Title
FORMATION OF 5,5-DIMETHYLHYDANTOIN UNDER CONDITIONS REPRESENTATIVE OF
CONDENSATE WATERS FROM COAL GASIFICATION

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Authors
Grant, T.M.
King, C.J.

Publication Date
1986-05-01
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T.M. Grant and C.J. King

May 1986
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FORMATION OF 5,5-DIMETHYLHYDANTOIN UNDER CONDITIONS
REPRESENTATIVE OF CONDENSATE WATERS FROM COAL GASIFICATION

Terry M. Grant and C. Judson King
Applied Science Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720
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The Bucherer-Bergs reaction is a likely source of 5,5-dimethylhydantoin (5,5-dmh) in coal-gasification condensate waters. The reaction rate was studied by means of measurements of concentrations of 5,5-dmh, acetone, cyanide, ammonia, and carbon dioxide in synthetic aqueous solutions. A rate model was derived from a proposed mechanism, and is consistent with a limited portion of the data. Variation of measured cyanide concentrations from values consistent with the model initiated a search for side-products. Formate ion was identified as a side-product. A hypothesis was advanced to explain deviations from the rate model, but the data taken are insufficient to characterize the reaction system fully. The data do indicate that the rate of 5,5-dmh formation is probably first-order in acetone, in ammonia, and in carbon dioxide. Further, cyanide was indicated as a limiting reagent in process condensates.
Chapter I  **Background: The Problem of Hydantoin Formation in Coal Gasification Condensates.**

A. The Nature of the Problem

Coal gasification has the potential to supply a large fraction of the United States energy requirements in the next few decades. U.S. coal reserves account for nearly twenty-one percent of the world's proven energy resources (Probstein and Hicks, 1982), and gasification can produce a high-purity, high-BTU, and environmentally acceptable fuel, as well as a chemical feedstock. Crude oil and natural gas prices are now low enough to swing the economic balance against coal gasification, but the 1970s showed that the balance can shift rapidly.

Several processes have been developed to carry out coal gasification, but all face obstacles to commercialization. Public acceptance and environmental regulations are two such obstacles, and consumption and pollution of water are key concerns. Much of this nation's coal is located in areas subject to water shortages, and the expense of transporting the coal away from these areas would be large.

A gasifier reacts coal with steam and oxygen and produces carbon monoxide, carbon dioxide, hydrogen and methane. These gases, together with volatiles pyrolyzed from the coal, are quenched, and excess steam condenses. A plant (Lurgi) generating $2.5 \times 10^8$ standard cubic feet per day of pipeline gas would consume more than $1.5 \times 10^6$ lb/hr of steam and would produce around $1.1 \times 10^6$ lb/hr of condensate water (Probstein and Gold, 1978). Although steam fed to a process must be very clean, condensate waters are highly contaminated with organics and with ammonia and the acid gases CO$_2$ and H$_2$S. These waters must be treated before reuse or release.
One class of organic compounds that require treatment when present is hydantoins. Several hydantoins have been found in condensates from low temperature gasification of lignite (Mohr and King, 1981; Olson et al., 1983; Mohr and King, 1985) and are listed in Table 1. 5,5-Dimethylhydantoin (5,5-dmh, Figure 1) is the predominant species, and has appeared at levels as high as 17,000 ppm in the blowdown from a cooling tower to which condensate has been recycled (Willson, 1984). Previous investigations have shown that 5,5-dmh forms in condensates rather than in the gas phase (Mohr and King, 1983; Olson et al., 1985). Most of the formation is probably in the quench-water circuit where residence times may be quite long.

The objective of this research was to characterize the kinetics of formation of 5,5-dimethylhydantoin under process conditions.

B. Project Impetus

There are several reasons why the formation of 5,5-dmh in condensates is of interest. First, as mentioned, hydantoins have accumulated to high levels in cooling tower blowdown and could thereby pose high chemical and biological oxygen demands. Second, although tests specific to this compound are needed, many hydantoins are physiologically active. Third, characterization of the mechanism and kinetics of formation could lead to quench system designs that minimize hydantoin formation. Further 5,5-dmh is hydrophilic and is less easily removed from condensates than are most other organic contaminants. Finally, reliable predictions of hydantoin concentrations would facilitate the design of effective treatment schemes. These issues are discussed more fully in the remainder of this chapter.
TABLE 1. HYDANTOINS FOUND IN CONDENSATE WATERS

<table>
<thead>
<tr>
<th>Component Identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,5-DIMETHYLHYDANTOIN</td>
</tr>
<tr>
<td>5-ETHYL-5-METHYLHYDANTOIN</td>
</tr>
<tr>
<td>5-ISOPROPYL-5-METHYLHYDANTOIN</td>
</tr>
<tr>
<td>5,5-DIETHYLHYDANTOIN</td>
</tr>
<tr>
<td>5-METHYL-5-PROPYLHYDANTOIN</td>
</tr>
<tr>
<td>5-METHYLHYDANTOIN</td>
</tr>
<tr>
<td>5-ETHYL-5-PROPYLHYDANTOIN</td>
</tr>
<tr>
<td>5-ETHYLHYDANTOIN</td>
</tr>
<tr>
<td>5-BUTYL-5-METHYLHYDANTOIN</td>
</tr>
<tr>
<td>SPIROPENTYLHYDANTOIN</td>
</tr>
<tr>
<td>SPIROHEXYLHYDANTOIN</td>
</tr>
</tbody>
</table>

(From Olson, et al., 1983)
FIGURE 1. STRUCTURE AND PROPERTIES OF 5,5-DIMETHYLHYDANTOIN

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point (°C)</td>
<td>178 - 182.5</td>
</tr>
<tr>
<td>Solubility in Water (wt %)</td>
<td></td>
</tr>
<tr>
<td>10°C</td>
<td>11.5</td>
</tr>
<tr>
<td>20°C</td>
<td>13.5</td>
</tr>
<tr>
<td>30°C</td>
<td>16.9</td>
</tr>
<tr>
<td>$P_{K_A}$ at 23.7°C</td>
<td>9.19</td>
</tr>
<tr>
<td>pH of 10% Aqueous Solution</td>
<td>4.65</td>
</tr>
<tr>
<td>pH of 2% Aqueous Solution</td>
<td>5.0</td>
</tr>
</tbody>
</table>

(Property values from Bateman, 1978)
i. Buildup in cooling towers

One motivation to understand 5,5-dmh formation (and removal options) is that the compound has accumulated in a cooling tower fed with recycled condensate. Closure of plant water cycles is a key goal for gasification processes, and reuse of treated condensate in a cooling tower is a measure to advance that goal. A preliminary assessment of the effectiveness of this measure (Willson, 1984) showed a buildup of 5,5-dmh to over 17,000 ppm in the blowdown from the cooling tower. This is a substantial organic loading that gives very high chemical and biological oxygen demands. A material balance shows that 5,5-dmh was probably not formed (or degraded) in the tower, but this conclusion could be affected by the volatility of the reactants. The formation reaction must be understood before a reasonable judgement is possible.

ii. Physiological activity

The fact that many hydantoins are physiologically active is suggested by their close relationship to \( \alpha \)-aminoacids. These two types of compounds are generally interconvertible under appropriate conditions (Ware, 1950). It has been suggested that hydantoins are present in proteins (Johnson, 1916), and they have been isolated from natural sources such as sugar beets and butterfly wings (Ware, 1950).

Table 2 summarizes known physiological actions of a number of hydantoins. The parent compound hydantoin is non-toxic (Lewis, 1912; Ware, 1950) and apparently has no medical uses. Phenyl substitution in the 5 position promotes activity, and although none of these compounds have been
<table>
<thead>
<tr>
<th>Compound</th>
<th>Medical Name</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydantoin</td>
<td></td>
<td>Non-toxic</td>
</tr>
<tr>
<td>5-alkyl 5-phenyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>methyl</td>
<td></td>
<td>Hypnotic (some narcotic effect)</td>
</tr>
<tr>
<td>ethyl</td>
<td>Nirvanol</td>
<td>Very Hypnotic</td>
</tr>
<tr>
<td>propyl</td>
<td></td>
<td>Treatment for Chorea</td>
</tr>
<tr>
<td>isobutyl</td>
<td></td>
<td>Slight Toxicity</td>
</tr>
<tr>
<td>isopropyl</td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>n-butyl</td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>5,5-dialkyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dimethyl</td>
<td></td>
<td>No or Low Toxicity</td>
</tr>
<tr>
<td>ethyl isobutyl</td>
<td></td>
<td>Low Teratogenicity</td>
</tr>
<tr>
<td>dipropyl</td>
<td></td>
<td>Moderately Hypnotic</td>
</tr>
<tr>
<td>propyl isobutyl</td>
<td></td>
<td>Moderately - Strongly</td>
</tr>
<tr>
<td>diisobutyl</td>
<td></td>
<td>Hypnotic, Low Toxicity</td>
</tr>
<tr>
<td>5,5-diphenyl</td>
<td>Dilantin, Epanutin</td>
<td>Anticonvulsant</td>
</tr>
<tr>
<td></td>
<td>(Accepted by AMA!?)</td>
<td>Non-narcotic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Slightly Hypnotic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Slight Toxicity</td>
</tr>
<tr>
<td>2,4-dithio dmn</td>
<td></td>
<td>Slightly Hypnotic</td>
</tr>
</tbody>
</table>
identified in condensates, phenol is abundant. 5-alkyl,5-phenylhydantoins are most active when the alkyl group is small, and Nirvanol was widely used as a hypnotic and as a treatment for chorea before its toxic effects were discovered. Dilatin is still considered a good antiepileptic drug even though it is slightly toxic, because it lacks the hypnotic effects of other anticonvulsants. The thiohydantoins are included because there is a substantial amount of sulfur compounds present in a typical condensate, and thiohydantoins could conceivably form. Comparison of Tables 1 and 2 shows that no 5,5-dialkyldantoin with known physiological activity has been identified in the condensates, although there are several "close cousins". Tests are needed for the compounds in Table 1.

