

# CHAPTER 6

## CHEMICAL MARKERS OF PREBIOTIC CHEMISTRY IN HYDROTHERMAL SYSTEMS

JAMES P. FERRIS

*Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180, U.S.A.*

### 1. Introduction

The goal of this chapter is to suggest some organic compounds which may be indicative of prebiotic processes in hydrothermal systems or laboratory simulations of them. While the exact processes which led to the origins of life are not known, studies of life's origins of the past forty years have uncovered a plethora of potential precursor molecules. Some of these same molecules were probably present in hydrothermal systems if chemical processes there had a role in the origins of life.

The types of molecules formed in primitive Earth simulation experiments and observed in the interstellar medium, on comets and meteorites will be reviewed in Section 2 of this chapter. Some reactions involving these molecules which may have been important in prebiotic syntheses will be outlined. Since near- to supercritical water is found in hydrothermal systems, its properties and aspects of organic chemistry in supercritical water at high temperature and pressure will be discussed in Section 3. Fischer-Tropsch type (FTT) reactions, which are a potential source of the building blocks of biological molecules in hydrothermal systems, are discussed in Section 4. In the concluding section, Section 5, the possible formation in hydrothermal systems of organic molecules that are believed to have been important for the origins of life is discussed.

### 2. Molecules Formed in Prebiotic Simulation Experiments and Observed in Extraterrestrial Environments

The molecules leading to the origins of life may have either been formed in the hydrothermal systems or transported to them after being formed elsewhere on earth or after being delivered to the earth by impacting carbonaceous meteorites or comets. This section gives a brief overview of the range of organics that may have been delivered to or possibly formed in hydrothermal systems. Although every attempt has been made to provide a comprehensive compilation of the organics that may have been present on the primitive earth, no attempt has been made to report on all the reactions that have been described in the literature for these compounds.

## 2.1. HYDROGEN CYANIDE (HCN) AND SIMPLE HCN ADDUCTS

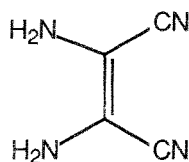
### 2.1.1. HCN

HCN is likely to have been present in prebiotic hydrothermal systems because it is formed by a variety of processes driven by thermal energy (Ferris and Hagan, 1984). Indeed, HCN has been observed in volcanic emissions and has been postulated to be present in hydrothermal systems (Mukhin, 1974). Most, if not all of this HCN is probably formed by the pyrolysis of contemporary biomolecules and not prebiotic precursors (Ferris and Hagan, 1984; Johnson and Kang, 1971; Morikawa, 1978). HCN is the product of passing an electric discharge through gaseous mixtures which contain carbon at the oxidation levels of CH<sub>4</sub>, CO and CO<sub>2</sub>, nitrogen as NH<sub>3</sub> and N<sub>2</sub>, hydrogen gas and water (Lemmon, 1970; Ferris and Hagan, 1984). Shock heating of comparable mixtures also generates HCN (Bar-Nun and Shaviv, 1975). Simple pyrolysis of CH<sub>4</sub>-NH<sub>3</sub> at 1200°C is a preparative source of HCN (Koberstein, 1973). HCN and nitriles are formed by the reaction of CO, NH<sub>3</sub> and H<sub>2</sub> (or the corresponding deuterated derivatives) in a FTT reaction at around 500°C (Hayatsu *et al.*, 1968, 1972). HCN is one of the products of the pyrolysis of formamide and nitriles (Yasuda, 1967; Ashworth, 1971; Brunmuller *et al.*, 1986). Photolysis of mixtures of CH<sub>4</sub> and NH<sub>3</sub> (Ferris and Chen, 1975a) or CO and NH<sub>3</sub> (Ferris *et al.*, 1974) also generates HCN. A model of chemical processes in the atmosphere of the primitive Earth is consistent with HCN formation if CH<sub>4</sub> and NH<sub>3</sub> were present (Zahnle, 1986) but an alternative model with carbon in the CO or CO<sub>2</sub> oxidation state and nitrogen as N<sub>2</sub> is more widely accepted (see Chapter 1; Cogley and Henderson-Sellers, 1984; Kasting, 1988). HCN has also been detected in the atmospheres of Titan and Jupiter, in comets, and in the interstellar medium. Thus the ease of formation of HCN under a variety of conditions strongly suggests that it, or adducts of it with other organic molecules (e.g., the formation of HOCH<sub>2</sub>CN by reaction with CH<sub>2</sub>O), were present in hydrothermal systems on the primitive earth. There it may have been complexed with iron as Fe(CN<sub>6</sub>)<sup>4-</sup> or Fe(CN)<sub>6</sub><sup>3-</sup> which is bound to insoluble minerals (Arrhenius *et al.*, 1989; Kuma *et al.*, 1989). Alternatively the HCN may have been combined with formaldehyde as the cyanohydrin (Section 2.1.3).

### 2.1.2. Diaminomaleonitrile (DAMN)

The self condensation of HCN in mildly basic solution (Sanchez *et al.*, 1967) results in the formation of DAMN, a central intermediate in the formation of the purine ring (Ferris and Orgel, 1966) and HCN oligomers (Ferris and Edelson, 1978; Ferris and Hagan, 1984). DAMN will be formed if the concentration of HCN exceeds 0.01 M and the pH is in the 7-10 range (Sanchez *et al.*, 1967). HCN is hydrolyzed to formate faster than it is converted to DAMN if the HCN concentration is lower than 10<sup>-2</sup> M. The effect of inorganic and organic substances on its formation has been investigated (Sanchez *et al.*, 1967).

DAMN formation is accelerated by the presence of formaldehyde (Schwartz and Goverde, 1982).

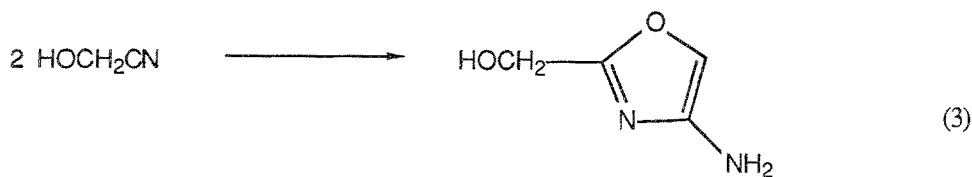
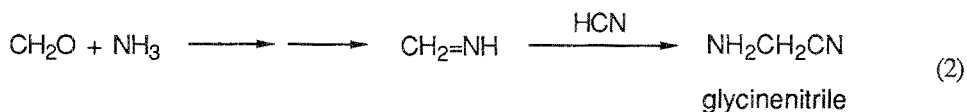


DAMN

### 2.1.3. Glycolonitrile and Other Cyanohydrins

HCN undergoes a facile addition to formaldehyde ( $\text{CH}_2\text{O}$ ) (equation 1) and other aldehydes to form glycolonitrile (Walker, 1964). The reaction proceeds at cyanide concentrations varying between  $10^{-2}$  to  $10^{-4}$  M depending on the reactivity of the aldehyde used. Aminonitriles (e.g., glycine nitrile) are formed if the free  $\text{NH}_3$  concentration is greater than  $10^{-2}$  M (equation 2) (Miller, 1957).

Glycolonitrile dimerizes to 2-hydroxymethyl-5-aminooxazole at  $0^\circ\text{C}$  and pH 8.0 and forms polymers at  $25^\circ$  and pH 8 (equation 3) (Arrhenius, 1990, pers. communication).



2-hydroxymethyl-5-aminooxazole

### 2.1.4. Simple Nitriles, Urea and Guanidine

#### 2.1.4.1. Acetonitrile (CH<sub>3</sub>CN)

CH<sub>3</sub>CN is detected in comets (Donn, 1982), the interstellar medium (Mann and Williams, 1980) and is formed in FTT reactions from CO, NH<sub>3</sub> and H<sub>2</sub> (Hayatsu *et al.*, 1968, 1972), by the photolysis of mixtures of acetylene and NH<sub>3</sub> (Ferris and Ishikawa, 1988) and the photolysis of acetamide (CH<sub>3</sub>CONH<sub>2</sub>) (Spall and Steacie, 1957). No studies suggest that CH<sub>3</sub>CN has a role in prebiotic synthesis so its presence is not indicative of processes leading to the origins of life but it may be formed in hydrothermal systems.

#### 2.1.4.2. Cyanoacetylene (HC≡CCN)

HC≡CCN is formed when an electric discharge is passed through a CH<sub>4</sub>/N<sub>2</sub> mixture (Sanchez *et al.*, 1966). It is present in the interstellar medium (Mann and Williams, 1980) and the atmosphere of Titan (Kunde *et al.*, 1981). HC≡CCN is a starting compound in a prebiotic synthesis of the pyrimidine ring system (Ferris *et al.*, 1968, 1974) and aspartic acid (Ferris *et al.*, 1968). It is readily converted to polymers in thermal and photochemical reactions (Ferris and Guillemin, 1990). Although cyanoacetylene may have had an important role in the origins of life, its high reactivity to nucleophilic addition suggests that it will be rapidly converted to a phosphate or other adducts in hydrothermal systems (Ferris *et al.*, 1970, 1974).

