ANNUAL REPORT

on

SPECTROSCOPIC AND PHOTOCHEMICAL STUDY OF MOLECULES IMPORTANT IN CHEMICAL EVOLUTION

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Corrected Summary of Results
Using Hot Hydrogen Atoms
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I. INTRODUCTION

The primary broad goals of this research are to investigate (1) the possible reactions responsible for generation of compounds important in chemical evolution, and (2) reactions of compounds important in chemical evolution. In both cases the interest includes molecules that exist in interstellar space as well as those present on or near other planets and those which were thought to be present on or near the primitive earth.

More specifically the research is directed towards the following goals:

(1) to postulate and verify a general mechanism by which complex molecules are made from simpler ones.

(2) to deduce which reactants and conditions are most meaningful and pertinent to model systems used for chemical evolutionary studies.

(3) to deduce the nature of the products producuced.

(4) to deduce any common denominators present for different reactions.

(5) to deduce the physical bases and sequence of reactions leading to products.

In the case of item 1 above, a good example of concern is how to postulate a general mechanism by which relatively complex organic molecules

(meaning those containing carbon) can be generated at very low ambient temperatures and very low molecular concentration, such as exists in interstellar space.

We are investigating photochemical reactions (those in which light is required) and thermal reactions (where heat is required). In the thermal case, subdivision is possible wherein in one case, all of the reactant molecules participating are of approximately the same temperature and another case, where one of the reactant molecules is at substantially higher temperature than the others. This latter case constitutes a unique kind of thermal reactions known as hot atom reactions which shall be discussed in more detail in a later section. We believe this type of reaction may constitute a unique mechanism for production of rather complex organic molecules under conditions where ordinarily no reactions would occur.

In those cases where light is involved, we direct our attention to:

(1) the utilization of the light absorbed in terms of whether light is re-emitted and/or used for photochemical reaction and when possible, the efficiency of use of the light for product formation.

(2) the dependence of the nature and quantity of products generated upon the wavelength of light used and the temperature at which the reaction is carried out.

Finally, it is worthwhile to point out that we expend considerable effort in the directions of employing unique techniques and instrumenta-

tion to ilucidate the mechanisms (pathways) of reactions and the identification of products of reactions. For example, from 2-4 instruments are commonly used to provide identification of products. In addition unique light sources of high intensity and short lifetime are utilized to aid in identification of intermediate species in a reaction sequence. Furthermore, these same light sources are used as energy sources for creation of new reactions.

II. Reactions Investigated Results and Conclusions

A. Hot H Atoms Reactions In Chemical Evolution

Some 23 molecules have been discovered in interstellar space and of these, 17 are organic molecules of varying complexity. In addition, there are indications that methane has been detected by absorption in the infrared. It has recently been stated that "there is no quantitative theory for formation of polyatomic molecules in interstellar space ... interstellar chemistry requires new insights into the basic understanding of chemical reactions."

Radio observations indicate that interstellar molecules are associated with clouds which contain gas and dust. Within clouds the temperature ranges between $-440^{o}F$ to $-100^{o}F$ and dust grains are estimated to be $-320^{o}F$. The gas density of clouds may vary from 1 to 10^{5} hydrogen atoms per cubic inch.

At least two major efforts indicate that polyatomic molecules were formed or released in the clouds where they now occur. The lifetimes of molecules in clouds with a few magnitudes of extinction become of the order of 10^{6} years.

The time scale for three molecules to collide in interstellar space under the conditions of the low density is greater than the age of the universe. Thus chemical reactions are limited to two-body gas phase processes or take place on surface of dust particles.

All of the conditions of extremely low density and low temperature would seem to preclude almost any type chemistry that could lead to complex organic molecules. However, we wish to propose one possibility that we believe is very reasonable for such molecules to be produced even under the extremely low pressure and temperature conditions.

