Abstract. The mechanism of the condensation of dilute aqueous solutions of HCN and the products formed by these reactions have been investigated. The initial HCN condensation reactions yield 3, a compound which is readily oxidized to 4. A similar oxidation of 5 to 6 was also observed. Urea is formed on hydrolysis of 4. The oxidation-reduction products formed from HCN may be in part a consequence of the oxidation of 3. It has been established by combination GC/MS that the amino acids glycine, dianinosuccinic acid, α-amino-isobutyric acid, aspartic acid, alanine and isoleucine are released on acid hydrolysis of the ‘HCN polymer’. Hydantoin (7), 5,5-dimethylhydantoin (8) and 5-carboxymethylenedehyedantoin (10) are also released on acid hydrolysis of the HCN condensation products. The direct conversion of the dicarbonyl derivative of dianinosuccinic acid to orotic acid via 10 at pH 8 has been observed. This conversion suggests a direct route to pyrimidines from HCN.

HCN is considered to have been one of the more important precursors of biological molecules on the primitive Earth (Sanchez et al., 1967). HCN could have been formed by a number of routes under possible prebiological conditions. Plausible routes to purines and amino acids have been demonstrated starting from HCN (Lowe et al., 1963; Oro and Kimball, 1961).

We have continued to explore the chemistry of HCN with the goals of determining the mechanisms involved in HCN oligomerizations in dilute aqueous solutions and identifying the compounds which are produced in these oligomerization mixtures. Complex mixtures are formed if 0.1–1.0 M aqueous solutions of cyanide are allowed to stand at room temperature (pH 9.2) for one month or longer. Oxalic acid, urea and the so-called ‘HCN polymer’** have been isolated from these reaction mixtures. The so-called ‘HCN polymer’ has been found to have a molecular weight of much less than 1000 so that it does not fall within the accepted definition of a polymer. It has been possible to fractionate this substance(s) into acidic, basic and neutral fractions. Urea is the main constituent of the neutral fraction (Ferris et al., 1973a). Amino acids are released on acid hydrolysis of the acidic and basic fractions, however, neither pronase nor carboxypeptidase catalyzed the release of amino acids from this material. The absence of cleavage by the proteolytic enzymes suggests that peptide links are not present in the ‘HCN polymer’ (Ferris et al., 1973a; Labadie et al., 1968).

The early stages of the HCN oligomerization reaction are well understood. HCN condenses to form the tetrameric species dianinomaleonitrile (DAMN) (3) via a dimer (1) and a trimer (2) (Sanchez et al., 1967; Ferris et al., 1972a, b). However, the conversion of these oligomers to urea, oxalic acid and the ‘HCN polymer’ is not understood. The possibility of subsequent nucleophilic condensation to cyanide with these

* Chemical Evolution XV. For the previous paper in the series see Ferris and Ryan (1973).
** The terms ‘HCN polymer’ and oligomerization mixtures are used interchangeably to describe those products formed by condensation of HCN in aqueous alkaline solution (Ferris et al., 1973a, b)
oligomers was probed by the addition of the nucleophiles to the reaction mixture. There was no observable effect on the rate of the oligomerization, when azide, monomethylamine, trimethylamine, hydroxide or phenoxide were substituted for ammonia in the condensation. The only difference that was observed was the formation of monomethylurea in addition to urea when the oligomerization was carried out in the presence of monomethylamine (Ferris et al., 1973b). This result suggests that cyanate, or a substance similar to cyanate, is formed during the course of the condensation. Cyanogen is a likely source of cyanate since it is hydrolyzed to both oxalic acid derivatives and cyanate at pH 9.

\[
\begin{align*}
\text{HCN} & \rightleftharpoons \text{HN} = \text{CHCN} \rightleftharpoons \text{NH}_2\text{CH(CN)}_2 \rightleftharpoons \text{NH}_2\text{CN} \rightleftharpoons \text{HN} = \text{CHCN} \\
1 & \quad \quad 2 & \quad \quad 3 \quad \quad 4
\end{align*}
\]

The occurrence of oxidation and reduction reactions during the course of the HCN oligomerization is required by the formation of urea and oxalic acid (HCN oxidation products) and, after hydrolysis of the 'HCN polymer', amino acids (HCN reduction products). We investigated the nature of these redox reactions by studying the reactions of diisopropyldiaminomaleonitrile (diisopropylDAMN) 5 in aqueous solution (Ferris and Ryan, 1973). Compound 5 is stable in aqueous solution in the absence of oxygen, however, it is readily oxidized to 6 in the presence of oxygen. No higher molecular weight oligomers were isolated in the reaction of 5 or 6 with cyanide.

\[
\begin{align*}
\text{RHN} & \quad \text{CN} \quad \text{RN} \quad \text{CN} \quad \text{O}_2 \\
5 & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
\end{align*}
\]

A similar oxidation of 3 to 4 appears to take place in the presence of oxygen. Compound 4 is converted to urea in the presence of ammonia. This suggests a possible pathway for urea formation during the oligomerization of cyanide. The direct oxidation of cyanide to cyanogen and cyanate which in turn react with ammonia to give urea is another possibility (Ferris et al., 1973a).

The facile air oxidation of 3 suggested that the oligomerization of cyanide might follow a different course in the absence of oxygen. The loss of cyanide from an aqueous (pH 9.2) solution proceeded more slowly in the absence of oxygen. However, we did observe the formation of the 'HCN polymer', urea and, after hydrolysis, amino acids when oxygen was excluded from the reaction solution (Ferris and Ryan, 1973). Thus, redox reactions leading to biomolecules from HCN could have taken place on the primitive earth in the absence of oxygen.