#### 2.1.4.3. Cyanogen (CN)<sub>2</sub>

(CN)<sub>2</sub> is formed from HCN photochemically (Airey and Dainton, 1966; Lohrmann, 1972), thermally (Harada and Fox, 1965), in electric discharges (Schavo and Winkler, 1959) and in FTT syntheses (Hayatsu *et al.*, 1968, 1972). It has been detected in the atmosphere of Titan (Kunde, 1981). It is also a very reactive compound and is not likely to be detected in hydrothermal systems but its formation may be inferred if cyanate

$$\begin{array}{c} \text{O} \\ || \\ (\text{N}=\text{C}=\text{O}^-) \end{array}$$

or urea (H<sub>2</sub>NCNH<sub>2</sub>) are observed (Naumann, 1910; Lohrmann, 1972).

#### 2.1.4.4. Cyanamide (NH<sub>2</sub>CN)

Cyanamide, a product of the photolysis of ammonium cyanide (Lohrmann, 1972) or the electron irradiation of CH<sub>4</sub>, NH<sub>3</sub> and H<sub>2</sub>O (Schimpl *et al.*, 1965), has also been observed in the interstellar medium (Mann and Williams, 1980). It dimerizes to dicyanamide

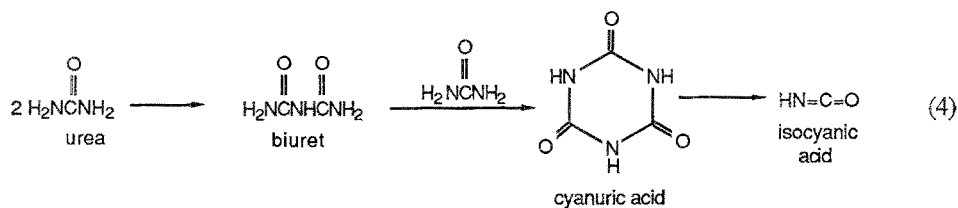


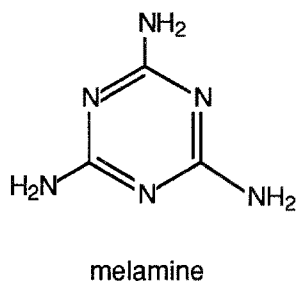
(cyanoguanidine) (  $\text{H}_2\text{NCNHCN}$  ) on heating in the dry state or in solution and is hydrolyzed to urea in aqueous acid and base (Prager *et al.*, 1910). It may have effected the condensation of amino acids to oligopeptides or nucleotides to oligonucleotides on the primitive earth (Ibanez *et al.*, 1971).

#### 2.1.4.5. Urea and Guanidine

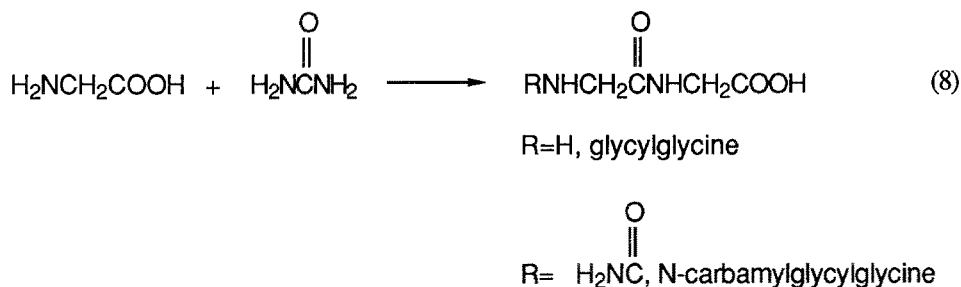
The first laboratory synthesis of a biological compound from simple inorganic materials was accomplished by Wöhler (1828) when he formed urea by heating ammonium cyanate. Urea has been obtained in a number of prebiotic studies using a spark discharge, UV light,  $\beta$ -rays and X-rays as the energy sources. Urea is also formed from HCN, nitriles and cyanamide ( $\text{NH}_2\text{CN}$ ). A recent review of the prebiotic formation of urea is given by Navarro-Gonzalez *et al.* (1989). Guanidine is formed by the thermal (Lowe *et al.*, 1963; Labadie *et al.*, 1968) and photochemical reactions (Lohrmann, 1972) of  $\text{NH}_4\text{CN}$  and by the reaction of cyanamide with  $\text{NH}_3$  (Blair and Braham, 1924).

Gamma irradiation of aqueous urea generates  $\text{CO}_2$ ,  $\text{NH}_3$  and  $\text{H}_2$  as the main products along with smaller amounts of oxalic [ $(\text{CO}_2\text{H})_2$ ] and malonic [ $(\text{CH}_2(\text{CO}_2\text{H})_2)$ ] acids (Navarro-Gonzalez *et al.*, 1989). Thermolysis of urea at temperatures as low as  $120^\circ\text{C}$  gives the triazine, cyanuric acid, via biuret (equation 4) (Smolin and Rapoport, 1959a). The yield increases as the temperature is raised to  $279^\circ\text{C}$  (Smolin and Rapoport, 1959a; Okazaki *et al.*, 1974). Pyrolysis of urea at  $350$ - $600^\circ\text{C}$  yields isocyanic acid, presumably via cyanuric acid (equation 4) (Takahasi and Ozako, 1974). Pyrolysis of urea in the presence of ammonia at  $310^\circ\text{C}$  (equation 5), pyrolysis of guanidine or cyanamide yields melamine (equations 6 and 7) (Smolin and Rapoport, 1959b).





Diglycine and N-carbamylglycylglycine (equation 8) are formed when a mixture of urea and glycine are heated at 105°C in aqueous solution containing a mixture of metal ions believed to have been present in the oceans of the primitive earth. Some of the same products are formed on heating mixtures of urea and formaldehyde under the same reaction conditions (Sakurai and Yanagawa, 1984).



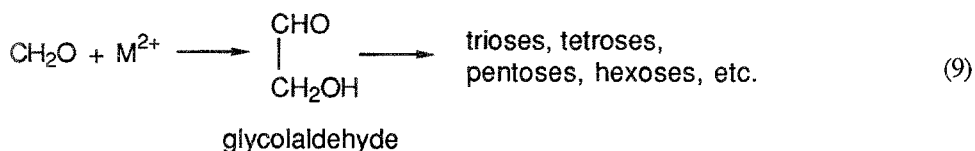
## 2.2. FORMALDEHYDE AND OTHER ALDEHYDES

Formaldehyde ( $\text{CH}_2\text{O}$ ) is a major product resulting from passing an electric discharge through mixtures of gases which simulate primitive atmospheres (Schlesinger and Miller, 1983). The yields of higher aldehydes decrease approximately in the order of their increasing complexity. Helium atom irradiation of mixtures of  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{Fe}^{2+}$  in a cyclotron yields traces of  $\text{CH}_2\text{O}$  and formic acid (Garrison *et al.*, 1951).

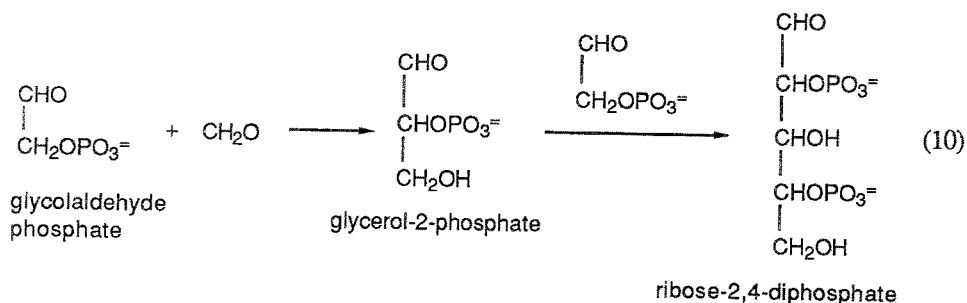
$\text{CH}_2\text{O}$  and higher aldehydes are also formed by the photolysis of  $\text{H}_2\text{O}$  in the presence of  $\text{CH}_4$  (Ferris and Chen, 1975b; Bar-Nun and Chang, 1983), the photolysis of  $\text{CO}-\text{H}_2\text{O}$  mixtures (Park and Getoff, 1988) and the photolysis of methanol (Allamandola *et al.*,

1988). It has been tentatively identified as a product of the photolysis of ferrous carbonate (Joe *et al.*, 1986) and  $\beta$ -irradiation of calcium carbonate (Albarran *et al.*, 1987). Formaldehyde has been detected in the interstellar medium (Mann and Williams, 1980) and the presence of polyoxymethylene, a polymeric form of formaldehyde, on Comet Halley has been inferred, but not proven, from mass spectral data (Huebner, 1987).

Aldehydes are reactive compounds and they may form adducts with other substances in hydrothermal systems. The reaction with HCN to form cyanohydrins (equation 1) and aminonitriles (equation 2) has already been discussed. The self condensation of formaldehyde proceeds in the presence of divalent metal ions to yield glycolaldehyde and eventually a mixture of sugars from trioses to hexoses (equation 9) (Miller and Orgel, 1974). A concentration of 0.01 M  $\text{CH}_2\text{O}$  or greater is required for the detection of sugars when alumina, kaolinite (Gabel and Ponnampuruma, 1967) and carbonate-apatite (Reid and Orgel, 1967) are used as catalysts. A 0.001 M formaldehyde solution apparently yielded only glycolaldehyde and no higher molecular weight compounds (Gabel and Ponnampuruma, 1967).