The proposition entails the use of hot hydrogen (H) atoms as reaction initiators and these are created by any number of ways including photolysis of organic molecules already present in interstellar space. Hot hydrogen atoms means atoms which are translationally hot (have high velocity or speed) and whose energy (kinetic) can vary over a wide range. Commonly for chemical interest this is from approximately 11 to approximately 230 kcal (per mole). It is believed that the probability for several types of reactions are highest in this energy region region. It is of primary importance to strongly stress the point that in interstellar space, hot H atoms stay hot and do <u>not</u> attain the ambient low temperatures until after multiple collisions. Because of the low molecular density, this could take many years. More will be said on this point shortly.

The observed chemical reactions of hot hydrogen atoms denoted as H^*, are as follows:

abstraction of hydrogen atoms (1)

$$RH + H^* \rightarrow R\cdot + H_2$$

where R· is a reactive chemical species known as a free radical,

substitution reactions (2)

$$H^* + CD_4 \rightarrow CD_3H + D$$

where D is a deuterium atom,

addition reactions (3)

$$H^* + C_2H_4 \rightarrow C_2H_5\cdot$$

where $C_2H_5\cdot$ is a chemical reactive fragment known as a free radical.

Changes in temperature have only a small affect on the average energy required for the foregoing reactions provided the energy of the hot hydrogen atom is not borderline for reaction to occur at all. The probability of a hot hydrogen atom reacting as in reaction 1 above (to abstract a hydrogen atom and leave a reactive free radical species) compared to that at room temperature (as for example 80^oF) is 100,000 to 1. Thus, it can be seen that the probability for such a reaction is dramatically increased by making the reacting hydrogen atom a hot one (one of high speed or kinetic energy).

In the laboratory, hot hydrogen atoms are created by irradiating certain molecules with light whereby a bonded hydrogen atom is ejected as from hydrogen sulfide (H_2S):

$$H_2S \xrightarrow{\text{light}} H^* + HS\cdot \qquad (4)$$

If the reactant molecule, such as H_2S, is carefully chosen the energy of the ejected hot hydrogen atom can simple be determined as the difference between the energy associated with the light and the energy of the original bond involving the hydrogen atom.[1]

[1] Even if the molecule were not carefully chosen, in many cases the proper correction factors are known so that the energy of the hot hydrogen atom can be ascertained.

Finally, before discussing the actual reactions we have investigated it is important to discuss the conditions referred to as thermal equilibrium and thermal non-equilibrium. For our particular interest, we are interested in this matter regarding temperature and its meaning. When a system is in thermal equilibrium, we mean that the molecules are colliding very frequently, and that there is an average speed or velocity for the molecules of the system and it does not change. This also means an average temperature can be defined for the system. This is the common circumstance for almost all systems where the density of molecules is high such as on earth. However, in interstellar space where the density of molecules is very low, molecules collide only rarely; therefore, if for some reason a molecule attained a high velocity (a hot molecule), it could remain this way for a very long time, and not be in thermal equilibrium with its surroundings (not have the same average velocity as the other molecules in the system). In such a case, this is a non-equilibrium system. Thus, despite the fact the ambient temperature of the surroundings (all other molecules and dust) may be very low, the "temperature of the high velocity molecule would be very high.[1] The foregoing is true for any situation until the hot molecule has had a sufficient number of collisions to slow it down to somewhere near the

[1] The term temperature is put in quotations since the term temperature can rigorously be used only for a system in equilibrium; however, it can be roughly used to describe the velocity of molecules, the higher the velocity of molecules, the higher the temperature.

average velocity (temperature of other molecules in the system. Thus, we can reproduce a non-equilibrium (thermal) system in the laboratory by irradiating molecules which eject a hydrogen atom of high velocity which until it has had a great many collisions, is hot and at a considerably higher "temperature" than the surroundings (other molecules). At least in this sense, we reproduce a non-equilibrium (thermal) equilibrium which must exist in interstellar space (including the gas-dust clouds).

It should be emphasized that since the ambient temperature in interstellar space is in the vicinity of -320^{o}F, most chemical reactions would not occur or would be extremely slow. However, it is just the possibility of a non-equilibrium condition where some atom(s) are hot and not in thermal equilibrium (at the same low temperature as the others) that permits reactions to occur that ordinarily could not. The basic idea of hot atoms as a reaction initiators is also valid for reactions occurring in the atmospheres of planets as well.