A limited amount is known about the effects of 5,5-dimethylhydantoin. 5,5-dmh is not acutely toxic according to RCRA standards (Anon. CFR, 1982; Tatken and Lewis, 1978; Semenova, 1982) and has probably not been tested for carcinogenicity or mutagenicity (Anon. Survey-USDHEW #80-453, 1978; Soderman, 1982; Anon. Index Medicus, 1978-85). 5,5-Dmh probably has a very low teratogenic activity, significantly less than aspirin, but the effects may be cumulative (Brown et al., 1982; Pavlovich, 1985). In short, there is evidence to suggest that 5,5-dmh should be removed from condensates before they are released, but further testing is needed.

iii. Quench circuit design

Temperature, residence time, and mixing patterns in the quench water circuit should affect the formation of 5,5-dmh and other hydantoins. Various authors have discussed the advantages of a two-stage over a one-stage quench circuit (Senetar and King, 1986; Parsons, 1980; Wohler, 1979).
The two-stage quench provides a separation of condensate solutes that could influence hydantoin formation. The reactants responsible for hydantoin formation might be separated, for example, or the properties of the reaction media (temperature and composition) might be substantially different.

iv. Properties of 5,5-dmh and its removal from condensates

Three properties of 5,5-dmh that affect its removal from condensates are suggested by the structure in Figure 1. First, the compound is hydrophilic because of the polar carbonyl groups and because of the hetero-atoms in the ring. Therefore, for small mole fractions, the activity of 5,5-dmh in water is low. This trait is reflected in the high aqueous solubilities, and suggests that solvent extraction of 5,5-dmh from condensates would be difficult.

Second, the high molecular weight and polarity make the compound relatively non-volatile. This fact, coupled with the high affinity for water, makes stripping unlikely to be effective for removing 5,5-dmh from aqueous solutions.

A third property suggested by the structure is acidity. The 3-position N-H group is flanked by electron-withdrawing carbonyls, giving a fairly high first acid dissociation constant. The dissociated hydantoin is stabilized by sharing electrons between the nitrogen and both carbonyl groups. Condensates are buffered between pH 8 and 9.5 by ammonia and bicarbonate, so a substantial fraction of 5,5-dmh can be ionized. Extraction with an organic solvent will be less effective at higher pH values.

The acidity of 5,5-dmh is also reflected in distribution coefficients for extraction from deionized water into organic solvents. Table 3a shows weight-
### TABLE 3. EQUILIBRIUM DISTRIBUTION COEFFICIENTS FOR EXTRACTION OF 5,5-DIMETHYLHYDANTOIN FROM WATER INTO VARIOUS SOLVENTS AT ROOM TEMPERATURE

#### 3A. (Mohr and King, 1983)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(K_D)</th>
<th>(K_X)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lewis Acids:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>&lt;0.05</td>
<td>0.14</td>
</tr>
<tr>
<td>25 wt% Di (2-ethylhexyl) Phosphoric Acid in Kerosene</td>
<td>&lt;0.05</td>
<td>----</td>
</tr>
<tr>
<td><strong>Lewis Bases:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl Isobutyl Ketone (MIBK)</td>
<td>0.25</td>
<td>1.39</td>
</tr>
<tr>
<td>Tricresyl Phosphate (TCP)</td>
<td>0.11</td>
<td>2.24</td>
</tr>
<tr>
<td>Tributyl Phosphate (TBP)</td>
<td>2.6</td>
<td>38.4</td>
</tr>
<tr>
<td>25 wt% Tri-n-Octyl Phosphine Oxide in Methyl Isobutyl Ketone (MIBK)</td>
<td>1.2</td>
<td>2.50</td>
</tr>
<tr>
<td>25 wt% Adogen 363 in Kerosene</td>
<td>&lt;0.05</td>
<td>----</td>
</tr>
</tbody>
</table>

#### 3B. (Senetar and King, 1986)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(K_D)</th>
<th>(K_X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexanone</td>
<td>0.95</td>
<td>5.17</td>
</tr>
<tr>
<td>4-methyl Cyclohexanone</td>
<td>0.54</td>
<td>3.36</td>
</tr>
<tr>
<td>2-Methyl Cyclohexanone</td>
<td>0.31</td>
<td>1.93</td>
</tr>
<tr>
<td>Methyl Isobutyl Ketone (MIBK)</td>
<td>0.24</td>
<td>1.33</td>
</tr>
</tbody>
</table>

\(K_D\) = **Weight-Fraction Based Equilibrium Distribution Coefficient**.  
\(K_X\) = **Mole-Fraction Based Equilibrium Distribution Coefficient**.
fraction-based and mole-fraction-based distribution coefficients for several Lewis-acid and Lewis-base solvents. 5,5-Dmh is virtually unionized in water and complexes most effectively with Lewis bases. The basic solvents are listed in order of increasing basicity as measured by the Gutmann donor number (Gutmann 1978), but the distribution coefficients do not follow the same order. The different order may be partly due to steric effects. Tricresyl phosphate is bulkier than methyl isobutyl ketone, for example, and Adogen 363 (a tertiary amine) is quite bulky. An effective extractant must not only be a strong Lewis base, but must also be able to interact easily with the 3-position N-H group. Table 3b confirms the effect of steric hindrance, since a methyl substituent lowers the $K_d$ and $K_x$ values for cyclohexanone. $K_x$ values are compared here, since they eliminate molecular-weight effects. The methyl group is more of a hindrance in the 2 position.

Process condensates released from the quench operation may contain up to two weight-percent organics (Mohr and King, 1983, 1985). Phenol, cresols and xylenols are the most abundant organics, but, unlike 5,5-dmh, these compounds are well removed by extraction with suitable solvents such as diisopropyl ether, methyl isobutyl ketone, and tributyl phosphate (Greminger et al., 1982; Senetar and King, 1986). There is also the possibility that a solvent or extractant (such as methyl isobutyl ketone or cyclohexanone) could participate in hydantoin formation. These facts suggest that hydantoin removal may require a treatment step separate from bulk removal of organics.

Although extraction is of limited effectiveness for removing 5,5-dmh from condensates, adsorption could provide an effective separation. 5,5-Dmh is well adsorbed onto activated carbon (Olson et al., 1983) and can be desorbed with methanol (Senetar and King, 1986). When condensates are treated with activated carbon, however, phenolics can adsorb irreversibly, which decreases
adsorption capacity upon reuse and prevents recovery of phenol. Consequently, synthetic resins may be more appropriate for treatment of condensate water than is activated carbon. The polyacrylic ester-based resin Rohm and Haas Amberlite XAD-7 adsorbs 5,5-dmh much less readily (Senetar and King, 1986), but interacts reversibly with phenolics. Regeneration can be accomplished with methanol (Senetar and King, 1986). Thus, polymeric resins hold promise for 5,5-dmh removal, but further information is needed for a cost-effective design.

v. Treatment design

In sum, 5,5-dmh is poorly removed from condensates by methods that remove the bulk of other contaminants. 5,5-Dmh, when it is present, must be considered in the design of a treatment scheme, and adsorption could be a key component of that scheme. Consequently, the concentration of 5,5-dmh will be a design parameter, and since the compound forms in the condensate, the kinetics of formation are of interest. Further impetus to study the formation reaction comes from the fact that the cost of an adsorption process is proportional to solute concentration, and the fact that 5,5-dmh might continue to form after treatment. Identifications of a limiting reagent and of potentially limiting reagents are, therefore, also of value.
Chapter II  **Preparation and Framework for Kinetic Studies.**

Several preliminary steps were taken before monitoring the kinetics of hydantoin formation. First, a probable reaction stoichiometry was identified. Together with published studies of the reaction, this stoichiometry suggested a potential mechanism. These premises, together with simplifying assumptions, led to a proposed rate expression. Analytical techniques were established to monitor reactant and product concentrations, and the limiting reagent for an actual condensate was identified. The information gathered during these steps was ultimately used to design kinetic studies.

A. Reaction Stoichiometry

The first task was to determine the reaction that forms 5,5-dmh in condensate waters. There are many compounds in the condensate, and many reaction paths are known (Ware, 1950; Smith, 1966) or can be imagined, but the primary candidate is the Bucherer-Bergs reaction (Bergs, 1933; Bucherer and Barsh, 1934; Bucherer and Brandt, 1934; Bucherer and Fishbeck, 1934). In this reaction, acetone, ammonia, carbon dioxide, and hydrogen cyanide combine to form 5,5-dmh and water:

$$\text{C}_3\text{H}_6\text{O} + \text{NH}_3 + \text{CO}_2 + \text{HCN} \rightarrow \text{C}_5\text{H}_8\text{N}_2\text{O}_2 + \text{H}_2\text{O}$$

The evidence that supports the premise that this is the important reaction includes the following:

1. All of the reactants are found in condensates.
2. Temperatures in a quench circuit are similar to those used for high yields in hydantoin syntheses.

3. 5,5-Dmh forms in condensates at pH 8.5, but not at pH 2.

4. 1:1 Acetone:5,5-dmh stoichiometry has been observed for high-pH waters (Mohr and King, 1983).

Table 4 shows that the Bucherer-Bergs reactants are present in a hydantoin-containing condensate. These reactants are involved in a number of equilibria, including those shown in Figure 2. Data for equilibrium constants (Dean, 1985) and studies by Taillades and Commeyras (1974c) indicate that, at pH values between 8.0 and 9.5, none of the reactants are primarily in the form shown for the Bucherer-Bergs reaction. Still, the stoichiometry is possible, and the absence of other compounds that could form 5,5-dmh lends support. In particular, analyses of condensates have shown that neither amino acids nor urea are present (Senetar and King, 1986).

Temperatures in a gasifier quench circuit are conducive to high yields of 5,5-dmh via the Bucherer-Bergs reaction. Typical aqueous phase quench temperatures range from 60°C to 90°C. A 91.6% yield of 5,5-dmh was obtained when acetone, hydrogen cyanide, and ammonium carbonate were heated to 60-66°C in water (Rogers, 1945). Acetone and cyanide were present in equimolar amounts, while ammonia and carbonate species were in slight excess at the start of the test. Various hydantoins have been synthesized by substituting different ketones and aldehydes for acetone, and the best yields are generally obtained in the 60-80°C range (Ware, 1950). Hydantoin yields at the end of each of three hours are reported by Henze and Speer (1942) for reaction of acetophenone at 55-60°C. The Bucherer-Bergs reaction should be facile in process condensates in the indicated temperature range.