The complex mixture of sugars formed from formaldehyde condensation reactions was considered to be a major flaw in the proposed prebiotic syntheses of RNA (Reid and Orgel, 1967; Ferris, 1987; Joyce *et al.*, 1987). Recent results from Eschenmoser's group (Müller *et al.*, 1990) have demonstrated that a very limited array of sugars, with ribose as the major product, are obtained in the condensation reaction of glycolaldehyde phosphate and formaldehyde in strongly alkaline solution (equation 10).



### 2.3. FORMIC, ACETIC AND OTHER CARBOXYLIC ACIDS

There are a host of different ways carboxylic acids may have accumulated on the primitive Earth. They have been reported to be the products of passing an electric discharge through CH<sub>4</sub> and H<sub>2</sub>O (Yuen *et al.*, 1981; Allen and Ponnampereuma, 1967), photolysis of CH<sub>4</sub>-H<sub>2</sub>O mixtures (Ferris and Chen, 1975b) and photolysis of CO, H<sub>2</sub>O, NH<sub>3</sub> under conditions which simulate reactions on grains in the interstellar medium (Agarwal *et al.*, 1985). Carboxylic acids and hydrocarbons are formed in the FTT reaction of CO and D<sub>2</sub> over a catalyst of meteoritic iron with either carbonaceous chondrite or ferric oxide and potassium carbonate as a promoter at 300-450°C (Nooner *et al.*, 1976; Leach *et al.*, 1978). Fatty acids of carbon number 6-18 were detected with a maximum yield at C<sub>9</sub> to C<sub>10</sub>. There was no preference for odd versus an even number of carbon atoms but the linear fatty acids predominated over the branched-chain fatty acids by factors ranging between 1.7-5.0. Autoradiolysis of <sup>14</sup>C-CaCO<sub>3</sub> (-β) yields formic (HCO<sub>2</sub>H), oxalic, glyoxylic (HO<sub>2</sub>CCHO), acetic and glycolic acids (HO<sub>2</sub>CCH<sub>2</sub>OH) (Albarran *et al.*, 1987). The identity of the acids requires confirmation by mass spectrometry or related techniques. Gamma irradiation of aqueous urea yields oxalic and malonic acids (Navarro-Gonzalez *et al.*, 1989) and oxalic acid is formed in processes leading to HCN oligomers from HCN (Ferris *et al.*, 1978). The corresponding acids are formed by hydrolysis of amides and nitriles; for example, HCN is hydrolyzed to formic acid at neutral pH (Sanchez *et al.*, 1967). Aliphatic, carboxylic acids (C<sub>1</sub>-C<sub>8</sub>); hydroxy acids (C<sub>1</sub>-C<sub>5</sub>) and dicarboxylic acids (C<sub>2</sub>-C<sub>9</sub>) were detected in the Murchison meteorite (Cronin *et al.*, 1988) and formic acid has been detected in the interstellar medium (Mann and Williams, 1980).

Pyrolysis of acids at 250-550°C in the absence of water and the presence of ThO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, MnO, or mordenite (a clay), generates ketones (Fuki *et al.*, 1974; Cornejo *et al.*, 1979; Sosnina, 1977). Heating formic acid at 282-415°C in the presence of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and other inorganics results in the formation of CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O (Schwab and Schwab-Agallidis, 1949). This decomposition proceeds on other mineral surfaces at temperatures as low as 150°C-200°C (Hinshelwood and Topley, 1923). Gamma irradiation of acetic acid (CH<sub>3</sub>CO<sub>2</sub>H) yields a mixture of dicarboxylic and tricarboxylic acids (Negrón-Mendoza and Ponnampereuma, 1982). The main photochemical reaction of carboxylic acids is the formation of alkane and CO<sub>2</sub> (equation 11) (Wilkerson and Guillory, 1977; Ferris and Joshi, 1979).



### 2.4. AMINO ACIDS AND AMINONITRILES

A voluminous literature developed on the prebiotic synthesis of amino acids in the wake of Miller's (1953) pioneering study. Amino acids are formed by the action of electric dis-



charges on almost any gaseous mixture of carbon, hydrogen and oxygen compounds so long as it is more reduced than  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{H}_2\text{O}$  (Schlesinger and Miller, 1983). Aminonitriles appear to be intermediates in the formation of some of the amino acids (Ponnampertuma and Woeller, 1967). Amino acids are produced when mixtures of simple carbon, nitrogen and oxygen compounds are subjected to shock heating (Bar-Nun *et al.*, 1970), ultraviolet radiation, ionizing radiation, high temperatures (Yanagawa *et al.*, 1984a; Harada and Fox, 1964; Lawless and Boynton, 1973; Lemmon, 1970) or proton irradiation (Kobayashi *et al.*, 1990). Glycine has been detected as a product of the photolysis of  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  at 10 K in a reaction designed to simulate synthesis in the interstellar medium (Briggs *et al.*, 1991). The self condensation of HCN in aqueous solution yields oligomeric products which release amino acids upon hydrolysis with 1 N HCl or at pH 8.5 (Oró and Kamat, 1961; Lowe *et al.*, 1963; Ferris *et al.*, 1978). These oligomers are not polypeptides since the amino acids formed constitute a small percent of the starting oligomers (Ferris *et al.*, 1978). Amino acids are also formed by the pyrolysis of formamide (Harada, 1967) and in reaction sequences starting from the sugars glucose or erythrose or from malic acid (Shen *et al.*, 1987, 1990). Amino acids are produced in small amounts in FTT reactions of  $\text{CO}$ ,  $\text{D}_2$  and  $\text{ND}_3$  over meteoritic iron or iron oxide or montmorillonite and alumina at 200-1000°C (Yoshino *et al.*, 1971; Hayatsu *et al.*, 1971). Tyrosine and histidine were detected as reaction products in addition to many of the same protein amino acids found in the electric discharge studies. Tentative identification of some non-protein amino acids was noted but no GC/MS confirmation was reported. Small amounts of amino acids have been detected in the Murchison and other meteorites. Seventy-four amino acids extracted from the Murchison meteorite have been conclusively identified (Cronin *et al.*, 1988). So far, amino acids have not been identified in the interstellar medium, however, the formation of glycine in simulation studies is suggestive of their presence (Briggs *et al.*, 1991).

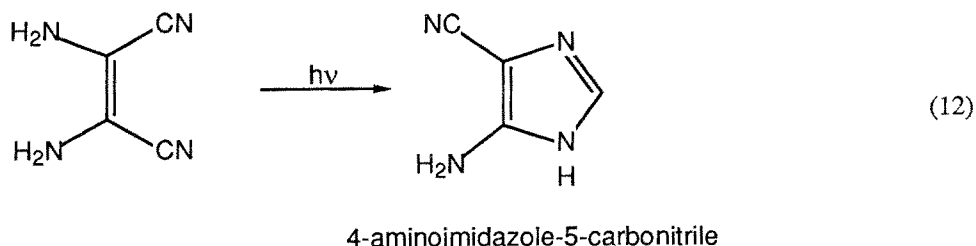
Pyrolysis of aminonitriles at 240°-300°C in the absence of water gives HCN and the corresponding imine (Guillemin and Denis, 1985, 1988). Pyrolysis of amino acid mixtures at 160°-200°C for 4-6 h gives UV absorbing compounds, some of which have been identified as pteridines (Heinz *et al.*, 1979). Diketopiperazine formation and decarboxylation was observed on heating amino acids in the presence of silica (Basiuk *et al.*, 1991). When glycine is heated with a mixture of  $\text{MnCO}_3 \cdot \text{Mn}(\text{OH})_2$  and  $\text{Al}_2\text{O}_3$  at 240°C under nitrogen and the product is hydrolyzed with 6 N HCl, ten protein and non-protein amino acids were separated and identified by nuclear magnetic resonance (Ivanov and Slavcheva, 1977). When glycine and alanine were heated between 310°-340°C HCN is formed. None was detected when leucine, phenylalanine and tyrosine were heated in this temperature range (Heyns and Pavel, 1957). Pyrolysis of sixteen amino acids at 700-1000°C (Johnson and Kang, 1971) or heating nitrogen-containing materials such as nylon at temperatures greater than 600°C generates HCN (Morikawa, 1978).

## 2.5 PURINES, PYRIMIDINES AND OTHER HETEROCYCLIC COMPOUNDS

The synthesis of adenine\* by the electron bombardment of a mixture of  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2$  was reported by Ponnampereuma *et al.* (1963). The formation of purine and pyrimidine bases by passage of an electric discharge through  $\text{CH}_4$ ,  $\text{N}_2$  and  $\text{H}_2\text{O}$  was reported in a meeting abstract (Kobayashi *et al.*, 1986) but the experimental details have not appeared in a refereed journal. Proton irradiation of a mixture of  $\text{CO}$ ,  $\text{N}_2$  and  $\text{H}_2\text{O}$  yields imidazole along with amino acids (Kobayashi *et al.*, 1990). The FTT reaction of  $\text{CO}$ ,  $\text{D}_2$  and  $\text{ND}_3$  at about  $500^\circ\text{C}$ , in the presence of a mixture of powdered iron meteorite and alumina or ferric hydroxide and alumina, yields an array of biologically important heterocycles including adenine, guanine, xanthine, thymine and uracil (Hayatsu *et al.*, 1972, 1968). In addition, the formation of dimethyluracil, the triazine melamine, pyridine, pteridines and pyrroles was also observed. The formation of the triazines ammeline and cyanuric acid was suggested by chromatography but it was not possible to confirm these findings by mass spectrometry.