We have investigated a variety of systems where two different molecules have acted as hydrogen atom (hot) donors, the latter of which were created by use of light (see equation 4). These hot hydrogen atoms have been permitted to impinge on a variety of substrate molecules such as methane (CH_4), ethane (C_2H_6), ammonia (NH_3), carbon monoxide (CO), and water (H_2O) or these in combination and products detected. Mercury was rigorously excluded from the systems so as not to introduce another pathway for reaction to occur. That is, mercury can absorb light, transfer energy by collision to a substrate molecule which can decompose or react with another molecule.

Another published study using ethane, ammonia, water plus hot hydrogen atoms found up to six amino acids could be produced. It was suggested that these amino acids did not occur primarily as free ones but were released upon reaction of a polymer or another precursor by hydrolysis (reaction with acidic water). Furthermore, mercury was not carefully excluded in several experiments and therefore some of the reactions would well have been induced by the mercury atoms that absorbed light. Finally, it was stated in the study that methane would not undergo reactions with hot hydrogen atoms and therefore no products resulted from mixtures of it with ammonia and water (and hot hydrogen).

The goals of our hot hydrogen atom study are (1) to determine if reactions do occur (2) the nature of the products formed with particular interest focused on biomolecules of prime interest in chemical evolution such as amino acids, (3) the mechanism or pathway of the reactions including what molecules may act as intermediates for the production of biomolecules of prime interest in chemical evolution and (4) determine the energy requirements for certain products to be created from mixtures of substrate molecules.

Table I presents a summary of the results obtained from a variety of experiments. We shall briefly describe the significance of these experiments.

In experiment I the results clearly indicated that it was possible to obtain significantly important biomolecules in the form of three amino acids. In order to be sure these products were formed by initiating reactions involving hot hydrogen atoms, experiment II was performed which

involved only heating of the initial reactants at an even higher temperature for the same length of time as in experiment I. The absence of amino acids proved that hot hydrogen atoms were necessary initiators of the reactions, finally producing amino acids. Also, in experiment I as well as several other of the experiments as VI, VII, certain additional products were formed which could not be identified.

Experiment III was similar to experiment I except H_2S was used as the source of hot hydrogen atom. More amino acids were obtained and in particular a sulfur containing one, cysteine was found. The use of H_2S as the hot hydrogen atom source makes analysis of the products easier since molecules do not arise from reactions of fragments of H_2S as they do for CH_3SH.

Experiments IV, V, VIII, IX were performed for a special reason. Since the mechanism or pathway for formation of the amino acids is too complex for elucidation at the present time, reactions involving two components only (plus hot hydrogen atom source) were carried out to get some insight into possible intermediates between the reactants (substrates) and the amino acids. Experiments IV and V indicated ethyl alcohol and organic acids (acetic and propionic) could be intermediates. Experiments VIII and IX indicated organic amines (methyl or ethyl amine) could also be intermediates.

On the basis of these reactions, ethyl alcohol was chosen as a new reactant because a sufficient amount of it would be present in the gas phase to at least potentially react (there would be significantly less in the gas phase in the case of the organic acids). Consequently

experiment V employed ethyl alcohol and ammonia (plus a hot hydrogen atom source, H_2S). Indeed, the results showed a substantial increase in the number of amino acids, from five (experiment III) to nine (experiment VI). Experiment VII was performed to determine the significance of water being present in addition to the ethyl alcohol. The result was very interesting in that although the same number of amino acids were produced as in experiment VI, there was a significant redistribution of the relative quantities. Whereas the amount of each amino acid was approximately the same in experiment VI, in experiment VII (added H_2O), 95% of the total quantity of amino acids was found as glycine. In fact a significant absolute quantity was found, namely 0.05 milligram.

