catalyzed reaction (Scheme 88).<sup>138</sup>

After 5 h at 400 °C in water, thiochroman-4-ol undergoes 70% conversion, with the products consisting primarily of benzothiophene (18%), methylbenzothiophenes (46%), and 2,3,5,6-tetramethylphenol (23%).<sup>53</sup> 1-Naphthyl octyl sulfide reacts primarily through radical reactions in both cyclohexane or aqueous environments to give a large number of products.<sup>135</sup> Increasing the reaction temperature in water from 250 °C (5 days) to 300 °C (3 days) increases conversion (from 34% to 96%) as well as loss of sulfur (from 58% to 82%). The major products under the harsher conditions are heptane (7%), 1-octene (38%), naphthalene (26%), and dioctyl sulfide (7%) (Scheme 89).<sup>135</sup>

Benzyl phenyl sulfide is virtually unreactive in water but quite reactive in cyclohexane after 5 days at 250 °C; its product slate consists of 69% starting material, 11% toluene, 4% thiophenol, and 7% diphenyl disulfide (Scheme 90).<sup>139a</sup> After 2 h at 300 °C, neat pyrolysis of benzyl phenyl sulfide gives a 96% conversion into toluene (50%), diphenyl sulfide (22%), diphenyl disulfide (6%), and thiophenol (8%), while in water the 100% conversion gives toluene (62%), thiophenol (18%), along with minor products including benzaldehyde.<sup>141</sup> After 7 min at 460 °C, 1-phenylthiotetralin undergoes complete conversion under both aqueous and nonaqueous conditions (Scheme 91).<sup>138</sup> In cyclohexane, the product slate is composed



Scheme 87. Products from Dioctyl Sulfide (250 °C, 5 days, cyclohexane)<sup>135</sup>



of tetralin (62%), naphthalene (14%), 1-naphthyl phenyl sulfide (11%), and each of benzene (3%), thiophenol, diphenyl disulfide, and 1-phenylnaphthalene. In 15% aqueous formic acid, the product slate is much simpler, consisting of benzene (45%), methylindane (1%), tetralin (24%), and naphthalene-(31%); all sulfur was extruded as  $H_2S$ .<sup>138</sup>

Phenyl 2-phenylethyl sulfide is quite reactive with <2% unreacted after 5 days at 250 °C in either water or cyclohexane (Scheme 92).<sup>139a</sup> In water, the major

Scheme 88. Products from Cyclohexyl Phenyl Sulfide (460 °C, 7 min, 15% HCO<sub>2</sub>H<sub>(aq)</sub>)<sup>138</sup>



Scheme 89. Aquathermolysis of 1-Naphthyl Octyl Sulfide (300 °C, 3 days, H<sub>2</sub>O)<sup>135</sup>



products are ethylbenzene (41%), thiophenol (15%), diphenyl sulfide (16%), diphenyl disulfide (7%), and acetophenone (10%), which is not found from the reaction in cyclohexane. However, after 5 days at 250

°C, phenyl 3-phenylpropyl sulfide undergoes only 16% conversion in cyclohexane and 7% in water to give a variety of products including disulfides, trisulfides, thiophenol, and alkenes (Scheme 93).<sup>139a</sup>



Scheme 91. Products from 1-Phenylthiotetralin (460 °C, 7 min, cyclohexane)<sup>138</sup>



#### 3. Diaryl Sulfides

Diphenyl sulfide is quite stable. It undergoes negligible conversion in cyclohexane, water, or 15% aqueous phosphoric acid after 1 h at 460 °C<sup>138</sup> or in an aqueous sulfite mixture for 22 h at 250 °C.<sup>133</sup> However, in 15% aqueous formic acid (1 h at 460 °C), diphenyl sulfide is converted to the extent of 76% almost exclusively into benzene. These results suggest that the cleavage of diphenyl sulfide is greatly enhanced by reducing media and that this cleavage is acid catalyzed.<sup>138</sup>

1-Naphthyl phenyl sulfide is completely desulfurized at 460 °C in 15% aqueous formic acid, giving benzene (43%) and naphthalene (56%) in 1 h. $^{138}$  1,1'-Dinaphthyl sulfide shows low conversions at 250 °C (<10% over 5 days) in cyclohexane or water but an 89% conversion at 300 °C over 3 days in pH 10.5 water containing nontronite<sup>135</sup> to give naphthalene (57%), 1-naphthalenethiol (6%), 1,2'-dinaphthyl sulfide (22%), and 2,2'-dinaphthyl sulfide (5%) (Scheme 94).