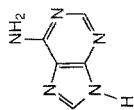
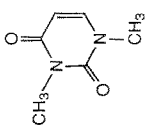
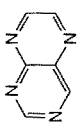
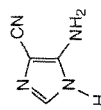
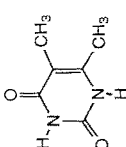

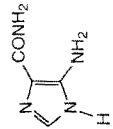
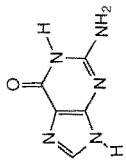

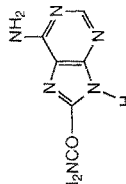
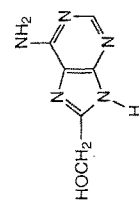
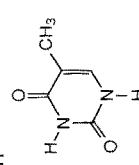
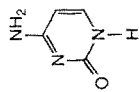
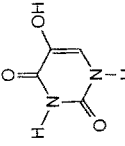
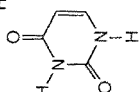
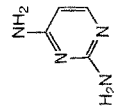
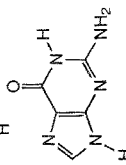
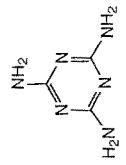
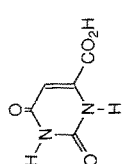
Adenine and substituted imidazoles are formed by the self condensation of mildly alkaline solutions of 0.1-15 M  $\text{NH}_4\text{CN}$  (Oró and Kimball, 1961, 1962). No free adenine was detected in the condensation of 0.1 M  $\text{HCN}$  but it was released on hydrolysis of the oligomeric reaction products (Ferris *et al.*, 1978; Ferris and Hagan, 1984). It has been suggested that the 8-cyano or 8-carbamyl derivative of adenine is formed first and this undergoes hydrolysis and decarboxylation to adenine (Voet and Schwartz, 1983; Schwartz *et al.*, 1984). The formation of 8-hydroxymethyladenine is observed if the condensation of  $\text{HCN}$  is performed in the presence of formaldehyde (Schwartz and Bakker, 1989). The pyrimidines 4,5-dihydroxypyrimidine, 5-hydroxyuracil, orotic acid (Ferris *et al.*, 1978) and uracil (Voet and Schwartz, 1982) are also formed on hydrolysis of products of the self-condensation of  $\text{HCN}$ .

Diaminomaleonitrile is a readily detectable intermediate in the self condensation of  $\text{HCN}$  (Section 1.2). It undergoes a facile photochemical rearrangement to 4-aminoimidazole-5-carbonitrile (equation 12) (Ferris and Orgel, 1966), a compound which reacts with  $\text{HCN}$  or simple derivatives of  $\text{HCN}$  to yield adenine, guanine, diaminopurine and hypoxanthine (Sanchez *et al.*, 1968).

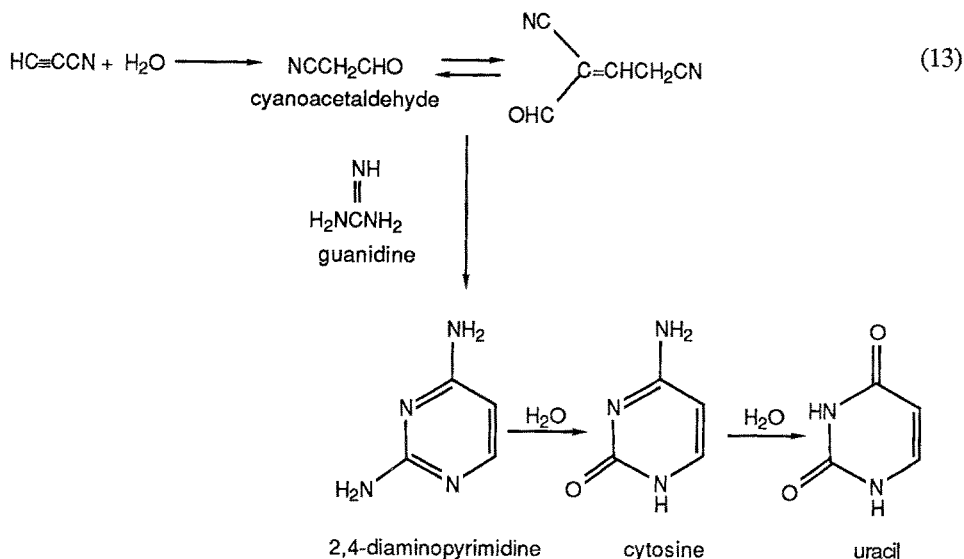


\*The structures of the heterocyclic compounds discussed in this section are given in Table 1.

TABLE I  
Potential prebiotic heterocyclic compounds

		
Adenine	1,3-Dimethyluracil	Pteridine
		
4-Aminoimidazole-5-carbonitrile	5,6-Dimethyluracil	Pyridine
		
4-Aminoimidazole-5-carboxamide	Guanine	Pyrrole
		
8-Carbamyladenine	8-Hydroxymethyladenine	Thymine
		
Cytosine	5-Hydroxyuracil	Uracil
		
2,4-Diaminopyrimidine	Hypoxanthine	Melamine
		
		Orotic Acid

The pyrimidine ring system has also been formed from cyanoacetylene (Section 1.4.2). Reaction of cyanoacetylene with cyanate ( $\text{N}=\text{C}=\text{O}$ ) yields cytosine, a compound which is hydrolyzed to uracil (Ferris *et al.*, 1968). Alternatively, the hydrolysis of cyanoacetylene yields cyanoacetaldehyde which reacts with guanidine to yield diaminopyrimidine which, in turn, is hydrolyzed to cytosine and uracil (equation 13) (Ferris *et al.*, 1974b).



Adenine, guanine, xanthine, hypoxanthine and uracil are found in small amounts in the Orgueil, Murray and Murchison meteorites (Hayatsu *et al.*, 1975; Van der Velden and Schwartz, 1977; Stoks and Schwartz, 1979, 1981; Cronin *et al.*, 1988).

## 2.6. SULFUR COMPOUNDS

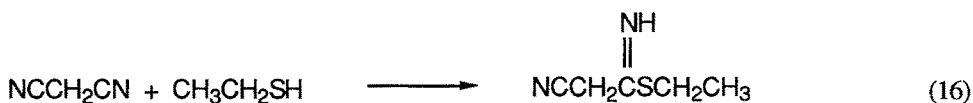
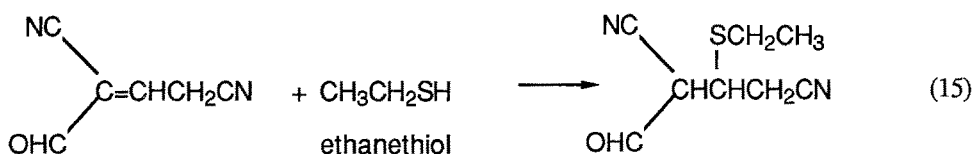
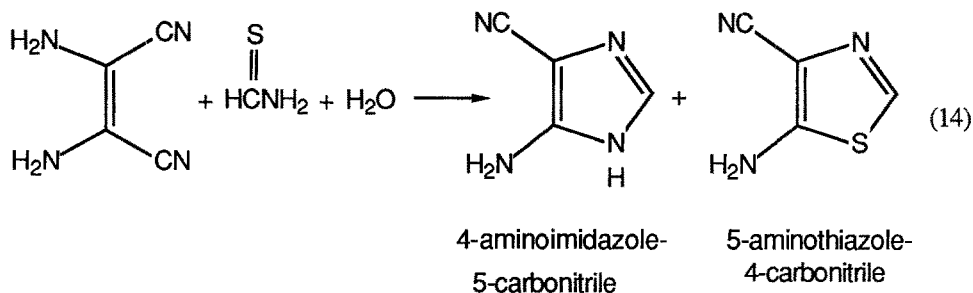
The presence of an abundance of inorganic sulfides suggests that organic sulfur compounds may have had a central role in the organic chemistry in hydrothermal systems (Shock, Chapter 5). The observation of heterocyclic sulfur compounds in contemporary hydrothermal systems has been discussed by Simoneit in Chapter 4. There have been very few studies on the formation of biomolecules containing sulfur under prebiotic conditions (for a review see Raulin and Toupance, 1977; see Table 2 for the structures of the compounds discussed in this section). When a Miller electric discharge experiment is performed in the presence of  $\text{H}_2\text{S}$ , methionine is observed as a reaction product (van Trump and Miller, 1972). Cysteic acid, taurine and cystamine were detected when  $\text{CH}_4$ ,  $\text{NH}_4\text{OH}$

and  $\text{H}_2\text{S}$  were irradiated with electrons. It was reported that cysteine and cystine were formed but were oxidized to cysteic acid (Choughley and Lemmon, 1966). Photolysis of mixtures of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}$  yields cysteine and cystine (Sagan and Khare, 1971; Becker *et al.*, 1974). Thus it appears likely that thiols and sulfur containing amino acids were available on the primitive earth and possibly in hydrothermal systems.