Direct evidence of the Bucherer-Bergs reaction in condensates came from studies of four freshly collected waters (Mohr and King, 1983; waters supplied
<table>
<thead>
<tr>
<th>Compound or Property</th>
<th>Concentration (mg/L) or Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>1,450</td>
</tr>
<tr>
<td>Ethanol</td>
<td>5</td>
</tr>
<tr>
<td>Acetone</td>
<td>40</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>1</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>420</td>
</tr>
<tr>
<td>Propionitrile</td>
<td>85</td>
</tr>
<tr>
<td>Phenol</td>
<td>4,560</td>
</tr>
<tr>
<td>O-Cresol</td>
<td>650</td>
</tr>
<tr>
<td>P-Cresol</td>
<td>880</td>
</tr>
<tr>
<td>M-Cresol</td>
<td>950</td>
</tr>
<tr>
<td>5,5-Dimethylhydantoin</td>
<td>2,280</td>
</tr>
<tr>
<td>5-Ethyl-5-Methylhydantoin</td>
<td>510</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>16</td>
</tr>
<tr>
<td>Propionic Acid</td>
<td>8</td>
</tr>
<tr>
<td>Butyric Acid</td>
<td>2</td>
</tr>
<tr>
<td>NH₃</td>
<td>7,890</td>
</tr>
<tr>
<td>Sulfide</td>
<td>370</td>
</tr>
<tr>
<td>Cyanide</td>
<td>75</td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>230</td>
</tr>
<tr>
<td>pH</td>
<td>8.3</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>23,200</td>
</tr>
<tr>
<td>COD</td>
<td>27,900</td>
</tr>
<tr>
<td>Resistivity</td>
<td>33</td>
</tr>
</tbody>
</table>

(From: Willson 1984)

* (The wastewater was produced from slagging fixed-bed gasification of lignite at the University of North Dakota Energy Research Center.)
FIGURE 2. SELECTED EQUILIBRIA OF BUCHERER-BERGS REACTANTS IN CONDENSATE WATERS

\[ \text{HCN} \rightleftharpoons H^+ + CN^- \]

\[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \]

\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + H^+ \]

\[ \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + H^+ \]

\[ \text{C}_3\text{H}_6\text{O} + \text{HN} \rightleftharpoons \text{C}_4\text{H}_7\text{ON} \]

\( \text{(ACETONE)} \quad \text{(ACETONECYANOHYDRIN)} \)

\[ \text{C}_3\text{H}_6\text{O} + \text{NH}_3 + \text{HCN} \rightleftharpoons \text{C}_4\text{H}_8\text{N}_2 \]

\( \text{(ACETONE)} \quad \text{(\(\alpha\)-AMINOISOPROPYLNITRILE)} \)
by Grand Forks Energy Technology Center, now University of North Dakota Energy Research Center). The condensates were collected under a nitrogen atmosphere, and a portion of each was adjusted to pH 2 with concentrated sulfuric acid. After shipment from Grand Forks North Dakota to Berkeley California by air freight, the samples were stored in dark glass bottles at 4°C. Table 5 shows how concentrations of 5,5-dmh changed with time in the mixtures. No time dependence was found for the pH-2 samples, but the concentration increased gradually in samples from Runs 106 and 120 at pH 8.5. The Bucherer-Bergs reaction should not occur at low pH because carbon dioxide and hydrogen cyanide have low solubilities in the unionized form.

To further test the conclusion regarding in-situ formation, the pH values of samples of the 500 day old, Run 78 waters were changed. The sample at pH 8.5 was acidified to pH 2, and sodium carbonate and sodium hydroxide were later added to the pH-2 sample to replenish the carbonate and to bring the pH to 8.5. After one month, no hydantoin had formed at low pH, but the sample now at pH 8.5 contained 1700 mg/l of 5,5-dmh. Note, however, that no cyanide was added to the samples. A possible explanation for these facts is that the absence of carbonate at low pH prevented hydantoin formation, but cyanide was present in a nonvolatile form. Specifically, acetonecyanohydrin and/or thiocyanate present at low pH could have supplied cyanide at high pH.

Further evidence for the Bucherer-Bergs reaction came from tests on the Run 106 condensate (Mohr and King, 1983). After several months, concentrations of acetone and 5,5-dmh differed between portions stored at the different pH values. The acetone concentration was 10.7 mmoles/l in the pH-2 sample and 8.7 mmoles/l in the pH-8.5 sample; a difference of 2.0 mmoles. The 5,5-dmh concentrations were 1.8 mmoles/l in the pH-2 sample and 3.6 mmoles/l in the pH-8.5 sample, a difference of 1.8 mmoles/l. Within an error of 10%,
TABLE 5. TIME DEPENDENCE OF 5,5-DIMETHYLHYDANTOIN CONCENTRATION IN CONDENSATES

<table>
<thead>
<tr>
<th>GFETC Run No.</th>
<th>Sample Stored at pH 8.5</th>
<th>Sample Stored at pH 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Age (Days)</td>
<td>Conc. (mg/l)</td>
</tr>
<tr>
<td>78</td>
<td>200</td>
<td>1720</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>1720</td>
</tr>
<tr>
<td>97</td>
<td>40</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>300</td>
</tr>
<tr>
<td>106</td>
<td>1.7</td>
<td>290</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>410</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>460</td>
</tr>
<tr>
<td>120</td>
<td>0.7</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>165</td>
</tr>
</tbody>
</table>

(From Mohr and King, 1983)
these numbers reflect the stoichiometry of the Bucherer-Bergs reaction.

Even with this evidence, there remain uncertainties about how hydantoins form. In particular, other reasonable precursors are available, substituted hydantoins other than 5,5-dmh form, and the chemistry of cyanide in condensates is poorly understood. Other potential precursors include carboxylic acids and alkyl nitriles (See Table 4). The presence of carboxylic acids is particularly interesting because several 5-alkyl and 5,5-dialkyl hydantoins have been identified (Table 1). If these hydantoins formed through the Bucherer-Bergs reaction, aldehydes and ketones other than acetone would be required, but none have been found. The identified carboxylic acids have the appropriate alkyl groups. Finally, the chemistry of cyanide in condensates is complicated, and it is not clear that HCN was even available in the pH adjustment experiments detailed earlier.

B. Proposed Mechanism

Despite these questions, the Bucherer-Bergs reaction is probably responsible for 5,5-dmh in condensates, and possible mechanisms were considered. Several investigators have studied parts of the mechanism, and the schemes in Figure 3 are consistent with published results. Scheme A was first suggested by Bucherer and Steiner (1934) after they found that cyanohydrins would react with ammonium carbonate or with ammonium carbamate to give hydantoins. They also treated α-aminonitriles with carbon dioxide to form hydantoins in aqueous solution. Support for the rearrangement shown in the last three steps comes from work by several investigators (Carrington, 1939; Catch et al., 1947; Cook et al., 1947, 1948ab; Jacobson, 1939, 1945) who treated α-aminonitriles with carbon disulfide to get 2,4-dithiohydantoins.
FIGURE 3. POSSIBLE MECHANISMS FOR 5,5-DMH FORMATION THROUGH THE BUCHERER-BERGS REACTION.
Bucherer and Steiner did not explicitly postulate the isocyanate (the species immediately prior to 5,5-dmh), but a recent study by Bowness, Howe, and Rao (1983) strongly supports its existence.

The initial steps of Scheme B were advanced by Taillades and Commeyas (1974abc), and Taillades et al. (1980). They argued that although "competition between the cyanide and amine for acetone first favors cyanohydrin formation", the reaction proceeds through an imine to the α-aminonitrile. They isolated intermediates in aqueous solutions of pH 8-12 to support their contentions. The imine is a stronger electrophile than the cyanohydrin, so Scheme B should be the more facile. Further, formation of acetonecyanohydrin is exothermic, and high quench circuit temperatures would favor dissociation. Scheme B, then, is probably the main pathway to 5,5-dmh in condensate waters.

C. Proposed Rate Expression

The participation of each of the Bucherer-Bergs reactants in a single fundamental step of the mechanism suggests a first order rate dependence on each reactant. The rate expression;

\[
\text{Rate of formation of 5,5-dmh} = k[\text{acetone}][\text{HCN}][\text{NH}_3][\text{CO}_2]
\]  

may be derived from the mechanism and suitable assumptions involving a rate limiting step and pseudo equilibria of other steps. Details are provided in Appendix A. Other rate expressions are possible, so the simple power-law expression should be viewed as a hypothesis.
D. Analytical Methods

Analytical techniques were established to study the Bucherer-Bergs reaction. 5,5-Dmh was quantitatively determined by reversed phase high performance liquid chromatography (HPLC). A Waters Associates Radial Pak C-18 cartridge provided the nonpolar stationary phase, and water buffered to pH-3 with H₃PO₄ and KH₂PO₄ was the mobile phase. Ultraviolet absorbance was detected at 214 nm. Cyanide ion was determined by a silver/sulfide specific ion electrode (Orion Model No. 94-16). The electrode responds to the dissociation of Ag(CN)₂⁻ provided as an indicator. Acetone concentrations were measured with gas chromatography using a Porapak-Q column (Waters Associates) and flame ionization detection. Ammonia and carbon dioxide concentrations were generally assumed constant, and were determined using specific electrodes (Orion Model No. 95-10 and Model No. 95-02). Further discussion of the analytical techniques is contained in Appendix B.