Thianthrene polymerizes thermally at 400 °C, but after 15 h at 400 °C in water, it has 17% of its sulfur eliminated.  $^{53}$ 

#### 4. Disulfides

After 5 days at 250 °C in cyclohexane, didecyl disulfide undergoes complete conversion through a





Scheme 93. Products from 1-Phenylpropyl Sulfide (250 °C, 5 days, cyclohexane and H<sub>2</sub>O)<sup>139a</sup>



variety of radical reactions into a multitude of products, with isomers of decanethiol (45%) and decene (32%) predominating.<sup>135</sup> Reaction of didecyl disulfide for 3 days at 300 °C in water gives complete conversion and 90% loss of sulfur, with decenes as the major products.<sup>135</sup>

Diphenyl disulfide is converted to the extent of 90% into diphenyl sulfide (37%) and thiophenol (52%) after 5 days at 250 °C in cyclohexane (Scheme 95).<sup>139a</sup> Under the same conditions in water, conversion is only 34% with thiophenol (4%), diphenyl sulfide (21%), and PhSO<sub>2</sub>SPh (9%) as the only products detected.

After 5 days at 250 °C in cyclohexane, 1,1'-dinaphthyl disulfide gives naphthalene-1-thiol (67%), 1,1'dinaphthyl sulfide (22%), and cyclohexyl 1-naphthyl sulfide (11%) as products with an 11% loss of sulfur (Scheme 96). Under these conditions in water, there is a 46% loss of sulfur with naphthalene (34%), naphthalene-1-thiol (43%), 1,2'-dinaphthyl sulfide (6%), and 1,1'-dinaphthyl sulfide (17%) as products.<sup>135</sup>

The main products (84% conversion) of thermolysis (5 days at 250 °C in cyclohexane) of di-2-pyridyl disulfide are 2-pyridinethione (57%) and di-2-pyridyl sulfide (24%). Di-4-pyridyl disulfide (93% conversion) gives 4-pyridinethione (16%), di-4-pyridyl sulfide (37%), and 2,7-diazathianthrene (25%).<sup>139a</sup> Under the same conditions in water, di-2-pyridyl disulfide is 97% converted into 2-pyridone (51%) and 2-pyridinethione (46%). Di-4-pyridyl disulfide is 92% converted into 4-pyridinethione (34%), 4-pyridone (39%), and di-4-pyridyl sulfide (19%).<sup>139a</sup>

#### Scheme 94. Aquathermolysis of 1,1'-Dinaphthyl Sulfide (300 °C, 3 days, H<sub>2</sub>O + clay additives)<sup>135</sup>



Scheme 95. Thermolysis of Diphenyl Disulfide (250 °C, 5 days, cyclohexane)<sup>139a</sup>



### **D. Sulfoxides and Sulfones**

Diaryl and alkyl aryl sulfones and sulfoxides have been treated at 460 °C in cyclohexane and aqueous media, where ionic reactions predominate.<sup>142</sup> Extensive desulfurization is observed in reactions of aryl sulfoxides and sulfones in aqueous formic acid and sodium formate solutions.

In cyclohexane, diphenyl sulfoxide is completely converted after 7 min at 460 °C, with thiophenol (22%) and diphenyl sulfide (72%) as major products (Scheme 97).<sup>142</sup> After 1 h in 15% aqueous formic acid, the major products are diphenyl sulfide (7%) and benzene (92%). Diphenyl sulfone is converted to the extent of 50% into cyclohexylbenzene (32%) and diphenyl sulfide (10%) after 1 h at 460 °C in cyclohexane but is completely converted in the same period in 15% aqueous formic acid into benzene (84%) and diphenyl sulfone (7%).<sup>142</sup>

Methyl phenyl sulfoxide, after 7 min at 460 °C in cyclohexane, is completely converted primarily into diphenyl sulfide (34%), methyl phenyl sulfide (13%), and thiophenol (37%).<sup>142</sup> After 1 h at 460 °C in 15% aqueous formic acid, the major products are benzene (85%), toluene (8%), and methyl phenyl sulfide (5%); the same conditions in water give diphenyl sulfide and thiophenol as additional major products.