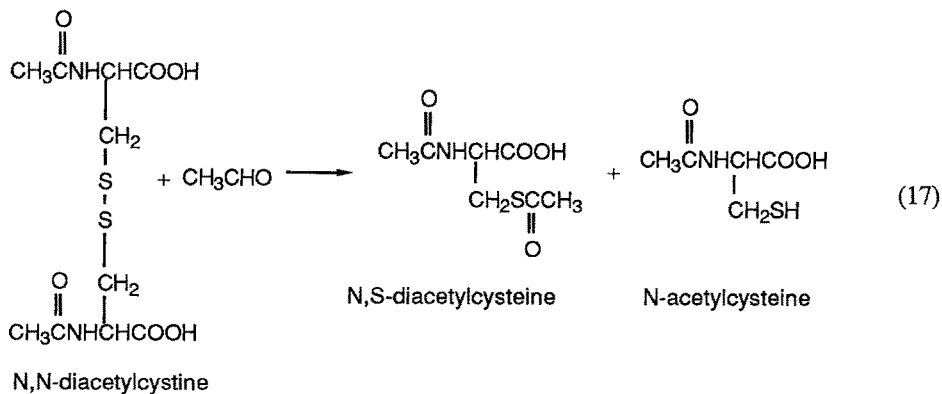
TABLE 2  
Sulfur containing amines and amino acids

$\begin{array}{c} \text{CH}_3\text{SCH}_2\text{CH}_2\text{CHCOOH} \\   \\ \text{NH}_2 \end{array}$ <p>methionine</p>	$\begin{array}{c} \text{HSCH}_2\text{CHCOOH} \\   \\ \text{NH}_2 \end{array}$ <p>cysteine</p>
$\begin{array}{c} \text{HOOCCHCH}_2\text{SSCH}_2\text{CHCOOH} \\   \qquad   \\ \text{NH}_2 \qquad \text{NH}_2 \end{array}$ <p>cystine</p>	$\begin{array}{c} \text{HO}_3\text{SCH}_2\text{CHCOOH} \\   \\ \text{NH}_2 \end{array}$ <p>cysteic acid</p>
$\text{HO}_3\text{SCH}_2\text{CH}_2\text{NH}_2$ <p>taurine</p>	$\text{H}_2\text{NCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{NH}_2$ <p>cystamine</p>

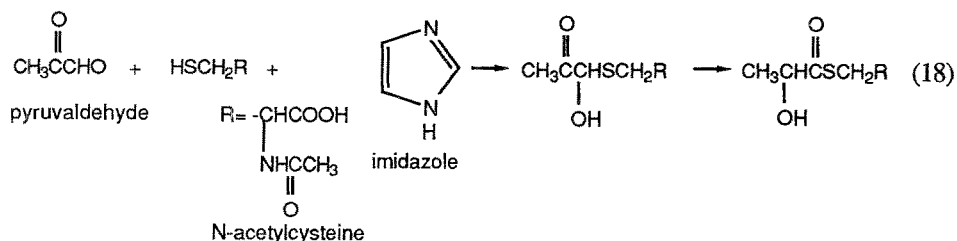
The possible role of hydrogen sulfide, thiols and thioamides on prebiotic reactions in aqueous solution has been studied only briefly.  $\text{HS}^-$  inhibits the tetramerization of HCN to DAMN (Section II.A.2) (Sanchez *et al.*, 1967). The reaction of DAMN with thioformamide yields 4-aminoimidazole-5-carboxamide and 5-aminothiazole-4-nitrile (equation 14) (Sanchez *et al.*, 1967). The addition of ethanethiol to activated double bonds and nitriles has also been observed (Raulin and Toupençe, 1977) (equations 15, 16). Presumably  $\text{H}_2\text{S}$  will undergo similar addition reactions in hydrothermal systems.



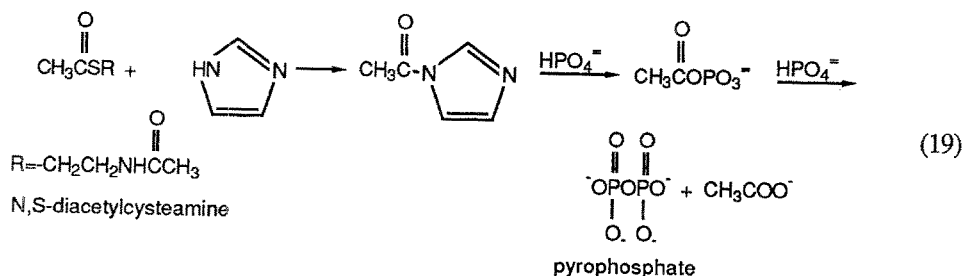
The central role of thioesters in contemporary biochemistry prompted a series of studies of the possible role of these compounds in prebiotic processes by A. L. Weber. He observed the photochemical formation of the thioester N,S-diacetylcysteine starting from the corresponding disulfide (equations 17) (Weber, 1981a).



The direct formation of a thioester in a thermal reaction from a ketoaldehyde and N-acetylcysteine has also been observed (equation 18) (Weber, 1982a). Ketoaldehydes may have been formed from sugars on the primitive earth.



The pyrophosphate bond, which provides the energy to drive many chemical reactions in contemporary biochemical systems, can be formed from the reaction between phosphate and thioesters (Weber, 1981b). Reaction of the thioester N,S-diacetylcysteamine with phosphate in the presence of imidazole yields pyrophosphate (equation 19). The insoluble phosphate mineral, hydroxyapatite, can be substituted for soluble phosphate in this reaction (Weber, 1982b). Thus, such a reaction of thioesters may generate pyrophosphate in hydrothermal systems.



### 3. Organic Chemistry in Near- to Supercritical Water

A key point of dispute in the discussion of the role of hydrothermal systems in the origins of life is whether biological molecules survived the high temperatures present there. Miller and Bada (1988) assert that "...the high temperature in vents would not allow synthesis of organic compounds, but would decompose them, unless the exposure time at vent temperatures was short." On the other hand, Shock (1990) reached the conclusion

that amino acids attain a metastable equilibrium at high temperatures based on his analysis of the experimental data of Miller and Bada (1988). Furthermore, the properties of supercritical water may favor the formation of complex molecules in hydrothermal systems (Simoneit, Chapter 4). Some insight into the possible prebiotic chemistry in hydrothermal systems can be obtained by inspection of organic chemical reactions investigated in supercritical water (Shaw *et al.*, 1991). It should be noted that the purpose of the studies discussed below was to investigate organic reactions in supercritical water and not to simulate the conditions in hydrothermal systems.

### 3.1. PROPERTIES OF SUPERCRITICAL WATER

Water is considered to be supercritical if its temperature is above the critical temperature (374°C) and its pressure is above the critical pressure (3200 psia or 22.1 MPa) (Note - 1 psia = 14.7 psi, 2 psia = 15.7 psi). The physical properties of water vary dramatically near the critical pressure and temperature. The variation in the dielectric constant and dissociation constant with the density of water (pressure) at 390°C is shown in Table 3 (Penninger and Kolmschate, 1989).

TABLE 3  
Some Physical Properties of Water<sup>a</sup>

Density gm/cm <sup>3</sup>	Temperature (°C)	$\epsilon$	$K_w$
0.997 <sup>b</sup>	25	78.5 <sup>b</sup>	$1 \times 10^{-14}$ <sup>b</sup>
0.25	390	3.59	$8.91 \times 10^{-18}$
0.35	390	5.89	$9.91 \times 10^{-16}$
0.45	390	8.20	$3.34 \times 10^{-14}$
-	350 <sup>c</sup>	-	$1 \times 10^{-11.8}$

<sup>a</sup>Adapted from Penninger and Kolmschate, (1989)

<sup>b</sup>At 25°C and 1 psia (Weast, 1964)

<sup>c</sup>Marshall and Franck (1981)

At the critical temperature and pressures lower than the critical pressure, water has the properties of steam where it has a low dissociation constant ( $K_w$ ) and dielectric constant ( $\epsilon$ ). At pressures above the critical pressure it behaves like liquid water except its dielectric constant and viscosity is much lower because there is less hydrogen bonding between the water molecules (Table 1). The dissociation constant of the water decreases as the density decreases (Table 3).



## 3.2. REACTIONS IN NEAR- TO SUPERCRITICAL WATER

At water densities greater than  $0.4 \text{ g cm}^{-3}$  the dielectric constant of water is sufficiently high so that reactions which proceed by ionic or polar transition states are observed. When the density of water is  $0.2 \text{ g cm}^{-3}$  or less it no longer stabilizes charged species by solvation so free radical reactions are favored over ionic processes. The solubility of organics is greatly enhanced and of inorganics suppressed in supercritical water as compared with ordinary water (Connolly, 1966; Josephson, 1982). It has been suggested that the solvent properties of water at  $300^\circ\text{C}$  resemble those of acetone (Siskin and Katritzky, 1991).

The different pathways for the reaction of organics in supercritical water are apparent in the data shown in Table 4. For example,  $\text{PhCH}_2\text{OH}$  is obtained by hydrolysis of the ether grouping in  $(\text{PhCH}_2)_2\text{O}$  when the density is greater than 0.4, while  $\text{PhCHO}$  and  $\text{PhH}$  are products of the free radical decomposition when the density is less than 0.4. In general, the greater the liquid-like properties of the water, the more predominant are the hydrolytic reactions.