The analytical techniques worked well for synthetic solutions of reactants, but problems arose for actual wastewaters. For example, the condensates contained considerable amounts of sulfur compounds. Silver compounds with lower dissociation constants than Ag(CN)⁻ interfere with the cyanide analysis, and silver sulfide is extremely insoluble. Lead and cadmium also form insoluble sulfides, so addition of either can remove the sulfide interference. PbCO₃ was the compound added. Fortunately, tests showed that thiocyanate does not interfere with the electrode analysis for cyanide.
E. Reaction Equilibrium

For the purposes of a kinetic study, the Bucherer-Bergs reaction may be considered irreversible. This postulate is reflected in the proposed mechanism, with one-way arrows for molecular rearrangement, and hence is reflected in the proposed rate expression. Evidence for this assumption is that very high yields are obtained, and that aqueous solutions of 5,5-dmh do not change concentration with time. Neither does acetone or cyanide appear at a detectable level when 5,5-dmh is dissolved in water (even after several months). Further, the free energy change for the Bucherer-Bergs reaction was estimated for all reactants and products in the gas phase at 298 K and 1 atmosphere pressure. To facilitate the estimate, the method of Benson et al. (1969) was used to approximate the free energy of formation of 5,5-dmh. The free energy change for the Bucherer-Bergs reaction is \(-14.6\) kcal/g-mol and corresponds to an equilibrium constant of \(5.27 \times 10^{10}\). The equilibrium constant for the Bucherer-Bergs reaction in the aqueous phase should be within a few orders of magnitude of the value for the gas phase. Because the reaction is irreversible, any of the reactants could act as a limiting reagent.

F. Limiting Reagent in Condensates

Characterization of aged condensates (GPGA-7/85 supplied by Great Plains Gasification Associates, North Dakota, and METC Run 104 supplied by Morgantown Energy Technology Center, West Virginia) showed that, while they contained little or no cyanide, they had substantial acetone (480 and 65 mg/l respectively). 'Spiking' experiments verified that cyanide is a limiting
reagent. Figure 4 shows the results of one such experiment. Samples of GPGA-7/85 condensate were spiked with acetone or potassium cyanide and then analyzed for hydantoin with high performance liquid chromatography. The figure shows chromatograms of the solutions that had been held at 60°C for at least twenty-four hours. 5,5-Dmh eluted at approximately 7.7 minutes, as shown by the second and fourth chromatograms. No hydantoin was found in a control solution or in a solution spiked with acetone. The solution spiked with cyanide yielded 15.1% conversion of the new limiting reagent acetone to 5,5-dmh after 28 hours. The same qualitative results were achieved with METC Run 104 condensate held at room temperature for 220 days. Cyanide was the limiting reagent for formation of 5,5-dmh in both waters.
FIGURE 4. SPIKING EXPERIMENTS WITH GPGA CONDENSATE WATER
(SOLUTIONS WERE HELD AT LEAST 24 HOURS AT 60°C)

Control Solution

5 ml GPGA condensate
5 ml MilliQ H₂O
5 ml MeOH

(No 5,5 dmh formed)

Control solution spiked to 6.7 ppm
5,5 dmh

15 ml control solution spiked with
1 ml acetone

(No 5,5 dmh formed)

5 ml GPGA condensate
5 ml 920 ppm KCN
5 ml MeOH

15.1% conversion of acetone to 5,5 dmh
Chapter III. Kinetic Studies

A. Model System and Revised Rate Expression

A model system was chosen for study of the kinetics of the Bucherer-Bergs reaction. In a typical experiment, standardized solutions of ammonium carbonate and of acetone and cyanide were mixed in the desired proportions. Cyanide was introduced as KCN and/or as acetonecyanohydrin. Most mixtures were similar in buffer capacity and pH to actual condensates, and the pH value for each mixture remained virtually constant during a trial. Each reaction vessel was sealed and held at constant temperature in an oil bath. Since ammonia and carbonate species were in excess, the concentrations of ammonia and carbon dioxide were approximately constant in each trial, and the proposed rate expression simplifies to;

\[ \text{rate} = k' [\text{acetone}] [\text{HCN}] \]  \hspace{1cm} (2)

If the initial formal concentrations of these reactants are equal, and acetone and hydrogen cyanide react 1:1, the rate expression becomes;

\[ \text{rate} = k'_2 [\text{acetone}]^2 \]  \hspace{1cm} (3)

where a new constant appears because HCN participates in an acid-base equilibrium. That is, a pseudo second-order rate expression is postulated. By the reaction stoichiometry,

\[ \frac{d[5,5\text{dmh}]}{dt} = - \frac{d[\text{acetone}]}{dt} . \]  \hspace{1cm} (4)
This means that:

\[
\text{rate} = \frac{d[5,5\text{ dmh}]}{dt} = -\frac{d[\text{acetone}]}{dt} = k'_2[\text{acetone}]^2
\]  

(5)

This expression may be integrated to give:

\[
\frac{1}{[\text{acetone}]} = \frac{1}{[\text{acetone}]_0} + k'_2t
\]  

(6)

The subscript 0 denotes an initial value. The analysis could as well have been carried out in terms of cyanide concentrations, so if we let the subscript R indicate a 'generic' reactant,

\[
\frac{1}{C_R} = \frac{1}{C_{R0}} + k''_2t
\]  

(7)

where the constant can again be different because of secondary (e.g., acid-base) equilibria.

B. Evidence and Parameters for a Pseudo Second-Order Rate Expression

In several experiments, 5,5-dmh and acetone measurements were consistent with Equation 7. Figure 5 shows experimental results for mixtures with initial formal concentrations of 0.25M ammonium carbonate, and held at the indicated temperatures. The initial formal concentrations of acetone and of cyanide were equal in each mixture and can be calculated as the reciprocal of the intercept with the ordinate. For each trial, the reciprocal values of reactant concentration for the ordinate were calculated from measured 5,5-dmh
FIGURE 5. TEST FOR PSEUDO SECOND-ORDER RATE BEHAVIOR IN SYNTHETIC MIXTURES AT VARIOUS TEMPERATURES

$\frac{1}{c}$ VS TIME

BASED ON HYDANTOIN DATA
concentrations \( C_H \) and from the initial acetone concentration \( C_{AO} \) as

\[
\frac{1}{C_R} = \frac{1}{C_{AO} - C_H}
\]  

(8)

The linearity of the plots is consistent with pseudo second-order behavior, although the test is not conclusive because of the low levels of conversion involved.

The information in Figure 5 can be used to characterize a pseudo second-order rate constant \( k_2^* \). Values of \( k_2^* \) at the various temperatures were determined as the slopes of lines in the figure. The results are summarized in Table 6. The square of the regression coefficient is very close to unity for each trial. The rate constant is a strong function of temperature. An activation energy of 18.9 kJ-mole was calculated from a plot of \( \ln k_2^* \) vs \( 1/T \). A pseudo second-order Arrhenius factor of 7.76 liter/mole-hr was also calculated and translates into a factor of \( 2.3 \times 10^5 \) liter\(^3\)/mole\(^3\)-hr for a fourth-order rate constant. The rate constant \( k_2^* \) is expected to depend on pH because of secondary acid-base reactions, but the fourth-order constant should not. The forth-order constant was calculated on the basis of the molecular forms of the reactants as indicated in Equation 1. The pH values of these solutions were close to 9.0 and were virtually constant throughout the trials (±0.1 pH units).

C. Determination of Individual Reactant Orders

The postulated orders for ammonia and for carbon dioxide were also tested. The trial at 60\(^\circ\)C was repeated with lower concentrations of these two reactants. The ammonium carbonate standard was diluted before mixing with the
TABLE 6. DETERMINATION OF A PSEUDO SECOND-ORDER RATE CONSTANT

\( k'_2 \) and least-squares fit at various temperatures

<table>
<thead>
<tr>
<th>t (°C)</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k'_2 ) L-mole(^{-1})-hr(^{-1})</td>
<td>2.04</td>
<td>2.58</td>
<td>3.46</td>
<td>3.59</td>
</tr>
<tr>
<td>( r^2 )</td>
<td>0.996</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
</tr>
</tbody>
</table>

**Derived Rate Constant**

\[ k'_2 = A \exp\left(-\frac{E_a}{RT}\right) \]

\[ A = 7.76 \text{ L-mole}^{-1}\text{-hr}^{-1} \]

\[ E_a = 18.9 \text{ KJ} \text{- mole}^{-1} \]

\[ r^2 = 0.945 \]
standard solution of acetone and cyanide. This method was chosen because the pH of an ammonium carbonate buffer is a function of the carbon to nitrogen ratio, but is almost independent of concentration. Table 7 summarizes the results and shows that the predicted and measured ratios of rate constants are virtually identical. Although these results do not prove a first order dependence for ammonia and for carbon dioxide individually, they strongly support that contention.

Initial rates of reaction (between zero and five to nine percent conversion) were measured to distinguish the orders for acetone and for hydrogen cyanide. Table 8 shows that doubling the initial concentration of either cyanide or acetone, individually, approximately doubles the rate. This is the expected result for first-order dependencies, and is a better test than Figure 5.

Results similar to those in Figure 5 have been obtained by other investigators (Diehl et al., 1985) using slightly different reaction conditions. They used temperatures of 50°, 70°, and 90°C and solutions of pH 8.4, while monitoring concentrations of 5,5-dmh. The ranges of conversions studied were generally much smaller than the ranges monitored for the results shown in Figure 5. Because of the low conversions, the inferences of Diehl, et al., with regard to reaction order cannot be considered conclusive. Further, their conclusions were based entirely on measured concentrations of 5,5-dmh. Also, a plot of ln $k_2$ vs. temperature based on their measurements is non-linear. These facts, together with evidence presented in the remainder of this chapter, cast some doubt on the validity of a power-law model, first-order in each of the Bucherer-Bergs reactants.
**TABLE 7. FIRST ORDER DEPENDENCE OF REACTION RATE ON AMMONIA AND ON CARBON DIOXIDE**

Initial Formal Concentrations (mole·liter\(^{-1}\))

<table>
<thead>
<tr>
<th>Species</th>
<th>Solution A</th>
<th>Solution B</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH(_3)</td>
<td>0.50</td>
<td>0.25</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>0.25</td>
<td>0.125</td>
</tr>
<tr>
<td>HCN</td>
<td>0.0117</td>
<td>0.0117</td>
</tr>
<tr>
<td>acetone</td>
<td>0.0117</td>
<td>0.0117</td>
</tr>
</tbody>
</table>

Measured \(k'_{2}\) (liter·mole\(^{-1}\)·hr\(^{-1}\))

<table>
<thead>
<tr>
<th>Solution A</th>
<th>Solution B</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.58</td>
<td>0.644</td>
</tr>
</tbody>
</table>