Experiment XI was carried out to determine if a substrate with only one carbon atom, namely methane, could serve as a reactant to ultimately produce amino acids all of which contain multiple carbon atoms. To be assured that any positive result was significant, extremely pure methane (99.97% minimum) was used such that no multiple carbon containing reactant would be present. Indeed, we identified the same 9 amino acids as found in experiment VI and even more than in experiment III where ethane (2 carbon atoms) was a reactant. The latter result may not be significant since variation in the amount of light and its wavelength distribution may affect the results. Nonetheless, the experiment proves methane as a reactant can lead to multiple carbon containing products (amino acids in this case).

Experiment X was performed to determine if it would be possible to produce from carbon monoxide and water (initiated by hot hydrogen) the

molecule formaldehyde (see section C) which is abundant in interstellar clouds. At least under the experimental conditions used, formaldehyde was not detected.

Several very significant conclusions can be drawn from these experiments.

(1) hot hydrogen atoms can initiate reactions among simple molecules to produce biomolecules of significance.

(2) The one carbon reactant, methane, can participate in reactions leading to multiple carbon containing biomolecules of significance (as amino acids). This is important because large amounts of methane existed on the primitive earth, is existent near some planets and may exist in interstellar space (clouds). The two carbon reactant, ethane, is not a necessary reactant.

(3) In none of our cases were hydrolysis conditions (acidic water solutions and heat) used prior to the identification of the amino acids. This indicates substantial amounts of amino acids exist as such and need not arise from a polymer precursor produced in the reactions (hot hydrogen atom initiated).

(4) In addition to amino acids, other significantly important molecules can be produced by reactions initiated by hot hydrogen atoms such as ethyl alcohol, acetic acid and organic amines. Furthermore it appears that some of these

are intermediates in the production of the amino acids.

(5) The first intermediate formed after attack by the hot atom is a reactive chemical fragment known as a free radical These in turn attack other reactants ultimately leading to the various products. The details of the nature of these reactions is not known at the present.

(6) Hot hydrogen atoms could be important initiators of reactions which ordinarily could not occur under the environmental conditions present (such as in interstellar space). However, the importance of such a possibility is not limited to these conditions but is also important in planetary atmospheres where the probability of occurrence of such reactions is still much higher because of the greater density of molecules.

TABLE I SUMMARY OF RESULTS USING HOT HYDROGEN ATOMS

Experiment	Reactants[a] (Pressure in cm Hg)	Lowest Temperature	Irradiation Time	Light Source	Amino Acids Detected	Other Products Detected
I	CH_3SH = 42.5 C_2H_6 = 12.5 NH_3 = 12.5 H_2O = 9	30°C	14 days	1 kw Xe lamp	Aspartic Glycine Cysteine	CH_3SSH, CH_3SSCH_3 and other amino compounds that are either more acidic or more basic than normal amino acids
II	CH_3SH = 42.4 C_2H_6 = 12.5 NH_3 = 12.5 H_2O = 9	50°C for 14 days	0	none	none	none
III	H_2S = 47.5 C_2H_6 = 12.5 NH_3 = 12.5 H_2O = 9	50°C	14 days	1 kw Xe lamp	Aspartic Glycine Glutamic Alanine Cysteine	Sulfur
IV	CH_3SH = 37.5 C_2H_6 = 37.5 (or CH_4) H_2O = 9.0	50°C	14 days	500 W High pressure Hg lamp I[c]	- - -	C_2H_5OH, CH_3SSH (or CH_3OH) CH_3SSCH_3
V	CH_3SH = 37.5 C_2H_6 = 37.5 H_2O = 9	50°C	14 days	500 W High pressure Hg lamp I[c]	- - -	CH_3COOH, C_2H_5COOH, CH_3SSH, CH_3SSCH_3, C_2H_5OH