The ether and amine functional groups in the first seven compounds listed in Table 4 are significantly more stable to hydrolysis than that of the peptide bond linking proteins (equation 20) or the phosphodiester bond linking nucleotides (equation 21). It can be inferred from these data that the reactive functional (e.g., peptides and nucleotide bonds) groups in biomolecules may undergo rapid thermolysis and hydrolysis (equations 20, 21) in hydrothermal systems. This appears to be confirmed by the facile decomposition of benzyl nitrile to benzene and 1,3-butanediol and glycerol to olefins and aldehydes (Table 4). Since nitriles are important products of prebiotic syntheses, it is likely that they would undergo rapid decomposition in supercritical water. The rapid reaction of 1,3-butanediol and glycerol suggests that the alcohol groups in sugars and nucleotides would also decompose rapidly.

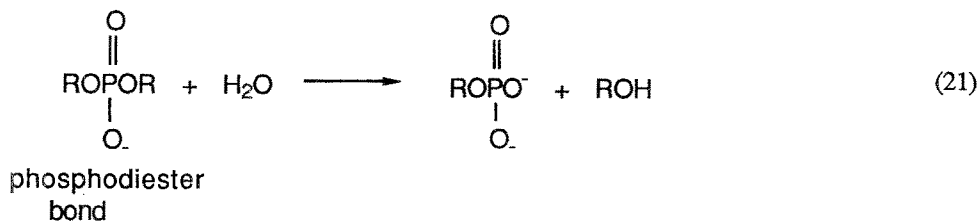
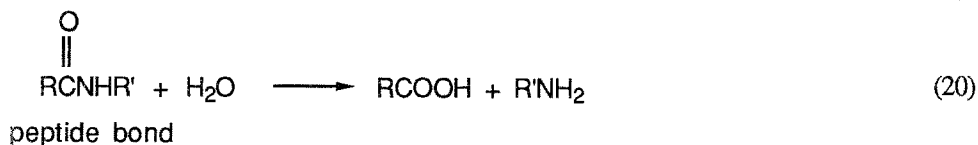
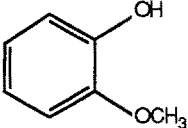
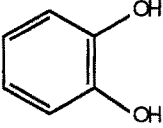
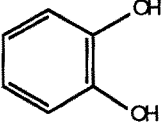
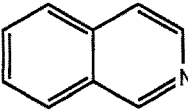


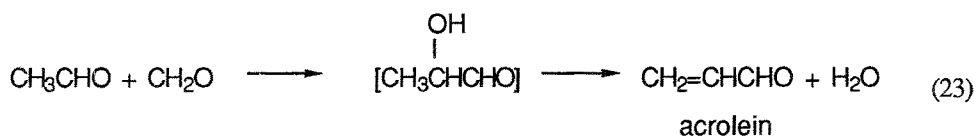
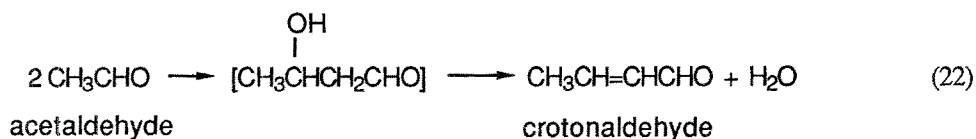
TABLE 4  
Some Representative Organic Reactions in Supercritical Water

Reactant	Major Products		Reference
PhCH <sub>2</sub> OCH <sub>2</sub> Ph	$\rho > 0.4$ PhCH <sub>2</sub> OH	$\rho < 0.4$ PhH, PhCHO	a
(PhCH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub>	NR	PhCH <sub>3</sub> , PhCH=CH <sub>2</sub>	a
	 CH <sub>3</sub> CH	 CH <sub>4</sub> , Char	
PhNHCH <sub>2</sub> Ph	PhNH <sub>2</sub> , PhCH <sub>2</sub> OH	PhNH <sub>2</sub> , PhCH <sub>3</sub>	a
	nd	PhCH <sub>3</sub> , PhCH <sub>2</sub> CH <sub>3</sub>	b
PhNH <sub>2</sub>	nd	PhOH, NH <sub>3</sub>	b
PhCH <sub>2</sub> NH <sub>2</sub>	PhCH <sub>3</sub> , Ph <sub>2</sub> CH=CHPh, (PhCH <sub>2</sub> ) <sub>2</sub>	PhCH <sub>3</sub> , PhCHO, NH <sub>3</sub>	c
PhCN	nd	PhH	b
HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>2</sub> O, CH <sub>3</sub> CHO, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> COCH <sub>3</sub> , polymers	CH <sub>2</sub> O, CH <sub>2</sub> =CHCH <sub>3</sub>	d
$\begin{matrix} \text{OH} \\ \text{HOCH}_2\text{CHCH}_2\text{OH} + \\ \text{H}^+ (0.005 \text{ M}) \end{matrix}$	CH <sub>2</sub> =CHCHO + CH <sub>3</sub> CHO	CH <sub>2</sub> =CHCHO	e

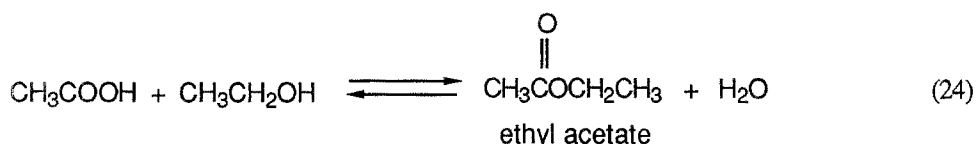
nd = Not determined

<sup>a</sup>Townsend *et al.*, 1988<sup>b</sup>Houser *et al.*, 1986<sup>c</sup>Houser *et al.*, 1989<sup>d</sup>West and Gray, 1987<sup>e</sup>Ramayya *et al.*, 1987

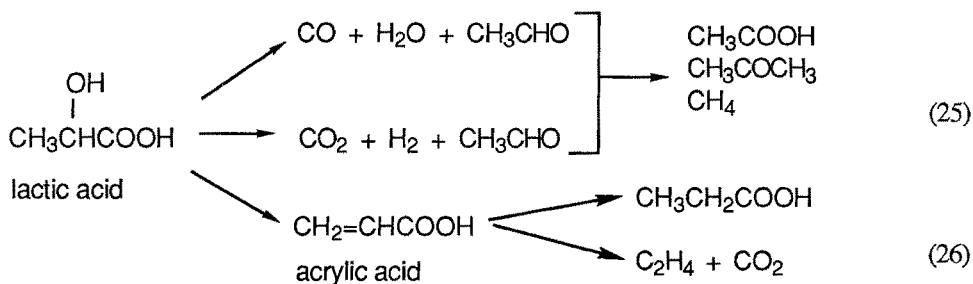
Synthetic processes have been reported in reactions performed in supercritical water which give some hope for the formation of more complex molecules under these conditions. The aldol condensation of 0.5 M acetaldehyde was observed at 385°C in a flow reactor to give a 37% yield of crotonaldehyde (Ramayya *et al.*, 1987) (equation 22). A mixture of acetaldehyde and formaldehyde generates acrolein and crotonaldehyde under the same reaction conditions (equation 23). These studies and other examples listed in Table 1 show that polyhydroxy alcohols are converted to aldehydes and ketones in supercritical water. The aldehydes and ketones may condense with themselves and with HCN and NH<sub>3</sub> to give aminonitriles which hydrolyze to amino acids.



The second synthetic example is the partial conversion of mixture of 1 M ethanol with 1 M acetic acid to ethyl acetate in a flow reactor where the residence time was less than 1 minute. About half of the ethanol that reacted was converted to ethyl acetate and most of the remainder was converted to ethylene and ethane (Antal *et al.*, 1987). The efficient formation of ethyl acetate in water, a reaction that requires anhydrous conditions and a strong acid catalyst at normal temperatures and pressures is significant (equation 24). This finding suggests that related condensations to form peptide or phosphodiester bonds from the corresponding monomers may occur in supercritical water. It should be emphasized that 1 M concentrations of reactants were used - higher concentrations than would be expected to occur under most prebiotic conditions. Also, the product ethyl acetate has much fewer reactive groups than do polypeptides or polynucleotides so its rate of decomposition in supercritical water may be appreciably slower than would the more complex biomolecules.



The decomposition of lactic acid to an array of other products is an example of the variety of reaction pathways available to a simple multifunctional molecule in supercritical water (Mok *et al.*, 1989). Decomposition to acetaldehyde followed by the further reaction of the acetaldehyde is shown in equation 25. Elimination of water to form acrylic acid followed by its hydrogenation or decarboxylation is shown in equation 26.



#### 4. Fischer-Tropsch Type Reactions (FTT) in Hydrothermal Systems

The reaction conditions in hydrothermal systems precludes the occurrence of many processes discussed in Section 1. For example, it is clear that reactions driven by photons or electric discharges will not be observed. Heat and ionizing radiation were probably the main energy sources driving chemical processes in hydrothermal systems on the primitive Earth. The prebiotic chemistry associated with ionizing radiation has been discussed in Section 2 and these chemical processes should not differ appreciably in hydrothermal systems. The thermally driven FTT reactions merit further discussion because the reaction conditions in hydrothermal systems are different from those described in Section 2 which were designed to simulate chemical events in the solar nebula.