Predicted Ratio: \[ \frac{k'_{2,A}}{k'_{2,B}} = 4.0 = \frac{k \left[ \text{CO}_2 \right]_{0, A} \left[ \text{NH}_3 \right]_{0, A}}{k \left[ \text{CO}_2 \right]_{0, B} \left[ \text{NH}_3 \right]_{0, B}} \]

Experimental Ratio: \[ \frac{2.58}{0.644} = 4.01 \]

Both solutions were maintained at 60°C.
TABLE 8.  
FIRST ORDER DEPENDENCE OF REACTION RATE  
ON ACETONE AND ON CYANIDE

<table>
<thead>
<tr>
<th>Species</th>
<th>Solution A</th>
<th>Solution B</th>
<th>Solution C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>HCN</td>
<td>0.0125</td>
<td>0.025</td>
<td>0.0125</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.0125</td>
<td>0.0125</td>
<td>0.025</td>
</tr>
<tr>
<td>Initial rate</td>
<td>(mmoles liter⁻¹ hr⁻¹)</td>
<td>0.393</td>
<td>0.762</td>
</tr>
</tbody>
</table>

Solutions were maintained at 60°C
D. Evidence Against a Pseudo Second-Order Kinetic Model

Initial doubts were raised by an experiment designed to monitor the Bucherer-Bergs reaction over a wide range of conversions. A mixture initially 1.67M in ammonium carbonate and 0.167M in both acetone and potassium cyanide was sealed in a reaction flask that was placed in an oil bath at 40°C. Figure 6 shows measured acetone concentrations as a function of time. These data were tested for pseudo second-order kinetics as shown in Figure 7. The plot of inverse concentration versus time might be considered linear over at least two regions, but with a different slope for each region. For lower conversions (t < 40 minutes, conversion < 33.5%) $k_2$ was estimated as 4.60 liter/mole-hr, with $r^2=0.979$. For higher conversions (40 < t < 600, 46.0% < conversion < 97.2%) the value of $k_2$ was 21.2 liter/mole-hr with $r^2=0.975$. This analysis reveals the danger of using only data for low conversions.

The upward curvature in Figure 7 suggests that the pseudo reaction order may be less than two. If a rate expression of the form

$$\text{rate} = k_0 [\text{acetone}]^m [\text{HCN}]^n = k_0 [\text{acetone}]^{m+n}$$

is hypothesized for reaction media of constant ammonia and carbon dioxide concentrations, $m+n$ is the pseudo reaction order. The expression may be integrated for various values of $m+n$ and the resulting equation tested with an appropriate plot of the data. Figure 8 shows a test for $m+n=1$. The downward curvature indicates that $m+n > 1$, so the power-law model that best fits the data has $1 < m+n < 2$. The 'best fit' value of $m+n$ is not as important as the conclusion that $m+n$ is not an integer. Analysis of Figures 7 and 8, then, casts doubt on the validity of a pseudo second-order power-law model for the
FIGURE 6
ACETONE CONCENTRATION VS. TIME FOR A SYNTHETIC MIXTURE AT 40°C.

INITIAL CONDITIONS:
- 1.67M AMMONIUM CARBONATE
- 0.167M ACETONE
- 0.167M KCN

MOLE PER LITER VS. TIME (MINUTES)
FIGURE 7. INVERSE ACETONE CONCENTRATION VS TIME FOR A SYNTHETIC MIXTURE AT 40°C.
FIGURE 8. TEST FOR PSEUDO FIRST-ORDER KINETICS FOR A SYNTHETIC MIXTURE AT 400°C
(-ln[ACETONE] VS TIME)
rate of formation of 5,5-dmh in the synthetic mixtures of interest.

The need for data over a wide range of conversions is supported by further consideration of Figure 5. The data shown in Figure 5 were tested for their fit to power-law expressions with pseudo reaction orders other than two. Table 9 shows that combined orders of one, two, and three all represent the data well. The power-law model is insensitive to order for conversions below 25-30%.

The strongest evidence against a simple pseudo second-order power-law model comes from measurements of cyanide concentrations. Figure 9 shows data for measured concentrations of cyanide, acetone, and 5,5-dmh for a synthetic mixture held at 60°C. This is the same trial represented in Figure 5, but includes measurements at much higher conversions. The curve marked with triangles was established by subtracting measured hydantoin concentrations from the initial concentrations of the limiting reagents (acetone and cyanide). While the acetone and 5,5-dmh curves reflect 1:1 stoichiometry, the cyanide curve does not. Rather, the cyanide curve quickly drops below the other two and remains lower throughout the trial. Careful calibrations and checks for interferences with the cyanide electrode confirmed that these results do not reflect an error in the analysis for cyanide. These same observations regarding cyanide concentrations were also true for mixtures held at other temperatures, as documented in Appendix C. The simple power-law model, first-order in all reactants, does not account for these facts, and the integral tests for order require 1:1:1 cyanide to acetone to 5,5-dmh stoichiometry.

Long-time measurements were made for the reaction run of Figure 9 and are shown in Table 10. The reaction vessel was allowed to cool to ambient temperature, and concentrations were monitored periodically. The cyanide
<table>
<thead>
<tr>
<th>Order $M + N$</th>
<th>50°C</th>
<th>60°C</th>
<th>70°C</th>
<th>80°C</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.997</td>
<td>0.998</td>
<td>0.998</td>
<td>0.996</td>
</tr>
<tr>
<td>2</td>
<td>0.996</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
<td>3</td>
<td>0.994</td>
<td>0.999</td>
<td>0.995</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Maximum % Conversion Used to Determine Least-Squares Fit: 22.3, 22.3, 25.5, 30.1
Figure 9. Time dependence of acetone, cyanide, and predicted reactant concentrations for a synthetic mixture at 600°C.

- Acetone concentration vs time
- Cyanide concentration vs time
- Reactant concentration vs time (based on hydantoin data)
TABLE 10. LONG-TIME MEASUREMENTS FOR A SYNTHETIC MIXTURE AT AMBIENT TEMPERATURE

<table>
<thead>
<tr>
<th>Days From Reaction Initiation</th>
<th>T = AMBIENT</th>
<th>8</th>
<th>34</th>
<th>49</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,5-DMH</td>
<td>8.24 x 10^-3</td>
<td>9.82 x 10^-3</td>
<td>1.02 x 10^-2</td>
<td></td>
</tr>
<tr>
<td>ACETONE</td>
<td>3.35 x 10^-3</td>
<td>1.88 x 10^-3</td>
<td>1.60 x 10^-3</td>
<td></td>
</tr>
<tr>
<td>CYANIDE</td>
<td>7.2 x 10^-4</td>
<td>2.9 x 10^-4</td>
<td>2.8 x 10^-4</td>
<td></td>
</tr>
</tbody>
</table>

ALL CONCENTRATIONS IN MOLES PER LITER
concentration fell to a very low level and then stayed approximately constant while hydantoin continued to form. Not only are the changes in cyanide concentration with time less than the corresponding changes in 5,5-dmh and in acetone, but also the absolute amount of cyanide measured is too small to account for the 5,5-dmh formed. Again, similar observations held true for other mixtures, as shown in Appendix C.

E. Tentative Explanation for Kinetic Data

Two ways to explain the anomalous values for cyanide concentration are

1. The measurement techniques might not reflect the actual reaction conditions.

and

2. One or more side-reactions might occur with other than 1:1 acetone:cyanide stoichiometry.

Several experiments were done to test these possibilities. The basic technique was to monitor the compositions of synthetic mixtures that were missing at least one of the Bucherer-Bergs reactants. These "component interaction studies" are listed in Table 11 and showed that the analytical techniques are generally adequate. Mixtures monitored at 30°C had compositions that were steady with time at the expected concentrations. Aqueous solutions of potassium cyanide and ammonium carbonate provided the only surprise. When such mixtures were maintained at 50°C, the cyanide concentration decreased with time. This fact, together with a consideration of the chemistry of cyanide in aqueous solutions, suggested the production of
<table>
<thead>
<tr>
<th>Analytical Method</th>
<th>Other Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas chromatography for acetone</td>
<td>a) cyanide; acetone cyanohydrin</td>
</tr>
<tr>
<td></td>
<td>b) ((NH_4)_2CO_3)</td>
</tr>
<tr>
<td></td>
<td>c) 5,5 dmh</td>
</tr>
<tr>
<td>HPLC for 5,5 dmh</td>
<td>a) acetone cyanohydrin</td>
</tr>
<tr>
<td></td>
<td>b) cyanide</td>
</tr>
<tr>
<td></td>
<td>c) acetone</td>
</tr>
<tr>
<td></td>
<td>d) ((NH_4)_2CO_3)</td>
</tr>
<tr>
<td>Electrode analysis for cyanide</td>
<td>a) acetone; acetone cyanohydrin</td>
</tr>
<tr>
<td></td>
<td>b) 5,5 dmh</td>
</tr>
<tr>
<td></td>
<td>c) ((NH_4)_2CO_3) T=30°C, 50°C</td>
</tr>
</tbody>
</table>
formic acid.

The presence of formic acid (pKa = 3.75) as formate ion in reaction mixtures was verified using high performance liquid chromatography with a Waters IC-PAK (quaternary ammonium functional group) anion exchange column. Interferences prevented quantification with either ultraviolet or refractive index detectors. The existence of formate ion and the observations made about Figure 9 and Table 10 led to a tentative explanation for the observed acetone:cyanide stoichiometry.

Figure 10 summarizes the hypothesis. The reaction of hydrogen cyanide and water to form formic acid and ammonia is known to proceed at temperatures greater than or equal to 50°C (Jenks, 1978). The reaction is exothermic, but has an appreciable activation energy. An equilibrium constant was calculated from free energies of formation and shows that the reaction is essentially irreversible. Formamide is expected to be an intermediate formed through a reversible reaction. Hypothetically, cyanide would be consumed by hydrolysis in parallel with the Bucherer-Bergs reaction. If the rate of formamide hydrolysis were small enough, a pseudo-equilibrium could be established for the hydrogen cyanide reaction (1). The Bucherer-Bergs reaction would continue to consume cyanide, shifting the equilibrium to the left. Initially, then, cyanide could disappear faster than hydantoin would form, and eventually the trend could reverse. This was the behavior observed in the experiments reported in this work.

