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CHEMICAL ORIGIN OF THE VENUSIAN CLOUDS

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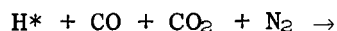
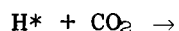
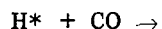
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Introduction

This project is a laboratory study of chemical reactions which may be important in the atmosphere of Venus. Because of the lack of a magnetic field, solar hydrogen must be expected to react with the components of the high Venus atmosphere as the solar wind streams in and penetrates the atmosphere. The primary reactions to be studied are:



In their studies of the reaction of $\text{H}(^2\text{P})$ with N_2 , Tanaka and McNesby¹ found ammonia to be the only product. They measured rates of ammonia formation in a number of experiments, and from their data we have estimated a rate coefficient of 10^{-15} cc molecules⁻¹ sec⁻¹ for the primary reaction between H^* and N_2 .

If, under the conditions found in the high Venus atmosphere, solar hydrogen does indeed react to a significant extent with the CO , CO_2 , and N_2 present, radicals containing oxygen-hydrogen, carbon-hydrogen, and nitrogen-hydrogen bonds will be produced. If photolysis of the primary reaction products is prevented, these radical species will condense and polymerize, forming water, hydrocarbons, and amino-compounds. Large amounts of condensed products accumulating from this source could produce the observed permanent cloud layer of the Venus atmosphere.

Summary

In work done on this project, it has been found that the reaction between excited hydrogen atoms and carbon monoxide (CO) yields intermediate radical and atom species which undergo rapid secondary reactions to produce water and organic compounds. The principal organic compounds formed are ethylene, formaldehyde, and glyoxal, all readily polymerizable substances. Since the reaction course proceeds in this fashion under laboratory conditions, with the formation of these reactive monomers, it is altogether possible that the same reactions and products are important in the high Venus atmosphere.

¹Tanaka, I., and J. R. McNesby, J. Chem. Phys. 36, 3170-73 (1962)

The reaction $\text{H}(^2\text{P}) + \text{CO} \rightarrow \text{products}$ was studied in a flowing system. The irradiation chamber was designed for maximum production of excited hydrogen atoms and the reaction tube with its CO inlet line was designed to provide optimum mixing conditions of $\text{H}(^2\text{P})$ and CO. The design proved to be a satisfactory one, as production rates of 10^{14} to 10^{15} molecules sec^{-1} were obtained.

From this, a minimum rate coefficient of 10^{-15} cc molecules $^{-1}$ sec $^{-1}$ can be estimated, but the actual rate coefficient is likely to be much larger.

Calculation of the Lyman- α flux based on photoionization current measurements gave values which were low when compared with product formation rates.

A detailed qualitative and quantitative analysis of the products was made. On a mole basis the products were 70% water and 30% organic compounds. The chromatograph showed 13 organic peaks of which five were positively identified, four tentatively identified, and four unknown. Half of the organic product was ethylene; two other major organic components were formaldehyde and glyoxal. In addition, methanol, ethane, acetylene, propylene, acetaldehyde, acetone, ethanol, and formic acid were positively or tentatively identified as being present. Acetaldehyde, if present, appeared at the same time as formaldehyde; ethanol and formic acid peaks were broad, difficult to analyze, and they interfered with the methanol peak.

Water was determined by passing the product gases through a calcium carbide (CaC_2) cartridge, which was heated to 160°C , then measuring the acetylene formed with the flame ionization detector.

A comparison of the water/organic product ratio (70/30) with the heats of reaction (ΔH) of the two reactions,



is of interest. Reaction (1) is probably the important water-producing reaction; it is exothermic by 75 kcal/mole. Reaction (2) is probably the organic-producing reaction; it is exothermic by 60 kcal/mole.

In view of the nature and distribution of the products, the two second-stage reactions which are probably most important are



The relatively large amount of ethylene produced is of theoretical interest in regard to the Venus atmosphere, because a significant production rate of ethylene provides the initial condition for making stable polymeric compounds. Such polymers are probable components of the Venusian cloud layer.