It is possible to prepare amino acids, heterocyclic compounds, and hydrocarbons and fatty acids with limited chain branching by the FTT reaction of  $\text{H}_2$ ,  $\text{CO}$  and  $\text{NH}_3$  (Hayatsu and Anders, 1981). FTT reactions are unique in providing a source of linear fatty acids essential for the formation of the bilayer membranes present in cell walls. It has not been possible to propose a prebiotic synthesis of linear fatty acids because there was no known place on the primitive Earth where both high temperatures and pressures required for FTT processes were present. The requisite conditions are found in hydrothermal systems.

The standard FTT reactions are usually performed using iron, nickel, cobalt and ruthenium catalysts under anhydrous reaction conditions (Anderson, 1958; Falbe, 1980). Platinum metals, Ir, Pd, Pt, Rh and Os, exhibit lower catalytic ability (Falbe, 1980). Basic compounds such as  $\text{K}_2\text{CO}_3$  and alumina promote some FTT reactions while  $\text{H}_2\text{S}$  and possibly  $\text{H}_2\text{O}$  serve as inhibitors (Asinger, 1968; Storch *et al.*, 1951; Anderson, 1956; Falbe, 1980). Commercial FTT reactions has been optimized for the synthesis of hydrocarbons from  $\text{CO}$  and  $\text{H}_2$ . Anders and coworkers (Hayatsu and Anders, 1981) extended the FTT reaction to biomolecules by adding  $\text{NH}_3$  to the mixture of gaseous reactants so that nitrogen-containing molecules are produced. Fatty acids are also formed in FTT reactions run under the conditions established by Anders and coworkers but without  $\text{NH}_3$  as a reactant (Nooner and Or6, 1979).

The FTT reaction may proceed in hydrothermal systems because the reactants are heated at high temperature and pressure in the presence of minerals. The CO needed may come from degradation of formic acid or its derivatives, formaldehyde (Section 2) or from equilibration processes in magma (Lilley *et al.*, 1982). The H<sub>2</sub> is formed from redox reactions of metals with water and the NH<sub>3</sub> is from the decomposition of nitrogenous organics or by the hydrogenation of nitrogen. Metallic iron, the standard catalyst for FTT reactions, has not been detected in contemporary hydrothermal systems, but it may have been present in such systems on the primitive earth. In addition, a variety of other metals and minerals can also serve as catalysts.

Miller and Bada (1988) concluded that the FTT reaction was not responsible for the synthesis of organic compounds in hydrothermal systems because the process is inhibited by H<sub>2</sub>S and H<sub>2</sub>O. It is proposed that hydrogen sulfide is an inhibitor because sulfide is chemisorbed to the surface iron atoms responsible for catalysis. The only way to regenerate the catalyst is to dissolve it in HNO<sub>3</sub> and then reprecipitate the metal. The inhibition of iron catalysis by H<sub>2</sub>S is permanent, i.e., it cannot be reversed by hydrogen or other FTT reactants (Anderson, 1956). The extent of H<sub>2</sub>S poisoning depends on the ratio of H<sub>2</sub>S to catalytic sites on the metal. The catalyst will continue to function until most of the catalytic sites have H<sub>2</sub>S bound to them. In hydrothermal systems fresh metallic and mineral surfaces are constantly generated deep in the oceanic crust or where fluid mixing occurs (Siskin and Katritzky, 1991). Therefore, it is possible that FTT reactions took place in the hydrothermal systems of the primitive Earth.

There are no data on the role of H<sub>2</sub>O as an inhibitor in FTT reactions but it is known to be a reversible inhibitor of the related reduction of nitrogen to ammonia on iron catalysts (Storch, 1951; Anderson, 1956). The reduction of nitrogen is also reversibly inhibited by CO, CO<sub>2</sub>, O<sub>2</sub> and SO<sub>2</sub> and is permanently inhibited by H<sub>2</sub>S. The observed inhibition by H<sub>2</sub>S and CO suggests that the catalysis of nitrogen reduction is comparable to that of CO reduction and oligomerization. If this is correct then it is likely that H<sub>2</sub>O is a reversible inhibitor of FTT reactions. What is not clear is whether supercritical water binds to the catalyst strongly enough to inhibit the binding and subsequent conversion of N<sub>2</sub> to NH<sub>3</sub> and CO to hydrocarbons and nitrogen-containing molecules. The reversible nature of water inhibition suggests the temperature may be sufficiently high in the hotter regions of these systems so that water may not bind to the catalyst and block the sites required for CO reduction.

It is of particular interest that the FTT reaction apparently does not require a metal catalyst but can also proceed on mineral surfaces. There are several reports of efficient syntheses proceeding on silica (Asinger, 1968), montmorillonite and montmorillonite-alumina mixtures (Yoshima *et al.*, 1971; Anders *et al.*, 1974). The montmorillonite used in the study by Yoshima *et al.* (1971) contains at most 2% Fe (Kerr *et al.*, 1951). It seems unlikely that this small amount of iron would be released from the octahedral layer of the montmorillonite so that it could serve as a catalyst. Clay minerals and silica are abundant in hydrothermal systems and may provide sites for FTT reactions. The mecha-

nisms of the silica- and clay-catalyzed reactions are not known so it is possible that the extent of inhibition by  $H_2S$  and  $H_2O$  is quite different from that observed with metallic iron.

In addition, molybdenum sulfide (Storch, 1951), nickel sulfide and tungsten sulfide (Asinger, 1968) have also been shown to be FTT catalysts. This is an especially surprising result since the inhibitory action of  $H_2S$  is believed to be due to formation of sulfide derivatives of metal atoms at active sites on the catalyst. Since metal sulfides are formed in great quantities in hydrothermal systems, it is possible that some of these sulfides are FTT catalysts and their formation does not inhibit but rather enhances the prospects for FTT synthesis.

## 5. Selected Chemical Processes in Hydrothermal Systems of Potential Importance to the Origins of Life

### 5.1. ASSUMPTIONS

It is assumed that synthetic processes driven by heating in the 100-390°C temperature range and reactions resulting from ionizing radiation were the most likely ones occurring in hydrothermal systems (Section 4). It is difficult to predict the extent of thermal degradation and hydrolysis since there have been only a limited number of experimental studies performed under controlled hydrothermal reaction conditions (Section 3). Consequently, the assumption will be made that only modification of the more reactive functional groups will occur such as hydrolysis of nitrile or amide groups to acids. A related assumption is that the synthetic processes will be rapidly quenched in hydrothermal systems before the reaction products undergo major degradation reactions such as breaking carbon-carbon bonds.

### 5.2. AMINO ACIDS AND PEPTIDES

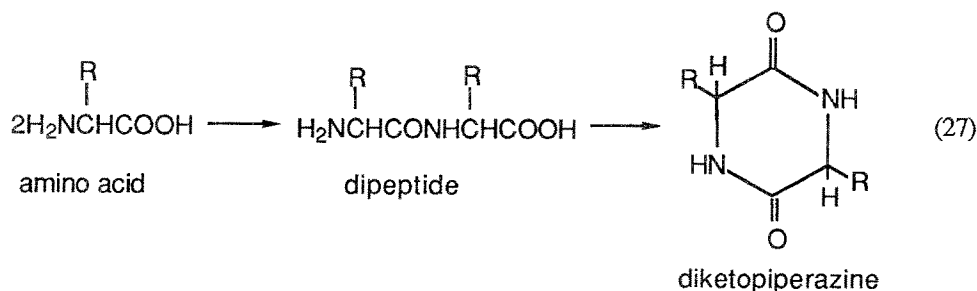
Amino acids are formed readily in thermal prebiotic simulation experiments (Ferris *et al.*, 1978; Yanagawa *et al.*, 1984a; Hayatsu *et al.*, 1971; Harada, 1967; Harada and Fox, 1964; Lawless and Boynton, 1973). Glycine, alanine and aspartic acids are among the more abundant amino acid products while smaller amounts of glutamic acid, threonine, serine, valine, leucine, histidine, phenylalanine and tyrosine were also produced in these studies. Glycine, alanine and aspartic acid are also the main amino acids formed by irradiation of a mixture of  $CO$ ,  $N_2$  and  $H_2O$  with protons (Kobayashi *et al.*, 1990). An array of amino acids which is not usually found in biological systems is also produced in the studies cited above. These include  $\beta$ -alanine,  $\alpha$ -amino-n-butyric acid,  $\beta$ -amino-n-butyric acid,  $\alpha$ -aminoisobutyric acid, N-methyl- $\beta$ -alanine and diaminosuccinic acid.

There have been few studies of the reactions of amino acids under hydrothermal conditions. In an investigation of amino acid stability a mixture of aspartic acid, serine, ala-

nine and leucine was heated at 250°C and 265 atm. It was observed that aspartic acid and serine decomposed within 1-2 h, alanine increased and then decreased in concentration, leucine decomposed after 5 h and glycine increased to a low steady state concentration (Miller and Bada, 1988). These data suggest the stability of amino acids in hydrothermal systems is different from that observed under standard conditions on the earth's surface (Shock, 1990a). Consequently, a different array of amino acids will probably emanate from hydrothermal systems than are observed in a "conventional" prebiotic syntheses on the earth's surface.