Evidence is needed to support the hypothesis in Figure 10 and to quantify the effects on the rate of 5,5-dmh formation. Formamide has been identified in actual condensates, but the kinetics of formation require study. The kinetics of formic acid formation must also be characterized before the Bucherer-Bergs reaction can be accurately modelled. It is possible that other
FIGURE 10. TENTATIVE EXPLANATION FOR OBSERVED ACETONE: CYANIDE STOICHIOMETRY

\[ \text{HCN} + \text{H}_2\text{O} \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} \text{HCONH}_2 \]  

(1)

\[ \text{HCONH}_2 + \text{H}_2\text{O} \overset{k_1}{\rightarrow} \text{HCOOH} + \text{NH}_3 \]  

(2)

\[ \text{HCN} + \text{C}_3\text{H}_6\text{O} + \text{NH}_3 + \text{CO}_2 \rightarrow \text{C}_5\text{H}_8\text{N}_2\text{O}_2 + \text{H}_2\text{O} \]  

(acetone)  

(3)  

(5,5-dmh)
cyanide 'sinks' and 'sources' exist and, if so, their kinetic behavior should also be established. After these side-reactions have been accounted for, studies of the 5,5-dmh formation reaction in synthetic mixtures should continue, with independent measurements for each reaction involved. The effects of pH on the various reaction rates should be established and the results extended to process condensates. This extension will require other kinetic studies since competing reactions are known; e.g., cyanide reacts with polysulfides to give thiocyanate (Senetar and King, 1986).

F. Further Analysis and Conclusions

While the participation of cyanide in side-reactions limits the value of studies based on only 5,5-dmh, acetone, and cyanide measurements, some conclusions are still possible. In particular, the dependence of the reaction rate on acetone can be determined if the rate is assumed to be first order in cyanide. The rate is found from the slope of the 5,5-dmh vs. time curve at a given time. This rate, divided by the cyanide concentration measured at the same time, is plotted against acetone concentration. Figure 11 shows such a plot for some of the data in Figure 9. A smooth curve was drawn through the 5,5-dmh vs. time data to help establish instantaneous reaction rates. There is significant scatter in Figure 11, but the linearity indicates a first-order dependence on acetone. The scatter is due primarily to uncertainty in the cyanide measurements, and the circled points correspond to particularly questionable values of cyanide concentration (values at 430 min. and 560 min. in Figure 9). Further, the best fit line through the data extrapolates to a 0,0 intercept as expected for a first-order dependence. A plot of reaction rate divided by measured cyanide concentration, vs. measured acetone
FIGURE 11. TEST FOR FIRST-ORDER DEPENDENCE OF THE REACTION RATE ON ACETONE CONCENTRATION

Best Linear Fit Excluding

\[ y = 0.0425 \times [\text{acetone}] + 0.0001 \]

\[ r^2 = 0.924 \]
concentration is also linear with a 0,0 intercept. Therefore, if the rate is assumed to be first-order in acetone, then it must be first-order in cyanide. These arguments are consistent with the postulated rate expression, but the expression needs corroboration.
Chapter IV Summary of Conclusions

The Bucherer-Bergs reaction is the likely source of 5,5-dmh in condensate waters. All of the reactants have been identified in condensates, process temperatures are favorable for high yields, and hydantoin forms at the same rate that acetone disappears. Further, the reaction does not occur at low pH (where \( \text{CO}_2 \) is only slightly soluble), and cyanide was a limiting reagent in aged samples.

A mechanism may be postulated from evidence in the literature and leads to a simple power-law model for the reaction rate. The rate was expected to be first-order in each of the reactants. Measurements of 5,5-dmh and acetone concentrations in synthetic solutions were consistent with the hypothesis for low conversions. Kinetic parameters were calculated from these data. The data fit models with other orders as well, however, so definite conclusions are not possible. Initial rate studies offer the strongest support for the proposed expression.

Measured cyanide concentrations were anomalous. While the 5,5-dmh and acetone measurements reflected the Bucherer-Bergs stoichiometry, the cyanide measurements did not. It was found that cyanide disappears from heated ammonium carbonate solutions even in the absence of acetone. Formate ion was identified as a side product in reaction mixtures. These facts lead to a hypothesis to explain the cyanide measurements, but experimental support for this hypothesis is still needed.

The fact that the cyanide concentration changed at a different rate than the acetone and hydantoin concentrations invalidates the integral tests that were used to establish kinetic parameters. The proposed power-law model may describe the Bucherer-Bergs reaction rate, but characterization of the side
reactions is required to interpret the rate data. The measurements do show that if there is a first-order dependence on cyanide, then there is a first-order dependence on acetone, and vice versa. Further, trials with differing initial ammonium carbonate concentrations showed that the rate is probably first-order in ammonia and first order in carbon dioxide.

Acknowledgement

This work was supported by the Morgantown Energy Technology Center, Morgantown, WV, through the Assistant Secretary for Fossil Energy, Office of Surface Coal Gasification, Advanced Process Research Program of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.
Appendix A  Derivation of Rate Expressions From the Proposed
Mechanism for the Bucherer-Bergs reaction.

To derive a rate expression from a mechanism, one assumes that the rate of an elementary step is proportional to the frequency of collisions of the reactants. This, in turn, requires that the rate be proportional to the product of the reactant concentrations raised to the power of their stoichiometric coefficients. In addition, simplifying assumptions are used to allow a mathematical solution in closed form. Four often used assumptions are that one or more steps are irreversible, that there is a rate limiting step, that there is a pseudo-steady-state concentration for one or more of the intermediates, and that there is a pseudo-equilibrium condition for one or more of the steps. Various combinations of these assumptions appear in the derivations that follow.

Derivation I.

This derivation allows for 5,5-dmh formation through Scheme A and/or Scheme B in Figure 3. The first step in the molecular rearrangement is assumed to be rate limiting, and all previous steps are assumed to be in pseudo-equilibrium. A later step could have as easily been chosen as rate limiting, with the result differing only in the form of the rate constant. Figure A1 shows a shorthand version of the mechanisms of interest and definitions for the symbols used.

Assume H $\rightarrow$ I is the rate limiting step.

rate = $\frac{dK}{dt} = \frac{dI}{dt} = k_{4}C_{H}$
Assume that each previous step is in pseudo-equilibrium.

\[ k_3 C_F C_G = k_{-3} C_H \quad \longrightarrow \quad C_H = \frac{k_3}{k_{-3}} C_F C_G \]

\[ k_2 C_E C_G = k_{-2} C_F \quad \longrightarrow \quad C_F = \frac{k_2}{k_{-2}} C_E C_G \quad \longrightarrow \quad C_H = \frac{k_3 k_2}{k_{-3} k_{-2}} C_E C_G \]

\[ k_1 C_B = k_{-1} C_D \quad \longrightarrow \quad C = \frac{k_1 C_B}{k_{-1} C_D} \quad \longrightarrow \quad C_H = \frac{k_3 k_2 k_1}{k_{-3} k_{-2} k_{-1}} C_B C_E C_G \]

and/or

\[ k_j C_F = k_{-j} C_B \quad \longrightarrow \quad C_B = \frac{k_j}{k_{-j}} C_F \quad \longrightarrow \quad C_H = \frac{k_3 k_j k_1}{k_{-3} k_{-j} k_{-1}} C_B C_E C_G \]

\[ k_1 C_E = k_{-1} C_L \quad \longrightarrow \quad C_L = \frac{k_1}{k_{-1}} C_E \quad \longrightarrow \quad C_H = \frac{k_3 k_j k_1}{k_{-3} k_{-j} k_{-1}} C_B C_E C_G \]

Combining the final equation for \( C_H \) for each scheme, with the first equation, gives;

\[ \text{rate} = \frac{k_4 k_3 k_2 k_1}{k_{-3} k_{-2} k_{-1} C_D} C_B C_E C_G \]

and/or

\[ \text{rate} = \frac{k_4 k_3 k_j k_1}{k_{-3} k_{-j} k_{-1}} C_B C_E C_G \]

Since \( C_D \) is practically constant, the reaction rate at a given temperature is a constant multiplied by the concentration of each of the Bucherer-Bergs reactants.
Derivation II.

This derivation is based on Scheme B in Figure 3 and retains the assumed rate limiting step, but uses the steady-state approximation for intermediates. A very different rate expression than in derivation I results.

Assume \( H \rightarrow I \) is the rate-limiting step.

\[
\frac{dK}{dt} = \frac{dI}{dt} = k_4 C_H
\]

Use the steady-state approximation for \( H \).

\[
\frac{dC_H}{dt} = 0 \quad \longrightarrow \quad k_3 F G C_G = k_{-3} C_H + k_4 C_H \quad \longrightarrow \quad C_H = \frac{k_3 F G C_G}{k_{-3} + k_4}
\]

So;

\[
r = \frac{k_4 k_3}{k_{-3} + k_4} F G C_G
\]

Use the steady-state approximation for \( F \).

\[
\frac{dC_F}{dt} = 0 \quad \longrightarrow \quad k_2 C_E C_G = k_{-3} C_H = k_{-2} C_F + k_4 C_G
\]

Then;

\[
C_F = \frac{k_2 C_E C_G + k_{-3} C_H}{k_{-2} + k_4 C_G} \quad \longrightarrow \quad C_F = \frac{k_2 C_E C_G + \frac{k_{-3} k_3}{k_{-3} + k_4}}{k_{-2} + \frac{k_{-3} k_4}{k_{-3} + k_4}} G C_G
\]
Rearranging:

\[ C_F(k_{-2} + k_3C_G) - C_F \frac{k_{-3}k_3}{k_3 + k_4} C_G = k_2C_CC_E \quad \Rightarrow \quad C_F = \frac{k_2C_CC_E}{k_{-2} + k_3C_G - \frac{k_{-3}k_3C_G}{k_3 + k_4}} \]

and:

\[ r = \frac{k_4k_3}{(k_{-3} + k_4)} \frac{k_2}{k_{-2} + k_3C_G - \frac{k_{-3}k_3C_G}{k_3 + k_4}} C_CC_E \]