Experiment	Reactants[a]	Lowest Temperature (°C)	Irradiation Time	Light Source	Amino Acids Detected	Other Products Detected
VI	H_2S = 25 NH_3 = 12.5 C_2H_5OH[e] = 7	30°C	21 hours	500 W High Pressure Hg lamp II[d]	Serine or Threonine Glycine Alanine Aspartic Valine Glutamic Leucine Isoleucine Proline	Sulfur and some other amino compounds which are either more acidic or more basic than normal amino acid
VII	H_2S = 25 NH_3 = 12.5 C_2H_5OH[d] = 7 H_2O = 3.2	30°C	37 hours	500 W High Pressure Hg lamp II[d]	Glycine Serine or Threonine Aspartic Valine Leucine Isoleucine Glutamic Proline (trace amount)	Sulfur and some other amino compounds which are either more acidic or more basic than normal amino acids
VIII	CH_3SH = 25 CH_4 = 25 NH_3 = 25	Room Temperature	14 days	1 kw Xe lamp	- - -	CH_3SSH, CH_3SSCH_3, and probably methylamine

Experiment	Reactants[a]	Lowest Temperature (°C)	Irradiation Time	Light Source	Amino Acids Detected	Other Products Detected
IX	CH_3SH = 25 C_2H_6 = 25 NH_3 = 25	Room Temperature	14 days	1 kw Xe lamp	- - -	CH_3SSH, CH_3SSCH_3 and probably ethylamine
X	H_2S = 37.5 H_2O = 9.0 CO = 37.5	50°C	14 days	1 kw Xe lamp	- - -	No detectable organic compounds were detected
XI	H_2S = 25 NH_3 = 25 CH_4[f] = 25 H_2O = 9	50°C	113½ hours	500 W Hg lamp I[b]	Aspartic Serine or Threonine Glutamic, Proline Glycine Alanine Valine Leucine Isoleucine	Sulfur

(a) In all experiments, the first molecule shown (H_2S or CH_3SH) is the source of the hot H atom by photolysis, eq. 4 of text.

(b) Identification based on analysis using a Technicon Amino Acid Analyzer.

(c) With no rear reflecting mirror in housing with average light collecting lens system.

(d) With rear reflecting in housing and excellent light collecting lens system.

(e) Absolute pure ethyl alcohol (US Industrial Co.).

(f) Ultra high pure grade, minimum purity is 99.97% (Linde Co.).

B. Photochemistry of Molecules Leading to Building Blocks for Nucleic Acids

In order for life to evolve and continue, nucleic acids including DNA must be present. In order for these to form, building blocks or subunits of the nucleic acids must have been synthesized from still simpler compounds. We have studied the photochemistry of five molecules which presumably could form products which would be a building blocks.

One of the five molecules can arise from hydrogen cyanide (hydrogen cyanide tetramer, molecule-1) which has been found in interstellar space and presumably existed on the primitive earth. Formulas for all five molecules to be discussed appear in Appendix 1. Another of the molecules, molecule-2, can arise from the reaction of cyanoacetylene (3-carbon, 1-nitrogen and 1-hydrogen atoms) and ammonia, both of which have been found in interstellar space. Although ammonia presumably existed on the primitive earth, no evidence for the coincident existence of cyanoacetylene has been presented. Another two of the molecules, molecule-3 and molecule-4, differ from molecule-2 in minor ways but these differences should not prevent formation of a building block but might alter the efficiency of the reaction. Finally, the fifth molecule, molecule-5, although similar to molecule-2 differs sufficiently in one respect that it could provide insight into the requirements for formation of a building block.

In the case of the primary molecule derived from hydrogen cyanide, there seems to be no doubt that a building block for nucleic acids can be produced in a solvent that was significant on the primitive earth, namely water. We have discussed the results of our research on this molecule in

the 1972 Annual Report.

The molecule-2 is an adduct or addition product of cyanoacetylene and ammonia. We have established the structure of this molecule; that is, the kinds of atoms present and their relative location, which had not been previously done. This is an important first step since if a building block were to be produced from it, the exact nature of the reactant responsible for this must be known. In addition we have determined all the light absorption characteristics of the adduct. This is also important since if a product were to be produced by the absorption of light the region of light absorption, the intensity of the absorption and the dependence upon the wavelength are all factors which can affect the results.