The detection of non-biological amino acids would provide support for the occurrence of prebiotic synthesis in contemporary hydrothermal systems. Such findings would not be conclusive because the non-biological amino acids may be formed from biological precursors. For example, when glycine was heated with  $\text{MnCO}_3\text{-Mn(OH)}_2$  and  $\text{Al}_2\text{O}_3$  at 240°C for 1 h and the product mixture is hydrolyzed with 6 N HCl  $\alpha$ -aminobutyric, norvaline, norleucine, sarcosine, N-ethylglycine, N-methylalanine and N-ethylalanine were detected as reaction products (Ivanov and Slacheva, 1977). Extreme care will be required to establish that the biological amino acids formed in simulation studies are not due to terrestrial contamination. The use of  $^{13}\text{C}$ - and  $^{15}\text{N}$ -labeled starting materials is recommended to prove that the amino acids detected resulted from synthesis and not from decomposition of contemporary biological materials (Briggs *et al.*, 1991).

It is possible that peptides will form in hydrothermal systems if the concentrations of amino acids is sufficiently high. Oligomers (molecular weight-1000-2000), which may contain peptide bonds, were formed by heating glycine, alanine, valine and aspartic acid (see Chapter 7). Glycine oligomers up to the dodecamer were obtained from glycine amide (Yanagawa *et al.*, 1984b). The synthesis of ethyl acetate from ethanol and acetic acid in supercritical water (Antal *et al.*, 1987) is consistent with peptide bond formation at high temperatures and pressures. Oligomer formation may proceed via diketopiperazines (Nagayama *et al.*, 1990; Basiuk *et al.*, 1991) which form spontaneously from dipeptides (equation 27) (Kopple, 1966). Mineral catalysis may be important in these and other condensation reactions discussed in Section 5 (Siskin and Katritzky, 1991).



### 5.3. HETEROCYCLIC COMPOUNDS

#### 5.3.1. *From HCN*

5-Aminoimidazole-4-carboxamide, 5-aminoimidazole-4-carboximidine, adenine, 8-carbamyladenine, orotic acid, 4,5-dihydroxypyrimidine, 5-hydroxyuracil and uracil have all been detected as products of the self condensation of HCN (Section 2.5). Triazine is formed by the acid catalyzed condensation of HCN but it is not likely to be detected in hydrothermal systems because it undergoes rapid hydrolysis in aqueous solution (Smolin and Rappoport, 1959c). Glycolonitrile, the HCN adduct of formaldehyde, dimerizes to an oxazole (Section 2.1.3). No data is available concerning the hydrolysis of this oxazole under conditions prevalent in hydrothermal systems.

The reaction of 5-aminoimidazole-4-carboxamide with cyanogen or cyanate yields guanine and with HCN a small yield of hypoxanthine is obtained (Sanchez *et al.*, 1968).

The main reaction products resulting from the self condensation of 0.1 M HCN *after acid hydrolysis* are adenine and 4,5-dihydroxypyrimidine. An unidentified precursor to 4,5-dihydroxypyrimidine, possibly 6-cyano- or 6-carbamyl-4,5-diaminopyrimidine, was detected before the reaction mixture was subjected to acid hydrolysis (Ferris *et al.*, 1978). 8-Cyano- or 8-carbamyladenine are likely precursors to adenine (Voet and Schwartz, 1983). If these precursors are formed, it is likely that they will be converted to adenine and 4,5-dihydroxypyrimidine when subjected to the reaction conditions in hydrothermal systems. Since 4,5-dihydroxypyrimidine has not been detected in any other prebiotic synthesis its detection in a contemporary hydrothermal system would provide strong evidence that HCN condensation reactions were responsible for it and some of the other hydrothermal products.

#### 5.3.2. *FTT Synthesis*

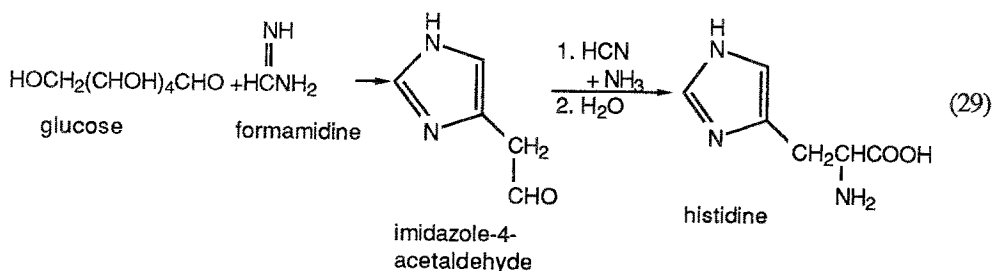
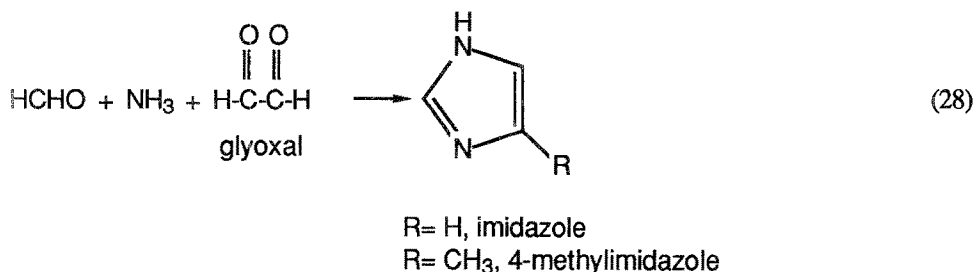
The yield of heterocycles formed in the FTT synthesis from CO, H<sub>2</sub> and NH<sub>3</sub> decreases in the order cyanuric acid>melamine>adenine, guanine>ammeline (Hayatsu *et al.*, 1968). Uracil and methylated uracils, thymine, xanthine, 2-methylpyrrole and histidine were also detected (Hayatsu *et al.*, 1972). Heterocycle formation by FTT synthesis requires the presence of NH<sub>3</sub> in the hydrothermal systems while their formation from HCN does not require NH<sub>3</sub>. If NH<sub>3</sub> is present then cyanuric acid is likely to be the most abundant heterocycle produced by FTT synthesis since it is also formed by the hydrolysis of the melamine and ammeline. The detection of adenine will not differentiate between its formation by a FTT synthesis or direct formation from HCN (see previous section). Cyanuric acid provides the best evidence for prebiotic synthesis via FTT reactions in contemporary hydrothermal systems but its detection does not provide unambiguous evidence since it is also produced by the thermolysis of urea (Section 2.1.4.5). Its absence could



also be due to its thermolysis of the cyanuric acid to cyanate or its hydrolysis to urea (Section 2.1.4.5).

### 5.3.3. Thermal Synthesis of Imidazoles From $\text{NH}_3$ and Aldehydes

Reaction of  $\text{NH}_3$  with formaldehyde and glyoxal results in the formation of imidazole (equation 28) (Oró *et al.*, 1984). Substitution of glucose for glyoxal yields 4-methylimidazole (Oró *et al.*, 1984; Bernhauer, 1929). Reaction of formamidine, the  $\text{NH}_3$  adduct of  $\text{HCN}$ , with erythrose yields imidazole-4-acetaldehyde (IAA). Histidine results when the amino nitrile derivative of IAA is hydrolyzed (equation 29) (Shen *et al.*, 1987, 1990).



Imidazoles may result if  $\text{NH}_3$  and aldehydes are present in appreciable amounts in hydrothermal systems. Imidazoles are readily detected by simple diazotization after chromatography (Oró *et al.*, 1984).

### 5.3.4. Thermolysis of Biological Molecules

The direct detection of abiotic synthesis in hydrothermal systems will be very difficult because compounds which are not prevalent in biological systems are formed by heating biological molecules (Section 5.2). Heterocycles are produced by the pyrolysis of amino

acids and proteins. Heating an equimolar mixture of glycine, alanine, valine, lysine, aspartic acid, and glutamic acid for 4-6 h at 160-200°C gives UV absorbing compounds which appear to be pteridines (Heinz *et al.*, 1979). Thermal degradation of proteins at 840°C generates pyrrole, indoles, pyridines, quinoline, pyrrole and isoquinoline (Higman *et al.*, 1970).

## 5.4. CARBOXYLIC ACIDS

### 5.4.1. Ionizing Radiation

Simple acids such as formic and acetic may be formed by the radiolysis of carbonates in hydrothermal systems (Albarrán *et al.*, 1987). More complex (branched) acids may result from the radiolysis of these simple carboxylic acids (Negron-Mendoza and Ponnampereuma, 1982). Dicarboxylic acids are formed by the irradiation of urea (Navarro-Gonzalez *et al.*, 1989).

### 5.4.2. FTT Synthesis

Linear and branched fatty acids are produced in FTT syntheses (Section 2.3). It will be possible to distinguish those acids produced by FTT processes from those formed from contemporary biological systems by the presence of both an odd and even number of carbon atoms and branched chains in those formed in FTT reactions.

Aliphatic carboxylic acids synthesized in hydrothermal systems will not undergo appreciable decarboxylation (Drummond and Palmer, 1985). The rate of the thermal decarboxylation of acetic acid is dependent on pH and surface catalysis by reaction vessel used (equation 30) (Palmer and Drummond, 1985). The half life for acetic acid decarboxylation is 10-100 years at 300°C. In one study it was established that the rate constant for the decarboxylation of butyric acid was about half that of acetic acid under roughly comparable reaction conditions. These kinetic findings are in agreement with qualitative studies performed in supercritical water (Swanson *et al.*, 1986).