After 1 h at 460 °C, methyl phenyl sulfone undergoes complete conversion in 15% aqueous sodium formate into benzene (54%), thiophenol (26%), and diphenyl sulfide (8%); formic acid gives a similar product slate, except there is more diphenyl sulfide (34%) and less benzene (30%).<sup>142</sup>

After 1 h at 460 °C in cyclohexane, dibenzothiophene sulfone is converted to the extent of 87% into a multitude of products including benzene (37%) and dibenzothiophene (12%).<sup>142</sup> It is unreactive after 7





Scheme 97. Aquathermolysis of Diphenyl Disulfide (460 °C, 1 h, 15% HCO<sub>2</sub>H<sub>(aq)</sub>)<sup>142</sup>



min at 460 °C in water, but after 1 h in 15% aqueous sodium formate, it is completely converted into dibenzothiophene (34%), 2-phenylphenol (31%), and biphenyl (30%). Recall (see section II.E) that dibenzothiophene is essentially unreactive to aquathermolysis.

Pyrolysis of styryl sulfoxides and sulfides leads to the formation of benzothiophene derivatives (40-50%yield) via intramolecular cyclization of thienyl.<sup>143</sup> Intramolecular cyclization of the styrylthienyl radical, which may be formed by homolysis of the S–OH bond of an intermediate sulfenic acid, is a favorable process.

# E. Sulfonic Acids

2-Phenylethane sulfonic acid is unaffected both by thermolysis and by a quathermolysis (250  $^\circ C,\ 5$  days).<sup>136</sup> Its sodium salt gives only traces of styrene under the same conditions.

2-(2-Pyridyl)- and 2-(4-pyridyl)ethanesulfonic acids are each more reactive than 2-phenylethanesulfonic acid, undergoing >94% conversion after 5 days at 250 °C.<sup>136</sup> In hexane, the major products from 2-(2pyridyl)ethanesulfonic acid are 2-methylpyridine (66%), pyridine (11%), and 2-ethylpyridine (12%) (Scheme 98); the 4-pyridyl analogue gives an anala-

# Scheme 98. Thermolysis of 2-(2-Pyridyl)ethanesulfonic Acid (250 °C, 5 days, hexane)<sup>136</sup>



gous product slate. In water, the methylpyridines and

pyridine itself are seen in increased amounts at the expense of the ethylpyridines, which become minor products. Additionally, high molecular weight products, e.g., di- and tripyridylthiophenes, are produced from these reactions, especially (>15%) for 2-(4-pyridyl)ethanesulfonic acid.<sup>136</sup>

### VI. Compounds Containing Other Elements

The destruction of toxins, such as chlorinated benzenes and organophosphorus and arsenic compound analogues of nerve gases, have been studied under aquathermolysis conditions. Heck reactions have also been examined in superheated water.<sup>92</sup>

#### A. Organophosphorus

Tripropyl phosphate, triethyl phosphonoacetate, triphenyl phosphate, diethyl 2-methylbenzylphosphonate, diethyl 1-naphthylmethylphosphonate, and diethyl (4-biphenylmethyl)phosphonate, chosen as analogues of military nerve gases, were subjected to neutral aquathermolysis both at sub- and supercritical temperatures. Triphenyl phosphate gives phenol as the main product (94%) at 350 °C after only 1 h (Scheme 99). At 300 and 350 °C, aromatic phosphonates, for example, 1-naphthyl methylphosphonate (Scheme 100), form mainly aromatic aldehydes and products resulting from cleavage of the C-P bond. The aquathermolysis at 460 °C leads to a wider variety of substituted aromatic compounds, including aryl phosphonates arising from partial hydrolysis of the original phosphonates. At temperatures >350 °C, the six organophosphorus compounds are highly reactive and completely converted to simpler nonphosphorus-containing products; <sup>31</sup>P NMR indicates

# Scheme 99. Aquathermolysis of Triphenylphosphate (350 °C, 1 h, H<sub>2</sub>O)<sup>144</sup>



Scheme 100. A quathermolysis of 1-Naphthyl Methylphosphonate (350  $^\circ C,$  1 h, H<sub>2</sub>O)  $^{144}$ 



that the phosphorus is largely converted into phosphoric acid.<sup>144</sup>

#### **B.** Organoarsenic

Six organoarsenic compounds were subjected to aquathermolysis at 300 °C for 1 h to assess the potential application of such treatment for the detoxification of warfare agents. Tetraphenylarsonium chloride hydrate is not reactive, whereas (3cyanopropyl)dimethyl(2-phenethyl)arsonium bromide undergoes nearly complete conversion to low molecular weight organics (Scheme 101). 5,10-Dihydro-10ethylphenarsazine forms a complex product slate of diphenylamines, small amounts of organoarsenic compounds, and arsenic oxide (Scheme 102). 4-Aminophenylarsine, 4-nitrophenylarsonic acid (Scheme 103), and 4-arsanilic acid form mainly aniline, phenol (only for the latter two), and arsenic oxide. 145