Use the steady-state approximation for C.

\[ \frac{dC_C}{dt} = 0 \quad \Rightarrow \quad k_1C_AB + k_{-2}C_F = k_{-1}C_CD + k_2C_CE \]

So;

\[ C_C = \frac{k_1C_AB + k_{-2}C_F}{k_{-1}C_D + k_2C_CE} = \frac{k_{-2}k_2C_CE}{k_{-2} + k_3C_G - \frac{k_{-3}k_3C_G}{k_3 + k_4}} \]

Rearranging:

\[ C_C(k_{-1}C_D + k_2C_CE) - \frac{k_{-2}k_2C_CE}{k_{-2} + k_3C_G - \frac{k_{-3}k_3C_G}{k_3 + k_4}} = k_1C_AB \]

and

\[ C_C = \frac{k_1C_AB}{k_{-1}C_D + k_2C_CE - \frac{k_{-2}k_2C_CE}{k_{-2} + k_3C_G - \frac{k_{-3}k_3C_G}{k_3 + k_4}}} \]
Therefore;

\[ r = \frac{k_4 k_3}{(k_{-3} + k_4)} \frac{k_2}{k_{-3} + k_3 C_G} - \frac{k_{-3} k_3 C_G}{k_{-3} + k_4} \frac{k_1}{k_{-3} + k_4} C_B C_E C_G \]

This can be put in other forms and may simplify, but it appears that the rate will not have a simple first-order dependence on either hydrogen cyanide or carbon dioxide.
**FIGURE A1** SHORTHAND REPRESENTATIONS OF BUCHERER-BERGS MECHANISMS

Scheme B (for Derivations I & II)

\[
\begin{align*}
A + B & \xrightleftharpoons[k_1]{k_{-1}} C + D \\
C + E & \xrightleftharpoons[k_2]{k_{-2}} F \\
F + G & \xrightleftharpoons[k_3]{k_{-3}} H \\
H & \xrightarrow[k_4]{k_5} I \xrightarrow[k_6]{k_5} J \xrightarrow[k_6]{k_5} K
\end{align*}
\]

Definitions

A ≡ C₃H₂O (acetone)
B ≡ NH₃
C ≡ \(\text{CH}_3\text{C}=\text{NH}\)
D ≡ H₂O
E ≡ HCN
F ≡ \(\text{CH}_3\text{NH}_2\)
G ≡ CO₂
H ≡ \(\text{CH}_3\text{C}^\text{NH}^\text{OH}\)
I ≡ \(\text{CH}_3\text{C}^\text{N}=\text{C}=\text{O}\)
J ≡ \(\text{CH}_3\text{C}^\text{N}^\text{C}=\text{NH}_2\)
K ≡ 5,5-dmh
L ≡ C₄H₇ON (acetonecyanohydrin)

Scheme A (for Derivation I)

\[
\begin{align*}
A + E & \xrightleftharpoons[k_1]{k_{-1}} L \\
L + B & \xrightleftharpoons[k_j]{k_{-j}} F \\
F + G & \xrightleftharpoons[k_3]{k_{-3}} H \\
H & \xrightarrow[k_4]{k_5} I \xrightarrow[k_6]{k_5} J \xrightarrow[k_6]{k_5} K
\end{align*}
\]
Appendix B Analytical Methods.

1. High Performance Liquid Chromatography (HPLC)

HPLC was used to quantify 5,5-dmh concentrations. A Spectra-Physics Model 3500B Liquid Chromatograph provided flow control. Detection was accomplished with a Waters Associates Model 400 Absorbance Detector with an Extended Wavelength Module. Preliminary tests with a Perkin Elmer Model LC-75 Variable Wavelength Spectrophotometric Detector revealed that 5,5-dmh has a relatively strong absorbance in the range of 210-220 nanometers, and so a fixed wavelength of 214 nm (zinc source) was chosen for the extended wavelength module. The fixed wavelength ultraviolet bulb has a greater intensity than a variable wavelength bulb at 214 nm so that detection is more sensitive.

The measurement of 5,5-dmh concentrations employed isocratic reversed-phase chromatography. The stationary phase was a C\textsubscript{18} Radial-Pak uBondapak column with 8 mm internal diameter, 10 cm length, and 10 μm irregular particles. This stationary phase is nonpolar and facilitates the separation of non-ionized solutes in a polar mobile phase. Radial compression of the column with a Waters Associates Z-Module enhanced the separation efficiency. A pH-3 phosphate buffer was used as the mobile phase and suppressed the ionization of acidic solutes. The buffer contained 0.544 g KH\textsubscript{2}PO\textsubscript{4} and 0.113 ml concentrated H\textsubscript{3}PO\textsubscript{4} per liter of water. Inorganic ions and organic contaminants were removed from the water through double-distillation followed by adsorption onto Millipore Milli-Q filters, before the buffer was prepared. Synthetic reaction mixtures were also prepared with this 'Milli-Q' water. The buffer was filtered to remove particles larger than 0.45 μm before being pumped through the column.
All samples were filtered through a Millex-SR 0.5 μm filter unit (Millipore Corporation) before injection. 20 μl aliquots were injected. Injection of condensate water for the limiting reagent experiments required pretreatment. A Waters Associates Sep-Pak C\textsubscript{18}-Cartridge was used to adsorb any compounds that could not be eluted from a C\textsubscript{18} chromatography column. The Sep-Pak was pretreated with Spectrophotometric grade methanol (Mallinckrodt) to wet the substrate. Condensate was pipetted into a syringe under nitrogen atmosphere and pushed through the cartridge into a glass vial. An equal volume of Milli-Q water was then passed through the cartridge and collected in the vial. Finally, a volume of methanol equal to the condensate volume was passed through the syringe and into the vial. These volumes of water and methanol were sufficient to elute all solutes of interest from the Sep-Pak. The final mixture had one-third of the initial condensate solute concentrations. Hydantoin concentrations were established by comparing peak areas with a calibration curve. 5,5-Dmh (97%) from Aldrich Chemical Company was used to establish the curve. Standard solutions had steady concentrations over time.

Formate was identified through co-chromatography with an IC-Pak A (Waters Associates) anion-exchange column. Milli-Q water was the mobile phase. More complete separation of formate from reaction mixtures was possible with a C\textsubscript{18} column placed upstream of the anion-exchanger. Refractive index detection (with a Waters Associates Differential Refractometer-R401 and Electronics Unit) and u.v. detection at various wavelengths showed peaks at the same retention time as a formate standard, but accurate quantitative measurements were not possible. When measured amounts of formate were added to reaction mixtures, anomalous peak areas were measured. This problem can probably be resolved with an appropriate choice of the mobile phase.
2. Gas Chromatography (GC)

Acetone concentrations were determined with a Varian Associates 3700 Gas Chromatograph. Flash injection and flame-ionization detection were used; nitrogen was the carrier gas (mobile phase). The column was a 3-foot long, 1/8-inch-o.d., 26-gauge stainless steel tube packed with Waters Associates Porapak-Q particles (100-120 mesh). These particles are porous polymer beads with polar monomers incorporated into the basic polymer structure. A column temperature of 140°C gave sharp reproducible peaks with low retention times (volumes). 1.0 μl injections were used, and peak areas were compared to a calibration curve to establish concentrations. The calibration curve was established with several aqueous solutions with known concentrations of Spectrophotometric Grade (Mallinckrodt) acetone.

3. Silver/Sulfide Electrode

Cyanide ion concentrations were determined with an Orion Model 94-16 Silver/Sulfide Electrode and silver potassium cyanide indicator. The electrode includes a solid silver sulfide membrane in which silver ions can migrate. When silver potassium cyanide is added to a sample, the ion $\text{Ag(CN)}_2^-$ liberates small amounts of silver and cyanide ions. The higher the activity of cyanide ions in a sample, the more migration within the membrane. Migration establishes a potential difference and the electrode potential (at a fixed location) is measured relative to a separate reference electrode. Since the degree of dissociation of $\text{Ag(CN)}_2^-$ depends on the cyanide ion concentration, this method provides an indirect measure of free cyanide.

The Nernst equation relates the measured potential ($E$) to the reference potential ($E_0$) as
\[ E = E_0 - \frac{RT}{(1)F} \ln \frac{(Ag(s))}{(Ag^+)} \]

\[ = E_0 - \frac{RT}{F} \ln \frac{1}{(Ag^+)} \]

\[ = E_0 + S' \log (Ag^+) \]

where \( S' \) has a value between 58 and 59 mv for typical room temperatures. The silver ion activity is related to that of cyanide by:

\[ \frac{(Ag^+)}{\beta_2 (CN^-)^2} = \frac{(Ag(CN)_2^-)}{\beta_2 (CN^-)^2} \]

\( \beta_2 \) is the overall formation constant of \( Ag(CN)_2^- \). Substitution gives:

\[ E = E_0 + S' \log \frac{(Ag(CN)_2^-)}{\beta_2 (CN^-)^2} \]

Activity coefficients for the three ions are constant for the measurements because the ionic strength was maintained at a constant level. Therefore:

\[ E = E_0 + S' \log \frac{\gamma_{Ag(CN)_2^-}^2}{\beta_2 \gamma_{CN^-}^2} + S' \log \frac{[Ag(CN)_2^-]}{[CN^-]^2} \]

\[ = E'_0 + S' \log \frac{[Ag(CN)_2^-]}{[CN^-]^2} \]

Dissociation of silver cyanide ion is very slight in aqueous samples (\( \beta_2 = 1.26 \times 10^{26} \)), so it's concentration is essentially constant. Further, the concentration of cyanide ion is essentially that of the original sample. These facts suggest that:
\[ E = E'_o + S' \log \frac{\text{constant}}{[CN^-]^2} \]

\[ = E''_o - 2S' \log [CN^-] \]

\[ = E''_o - S \log [CN^-] \]

S is called the electrode slope and is the potential change caused by a factor of ten increase in cyanide activity.

The experimental procedure for measuring cyanide concentrations in a reaction mixture included several steps. 100, 10, 1, and 0.1 ppm CN\(^-\) standards were prepared by serial dilution of a standardized KCN stock solution containing 1000 ppm CN\(^-\). The diluent was 0.625 M NaOH.