Experimental and Discussion

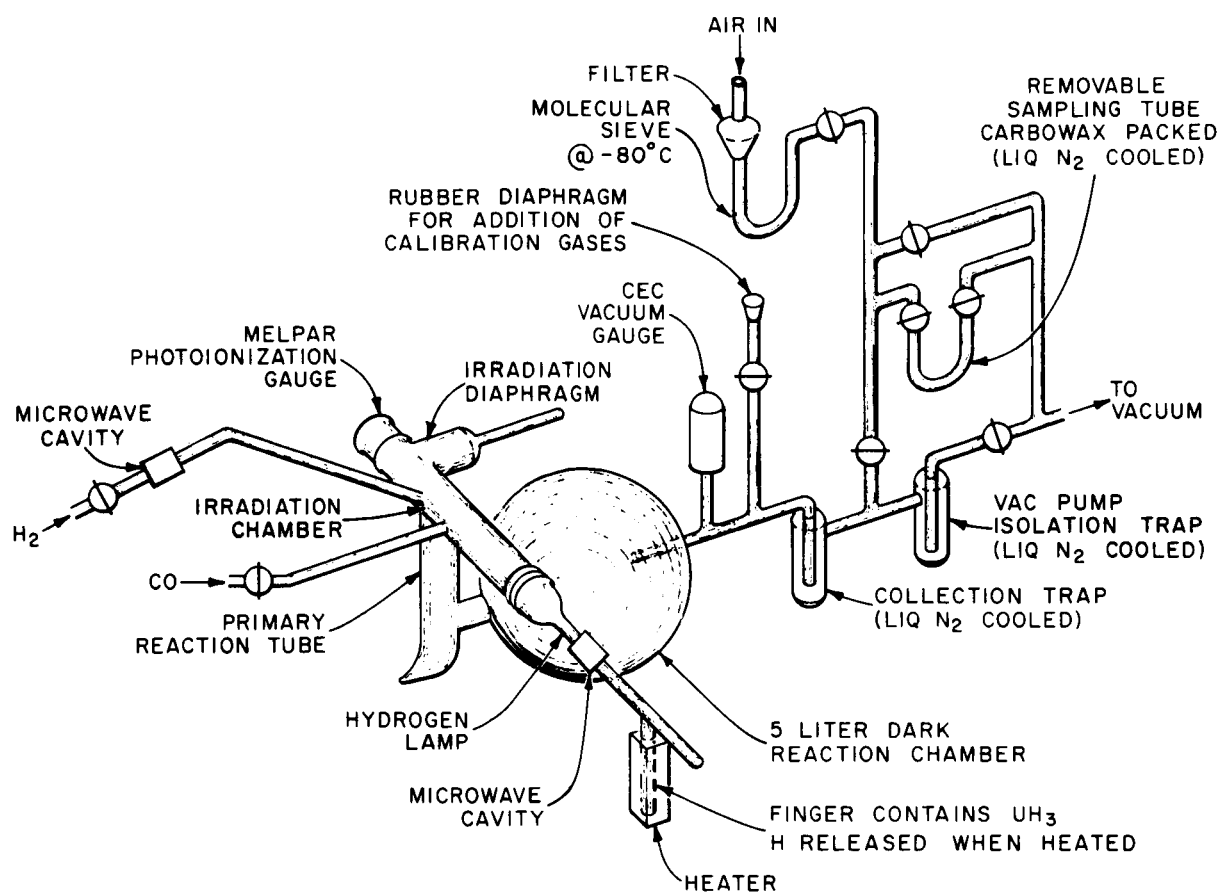
The first, and one of the most important objectives of this study, is the investigation of the reaction $\text{H}(^2\text{P}) + \text{CO} \rightarrow \text{products}$, because this reaction must have a primary role in any production of hydrocarbon or water, or both, in the Venus atmosphere. It is recognized that the radiative lifetime of $\text{H}(^2\text{P})$ is a very small fraction of the time between particle collisions in low pressure gas systems. Therefore, if there is to be enough excited hydrogen to provide for an appreciable rate of reaction, resonance trapping of the exciting radiation, i.e., Lyman- α , must occur.