#### C. Halogens

The use of aquathermolysis to remove chlorine from organics has also been studied. The decomposition of 3-chlorobiphenyl by 1 equiv of  $H_2O_2$  at 400 °C is greater than 99.9%. Complete analysis of the complex product slate formed when only 0.5 equiv of  $H_2O_2$  is used indicates that OH radicals are important species in this process.<sup>146</sup> Reaction of poly(vinyl chloride)<sup>147a</sup> and rubber materials<sup>147b</sup> with neutral water at temperatures greater than 200 °C results in removal of 30 and 64 wt % chlorine, respectively, without the release of chlorine or hydrogen halide gases. Methylene chloride hydrolyses more rapidly in sub- than in supercritical conditions, a result

Scheme 101. A quathermolysis of (3-Cyanopropyl)dimethyl (2-phenethyl)arsonium Bromide (300 °C, 1 h,  $\rm H_2O)^{145}$ 



Scheme 102. Aquathermolysis of 5,10-Dihydro-10-ethylphenarsazine (300 °C, 1 h, H<sub>2</sub>O)<sup>145</sup>



explained qualitatively due to the dielectric constant of the medium and quantitatively by calculations;  $^{148a}$  product distribution and mechanistic pathways have been studied.  $^{148b,c}$ 

Heck reactions between a variety of activated arenes and alkenes bearing electron-withdrawing groups proceed in low yields, because of loss of catalyst activity, but with regiocontrol in water at 260 °C; the nature of the ligands appears to be unimportant. Hydrogenation and hydrogenolysis side reactions are halted by the use of NH<sub>4</sub>HCO<sub>3</sub> and are exacerbated at supercritical temperatures.<sup>149</sup> Hightemperature water Heck reactions, including the use of alcohols as masked alkenes (Scheme 104),<sup>150</sup> have been summarized.<sup>92</sup> Recently, Heck reactions with cycloalkenes in water with sodium acetate at 260 °C

Scheme 103. Aquathermolysis of 4-Nitrophenylarsonic Acid<sup>145</sup>



Scheme 104. Potential Alkene Synthons Examined in the Heck Coupling Reaction in Superheated Water<sup>150</sup>



for 20 min gave products in up to 54% yield.<sup>151</sup> The aqueous Heck reaction of 5-iodo-2,4-dimethoxypyrimidine with thiophene for 24 h at 150 °C gave a 23% yield of 6-(2-thienyl)-2,4-dimethoxypyrimidine.<sup>152</sup>

1,2-Dichlorobenzene after 6 h at 410 °C in  $D_2O$  gives a variety of products containing oxygen.<sup>93</sup>

1-Chlorohexane is completely dehalogenated after 30 min at 400 °C in water; product distribution is altered by interactions between the formed HCl and the walls of the metal reactor.<sup>50</sup>

#### VII. Conclusions

It is clear that while the typical homolytic bond cleavages so common in dry pyrolysis can and do also occur in aqueous media, a whole additional range of ionic/ heterolytic chemistry also takes place in water. Much of this is dependent on the relatively high dielectric constant which applies to subcritical water; above the critical point, the dielectric constant depends largely on the pressure and the ionic chemistry falls off as the pressure drops.

The significant increase in the dissociation constant of water with increasing temperature means that water becomes both a stronger acid and a stronger base. Thus, in addition to the normal rate increase expected with rise in temperature, there is superposed on this an additional rate increase for both acid- and base-catalyzed reactions. That important class of reactions which requires both acid and base catalysis is thus triply accelerated by rising temperature.

In general, substituents are more reactive than heterocyclic rings. The cleavage of C-O bonds in esters and ethers has come to be expected under relatively mild conditions in aqueous media; C-S and C-N bonds are also fairly easily broken. Less expected is the wide range of C-C, C-O, and C-N bond-forming reactions which have been found to take place, usually by ionic mechanisms. At higher temperatures or in the presence of acids or reducing agents, heterocyclic rings react quite readily; surprisingly, ring opening is found to occur by breaking of C-C bonds, in addition to the more common-place C-S and C-N bond cleavage. More recent work has demonstrated aquathermolysis to be a promising alternative for the detoxification of military nerve agents.

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