An indicator/buffer solution was prepared with 33 g of disodium hydrogen phosphate heptahydrate added to 75 ml Milli-Q water. This mixture was stirred for thirty minutes to saturate the liquid with phosphate. 2.2 g of sodium hydroxide, 0.1 gm of silver potassium cyanide, and 3.4 ml of ethylenediamine were then added. Continued stirring was required to dissolve the solids.

Ethylenediamine and silver potassium cyanide are toxic chemicals and must be handled with care. Rubber gloves were required and mixing was done under a fume hood. Indicator solutions tended to precipitate Ag\(_2\)(CN)\(_2\), sometimes within twentyfour hours of preparation. Measures to prevent this included storage in a brown glass bottle and in a darkened area, storage in an agitated water-bath thermostatted to a temperature between 25 and 30° C, and/or addition of 1% excess cyanide. The latter precaution requires a correction to measured cyanide concentrations.

One ml of indicator-buffer was added to 50 ml of a standard and the
millivolt response of the electrodes recorded. Repetition of this process established a calibration curve used to interpret sample measurements. A sample consisted of 2 ml of the reaction mixture diluted to 50 ml with NaOH diluent, and 1 ml of indicator-buffer. Dilution with NaOH not only converted HCN to cyanide ion allowing a measurement of total 'free' cyanide, but also served to quench the Bucherer-Bergs reaction by lowering the solution temperature and the reactant concentrations. Measurements were made for dilute aqueous samples of acetone cyanohydrin, and showed that all of the cyanide was in the free form after dilution with NaOH. Magnetic stirring was used throughout the trials, and samples and standards were at approximately the same temperature.

4. Ammonia Electrode

Aqueous concentrations of ammonia were measured with an Orion Model 95-10 specific gas electrode. The pH's of samples and standards were adjusted with ~1 ml of 10 M NaOH per 100 ml of sample. Since the resulting pH's were greater than 11, all of the ammonia species were converted to NH$_3$, the form sensed by the electrode.

The electrode has a hydrophobic gas-permeable membrane through which NH$_3$ diffuses, but the sensing element is a pH electrode. The gas diffuses into a filling solution of constant ammonium ion activity until the NH$_3$ activity is the same on both sides of the membrane. The NH$_3$ activity is proportional to the hydroxide ion activity in solutions of constant ammonium ion activity. The Nernst equation for the pH electrode can therefore be written in terms of NH$_3$:

$$ E = E_0 - \frac{RT}{(1)F} \ln (OH^-) $$
\[
E = E'_0 - \frac{RT}{F} \ln \frac{(NH_3)_b}{(NH_4^+)}
\]

\[
= E'_0 - S \log(NH_3)
\]

\(E'_0\) is established by an internal reference electrode that responds to a fixed level of chloride in the filling solution. \(S\) is between 56 and 58 mv at typical room temperatures.

Measured potentials were compared to a calibration curve to establish ammonia concentrations. The curve was prepared by measuring potentials of ammonium chloride standards. Standards and samples were at the same temperature and had approximately the same ionic strength. These precautions kept activity coefficients fairly constant and allowed calibration based on ammonia concentration rather than on ammonia activity. Ammonia concentrations remained almost constant in the synthetic reaction mixtures monitored in this work.

5. Carbon Dioxide Electrode

Total carbonate concentrations were monitored with a carbon dioxide gas-sensing electrode. Five ml of a buffer solution were added to 50 ml samples to lower the pH and convert all carbonate species to the CO\(_2\) form. The buffer contained 294 g of sodium citrate, and enough Milli-Q water to make one liter of solution. Enough concentrated HCl was added to this mixture to bring the pH to 4.5. The final pH of most samples with buffer was close to 5.
The electrode membrane is permeable to CO₂. The gas diffuses into a filling solution of constant bicarbonate ion activity causing a proportional increase in hydrogen ion activity. The sensing element is a pH electrode and the Nernst equation can be written as;

\[ E = E_0 + \frac{RT}{(1)F} \ln (H^+) \]

\[ = E_0 + \frac{RT}{F} \ln \frac{(CO_2) K_a}{(HCO_3^-)} \]

\[ = E'_0 + S \log (CO_2) \]

\(E'_0\) is established by an internal reference electrode that responds to a fixed level of chloride in the filling solution. \(S\) is between 55 and 57 mv at typical room temperatures.

Measured potentials were compared to a calibration curve to establish CO₂ concentrations. Sodium bicarbonate standards were used to prepare the curve. Standards and samples were at the same temperature and had approximately the same ionic strength. These precautions kept activity coefficients constant so that calibration could be based on bicarbonate concentration. Carbonate concentrations were virtually constant in synthetic reaction mixtures.
Appendix C  Additional Experimental Results

The primary purpose of this appendix is to document additional experimental results that support the conclusions reached in this report. In particular, measured 5,5-dmh, acetone, and cyanide concentrations for synthetic mixtures held at various temperatures, are plotted in Figures C1, C2, and C3. Some of the 5,5-dmh measurements were used to establish Figure 5 in Chapter III. Long-time measurements for a solution at ambient temperature are reported in Table C1.

Figure C1 presents measured acetone, cyanide, and 5,5-dmh concentrations as a function of time for a synthetic mixture held at 50°C. Initial formal concentrations in the mixture were

\[
[\text{acetone}]_o = [\text{cyanide}]_o = 11.80 \times 10^{-3} \text{M} \\
[\text{NH}_3]_o = 0.50 \text{M} \\
[\text{CO}_2]_o = 0.25 \text{M}
\]

The curve marked with triangles was established by subtracting measured 5,5-dmh concentrations from the initial concentrations of acetone and cyanide. Coincidence of this curve with the curve for acetone, shows that there was 1:1 acetone to 5,5-dmh stoichiometry. The cyanide curve is not coincident, and this fact supports conclusions drawn in Chapter III about Figure 9.

Figure C2 was developed in the same way as Figure C1, under slightly different experimental conditions. A synthetic mixture was held at 70°C and had the following initial formal concentrations.

\[
[\text{acetone}]_o = [\text{cyanide}]_o = 11.33 \times 10^{-3} \text{M}
\]
\[
\begin{align*}
[NH_3]_0 &= 0.50M \\
[CO_2]_0 &= 0.25M
\end{align*}
\]

Again, the curve for cyanide falls below those for measured acetone and 5,5-dmh concentrations. The cyanide measurements in this trial are subject to more doubt than those reported in Figure 9 and in Figure Cl. A precipitate formed in the indicator/buffer solution approximately 3 hours after the trial began.

Acetone and 5,5-dmh concentrations were also measured for a synthetic solution held at 80°C. No cyanide measurements were made. Initial formal concentrations were calculated as,

\[
[\text{acetone}]_0 = [\text{cyanide}]_0 = 12.35 \times 10^{-3} M
\]

\[
[NH_3]_0 = 0.50M \\
[CO_2]_0 = 0.25M
\]

Initial concentrations were calculated, (for all kinetic experiments detailed in this report), rather than measured directly, because standardized solutions were mixed to initiate 5,5-dmh formation.

Figure C3 shows the measured values of concentration in the same form as in Figures 9, Cl, and C2. The separation between the two curves may be due to an error in the calculated value of the initial concentration of acetone. More of the ammonium carbonate standard or less of the acetone and cyanide standard than believed, may have been introduced to the reaction vessel. Nevertheless, the calculated value of the initial cyanide concentration, and the measured 5,5-dmh concentrations, were used in constructing Figure 5.

Long-time measurements were made for the synthetic solution held at 70°C
and discussed above. After ~27 hours at 70°C, the reaction vessel was allowed to cool to ambient temperature, and concentrations were monitored periodically. The results are reported in Table C1.

Between 8 and 40 days, the 5,5-dmh concentration increased approximately as much as the acetone concentration decreased. The cyanide concentrations for 17 days and for 40 days may be regarded as approximately equal to each other, within the accuracy of the measurement technique. As was true for the long-time measurements discussed in Chapter III, section D, the changes in cyanide concentration with time were less than the corresponding changes in 5,5-dmh, and in acetone. Further, the absolute amount of cyanide measured is too small to account for the 5,5-dmh formed.
FIGURE C1  TIME DEPENDENCE OF ACETONE, CYANIDE, AND PREDICTED REACTANT CONCENTRATIONS FOR A SYNTHETIC MIXTURE AT 50°C

- Acetone Concentration vs Time
- Cyanide Concentration vs Time
- Reactant Concentration vs Time (based on hydantoin data)
FIGURE C2  TIME DEPENDENCE OF ACETONE, CYANIDE, AND PREDICTED REACTANT CONCENTRATIONS FOR A SYNTHETIC MIXTURE AT 700°C

- Acetone Concentration vs Time
- Cyanide Concentration vs Time
- Reactant Concentration vs Time (based on Hydantoin Data)
FIGURE C3  TIME DEPENDENCE OF ACETONE AND PREDICTED REACTANT
CONCENTRATIONS FOR A SYNTHETIC MIXTURE AT 80°C

- Acetone Concentration vs Time
- Reactant Concentration vs Time
  (based on hydantoin data)
### TABLE C1. Long-Time Measurements for a Synthetic Mixture at Ambient Temperature

<table>
<thead>
<tr>
<th>Days From Reaction Initiation</th>
<th>T = Ambient</th>
<th>8</th>
<th>17</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,5-DMH</td>
<td></td>
<td>8.18 x 10^{-3}</td>
<td>9.94 x 10^{-3}</td>
<td>1.01 x 10^{-2}</td>
</tr>
<tr>
<td>ACETONE</td>
<td></td>
<td>3.46 x 10^{-3}</td>
<td>1.65 x 10^{-3}</td>
<td>1.59 x 10^{-3}</td>
</tr>
<tr>
<td>CYANIDE</td>
<td></td>
<td>1.02 x 10^{-3}</td>
<td>3.57 x 10^{-4}</td>
<td>3.35 x 10^{-4}</td>
</tr>
</tbody>
</table>

All concentrations in moles per liter
REFERENCES


Wohler, F. CHEMSA, 1979, 5, 71-73.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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