The number of hydrogen atoms per unit cross section which are being irradiated in the laboratory system ($\sim 10^{14} \text{ cm}^{-2}$) is a reasonable analog for the high Venus atmosphere if we take the effective thickness of the reaction layer to be 10^6 cm and the hydrogen atom concentration to be 10^8 cm^{-3} .

Apparatus and Procedure

The laboratory apparatus which was used is shown in Fig. 1. The total pressure in the flow system was maintained at 2 torr and the relative flow rates of the H_2 and the CO were varied between 1 H_2 /1 CO and 100 H_2 /1 CO .

The hydrogen used was purified by passing it through a palladium-silver alloy thimble. The CO was purified by passing it through magnesium



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FIG. 1 EXPERIMENTAL APPARATUS

perchlorate to remove water vapor and oxygenated hydrocarbons, then through ascarite to remove any CO_2 . Small amounts of methane and ethane were the only impurities remaining in the CO .

The hydrogen lamps used contained uranium hydride. The hydrogen pressure and the irradiation intensity were controlled by controlling the temperature of a well containing the uranium hydride. The uranium in these lamps served the dual purpose of supplying the hydrogen and of continuously reacting with and removing any foreign gases which might appear in the gas phase by desorption from the walls. Both lithium fluoride (LiF) and magnesium fluoride (MgF_2) windows were used. While the Lyman- α transmission of the LiF windows slowly decreased with use, the MgF_2 did not appear to be affected by the radiation from the hydrogen lamp.

Operating Parameters

The irradiation chamber, 12 cm long, had a Lyman- α lamp at one end and a photoionization tube at the other. In this arrangement, determination of radiation adsorbed by H atoms was of secondary importance and the detected photoionization current was greatly attenuated, chiefly by divergence of the radiation. The divergent loss factor for this system was found to be about 5×10^2 . The measured photoionization current was 2×10^{-8} amp at 12 cm from the lamp. When hydrogen atoms were added to the irradiation chamber, the decrease in current was between 5 and 15%, averaging about 10%.

The calculated Lyman- α current was then $(2 \times 10^{-8}) \times (5 \times 10^2) \times 10^{-1} \sim 10^{-6}$ amp, giving a calculated flux,

$$F = \frac{i}{1.6 \times 10^{-19}} \times \frac{q}{A}$$

$$= 2.5 \times 10^{12} \text{ quanta sec}^{-1} \text{ cm}^{-2}$$

where i is the detector current.

q is the quantum efficiency of the gauge.

A is the area.

Based upon product yield, assuming a quantum efficiency of 1 and neglecting any chain branching effects in the intermediate radical reactions, the Lyman- α flux was 10^{14} to 10^{15} quanta $\text{sec}^{-1} \text{ cm}^{-2}$.

The flow rate through the system was 250 cc sec^{-1} at 2 torr pressure. Thus the residence time in the 50-cc irradiation chamber was 0.2 sec and the residence time in the 5-liter dark reaction chamber was 20 sec. After leaving the dark reaction chamber, the product mixture passed into a trap cooled with liquid nitrogen where all of the reaction products were condensed and collected. Following the reaction period, which was generally 15 minutes, the collected products were transferred to a small copper loop trap, packed with Carbo-Wax supported on firebrick. The transfer was made by cooling the copper loop with liquid nitrogen, warming the collection trap with hot water, and carrying the products in hydrogen gas with about 100 torr pressure drop across the copper loop. Fifteen minutes were required for the transfer. Then the liquid nitrogen-cooled loop was removed from the system and carried to a flame ionization detector, where the loop was connected into the carrier gas stream and the sample analyzed.

Analysis of Products

Two analytical procedures were used for organic components: in the first procedure, the sample was carried directly into the flame ionization detector from the loop trap with no chromatographic column; in the second procedure, a 6-ft Carbo-Wax column was added to enhance component resolution.