In the particular case of molecule-2 in water, a building block is photochemically produced but the efficiency is very low, approximately 0.0005%, based on the amount of light absorbed. In addition for this case as well as for a similar molecule containing only an extra carbon atom, molecule-3, we found that (1) the presence of oxygen strongly inhibits the rate of formation of a building block, (2) the presence of oxygen plays an important role in the ultimate photodecomposition of the reactants to ammonia and hydrogen cyanide and (3) the wavelength of light used to irradiate the reactant affects the nature of the photochemical reaction giving generally either only photodecomposition or a very small amount of a building block plus formation of unknown products.

For a fourth reacting molecule, molecule-4, additional grouping of atoms are present compared to the two just discussed in the previous

paragraph; however, these are not in locations that should affect the possibility of formation of a building block. Indeed, this proved to be true and a building block was photochemically formed. However, the additional groups apparently increase the efficiency of the formation of the product building block.

Finally for the fifth reacting molecule, molecule-5, one important difference exists compared to all others. On one of the nitrogen atoms in the molecule, two hydrogen atoms are replaced by two carbon-containing groups. In this case, even after 15 hours of irradiation with high intensity light, no building block was produced. This provides us with the important clue that at least one and possibly two hydrogens must be on the nitrogen atom in order that a building block be photochemically synthesized.

C. Formaldehyde

Formaldehyde is a small 4 atom gaseous compound containing 2-hydrogen, 1-oxygen, and 1-carbon atoms. It can act as a precursor to the formation of biologically important compounds as sugars, amino acids and building blocks for nucleic acids (including DNA). Formaldehyde is not only potentially important for such synthesis that may have occurred during the primitive state of the earth but has been found to co-exist with ammonia in the galaxy. The latter fact is interesting since light could potentially induce reactions between ammonia and formaldehyde to produce some biologically significant molecules and/or building blocks to synthesis of still more complex molecules via chemical evolution.

Formaldehyde readily and spontaneously forms a solid polymer, paraformaldehyde, at temperatures below 176^{o}F and in the presence of a trace of water this occurs at still higher temperatures. We point this out since water was obviously present on the primitive earth and it is doubtful if gaseous formaldehyde was present in an amount much greater than 0.4 percent. Furthermore, there does not appear to have been any published studies of the thermal reactions of formaldehyde (gas) or the paraformaldehyde (polymer) in the presence of inorganic materials (non-carbon containing) which might promote increased reactivity of formaldehyde (or paraformaldehyde). Both because of the possibility that much of the formaldehyde existed as a polymer on the primitive earth and perhaps elsewhere, and because no studies with formaldehyde or its polymer with reactivity enhancing inorganic materials have been done, we investigated the subject.

To briefly anticipate the results, we have found that formaldehyde and paraformaldehyde react in the presence of several inorganic materials to give a wide variety of simple organic compounds (carbon containing) which in themselves could be important reactants in subsequent chemical evolutionary reactions. Many of these have not been found before. In addition, three of the products have been found in interstellar space, and we predict that some of the others will be found in interstellar space and in the atmospheres of other planets.

The inorganic materials used to react with formaldehyde and paraformaldehyde are models for soil and rock-like substances found on planetary surfaces and in interstellar space. The temperature under which the reactions were carried out were purposely kept relatively low to simulate conditions likely on other planets such as 132 degrees and 248 degrees Fahrenheit (^{o}F). In addition we studied the effect of temperature change upon the total quantity of volatile products produced as well as the variation in the percentage distribution of the various products which arose. Finally, in the case of the paraformaldehyde (polymer), we varied the relative quantity of this to the activating materials to determine the effect upon the quantity of volatile products produced and their percentage distribution.

We have reported some results in the last annual report (July, 1972). However, later we were concerned about (1) the possible loss of products because of the method of collecting samples for analysis and (2) whether different results for the product analysis would be obtained as a function of time at which the analysis was done after the reaction was completed.

For one reaction condition, we have found that the nature of the final products are somewhat different than those obtained earlier and apparently depends upon both of the concerns noted above. Nonetheless we now know the complete range of products produced for one reaction condition when analysis was done from 2 hours to approximately 15 hours after completion of the reaction. The results based on the one reaction condition involving zinc oxide as the inorganic activating agent and paraformaldehyde at 248^{o}F for two hours is that 9 volatile products were produced.

A wide variety of inorganic activating materials were used including zinc oxide, zinc chloride, magnesium oxide, magnesium chloride, silicon dioxide, ferric oxide and ferrous oxide. Products were detected only when using the zinc and magnesium compounds. Also a variety of temperatures, ratios of inorganic material to paraformaldehyde and times of reaction were employed. Overall, a total of seventeen different organic compounds were detected from the various reaction conditions. Appendix I gives a list of the organic compounds detected.

The total quantity of volatile products depended upon:

(1) the nature of the activating material

(2) the ratio of activating material to paraformaldehyde

(3) the temperature

(4) whether formaldehyde or paraformaldehyde was used as the reactant

(5) time of reaction

(6) the time of analysis after the products were distilled.

The percent distribution of the various products depended upon:

(1) the nature of the activating material

(2) whether formaldehyde or paraformaldehyde was used as the reactant

(3) the temperature

(4) the time of analysis after the products were distilled.

In summary, using paraformaldehyde as the reactant to produce organic products:

(1) Zinc oxide was the most activating material of the seven inorganic activating materials used.

(2) At lower temperatures and a given reaction time, the total yield of volatile products is less than at higher reaction temperatures.

(3) Although the reaction proceeds more slowly at lower temperatures (as for Zinc oxide), allowing a longer time for the reaction gives even a higher yield of volatile products than at the more elevated temperatures.

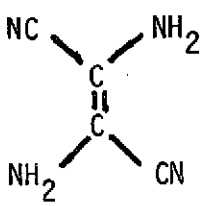
(4) The percent conversion of paraformaldehyde to volatile products can be high, as high as 75% on the basis of experiments to date.

Two of the products generated are methyl alcohol and acetaldehyde which are reactive compounds and also are found in interstellar space. Formic acid (as a derivative) has also been detected. Formic acid and a derivative of formic acid also have been found in interstellar space. Six

other products generated are also reactive compounds, one of which is known to be important in the synthesis of sugars.

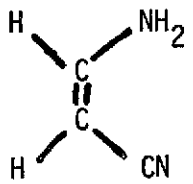
APPENDIX 1

Formulas for the Five Molecules of Interest for Photochemical Transformation to Building Blocks for Nucleic Acids

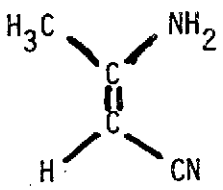


hydrogen cyanide tetramer

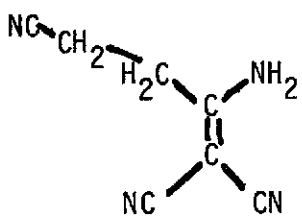
Molecule-1



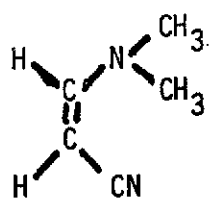
Molecule-2



Molecule-3



Molecule-4



Molecule-5

APPENDIX 2

Organic Compounds Detected from Reaction of Paraformaldehyde with Various Inorganic Materials

Acrolein [$H_2C = CH-CHO$]
Acetaldehyde [CH_3CHO]
Formic acid[1] [HCOOH]
Methyl formate [$HCOOCH_3$]
Glycolaldehyde [$HO-CH_2-CHO$]
Glycolaldehyde methyl ether [CH_3O-CH_2-CHO]
Methoxymethanol [CH_3O-CH_2-OH]
2-methoxyethanol [$CH_3O-CH_2-CH_2-OH$]
Dimethyoxymethane [$CH_2(OCH_3)_2$]
Trimethoxymethane [$CH(OCH_3)_3$]
Dimethyl ether [CH_3-O-CH_3]
p-dioxane
s-trioxane
carbon dioxide [CO_2]
β,β' dihydroxydiethyl ether[2] [$HO-CH_2-CH_2-O-CH_2-CH_2-OH$]

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[1] detected as the metal formate.

[2] likely product but structure not unequivically verified.