The experimental procedure was to make 15-minute runs with selected H_2 and CO flow rates, followed by 15-minute transfers to the sample loop, and then to analyze the collected products using the flame ionization detector.

System blanks were obtained by making complete 15-minute runs and 15-minute collections with all experimental conditions identical to the conditions of a reaction experiment except that the microwave units were not operating; therefore no H atoms were being produced and the irradiation chamber was not being irradiated. These system blanks were checked very carefully for reproducibility. Blank runs were made immediately

before and after reaction runs, and this three-part sequence was repeated several times under each set of operating conditions.

Analysis of the blank run chromatograms showed that the background spectrum of components was very reproducible. While there were five small peaks, the variation in peak height from blank to blank was less than 20%. Comparison of the blank run chromatograms with reaction run chromatograms showed that all of the methane and part of the ethane were impurities in the CO reactant. Later, when a quantitative analysis was made possible by means of a water vapor calibration, the concentration of methane in the CO was calculated to be 50 ppm.

Two definitive experiments were made to confirm the assumption that ground state H atoms do not react with CO. In the first, a 15-minute blank run was made with ground state H atoms being produced by the microwave unit for that purpose. Analysis of the collected sample was essentially identical with the analysis of the normal blank runs. In a second 15-minute run with ground state H atoms, the condensible components were collected with the trap cooled by liquid oxygen (to prevent condensation of CO). When the collection trap was warmed the pressure increase in the isolated system was 2 microns. This was attributed to the methane and ethane from the CO.

When a 15-minute reaction run was made, using a liquid oxygen trap, vaporization of the condensed products resulted in a pressure increase of 28 microns. The condensed yield of $28 - 2 = 26$ microns, assuming perfect gas law, is 8 micromoles:

$$26 \times 1.3 \times 10^{-6} \text{ atm} \times 6 \times 10^3 \text{ cc} = 0.2 \text{ cc (1 atm)}$$

$$\frac{0.2}{2.4 \times 10^{-3}} = 8 \text{ } \mu\text{moles}$$

This number gives a very approximate indication of the total quantities of reaction products.

Between the extremes of flow ratios of H_2 and CO used, twice as much product was formed at 100 H_2 /1 CO (2 torr H_2 /20 micron CO) as at 1 H_2 /1 CO (1 torr H_2 /1 torr CO). However, even at 100 H_2 /1 CO the ratio of $\text{H}(^2\text{P})$

to CO was probably about $1[\text{H}(^2\text{P})]/100 \text{ CO}$, so the amounts of product formed were proportional to the $\text{H}(^2\text{P})$ concentrations.

When the sample was added directly to the flame ionization detector, it was allowed to warm up slowly by simply removing the loop from liquid nitrogen. This produced a quite reproducible "temperature-programmed" series of component peaks. Seven separate peaks appeared as the temperature rose to room temperature, and two more were seen by heating the trap with boiling water.

Several of the peaks were easily identified. The first four, completely separated, were methane, ethane, ethylene, and acetylene. The next three peaks were possibly combinations of components. For example, formaldehyde and acetaldehyde came out together. The last two "hot water" peaks were apparently a mixture of alcohols and other less volatile components.

From the organic component analysis by direct injection of the sample into the flame ionization detector, the relative importance of ethylene, formaldehyde, and glyoxal production by the $\text{H}(^2\text{P}) + \text{CO}$ reaction was shown.

The quantitative determination of the water produced was next attempted. Using the same basic experimental and analytical procedure as was used for the organic compounds, the apparatus was modified by adding a calcium carbide (CaC_2) cartridge between the sample transfer valve and the sample loop. The CaC_2 will produce a molecule of acetylene for every two molecules of water. At first, there were two sources of trouble. It was necessary to condition the glass surfaces of the apparatus by adding an adsorbed monolayer of water molecules (about 10 micromoles) before reproducible amounts of water vapor could be transferred from the apparatus into the sampling section. The second problem concerned the behavior of the CaC_2 cartridge. Operating at room temperature, it gave completely nonreproducible acetylene measurements. This unreliability was caused by the absorption of water vapor by the calcium hydroxide $[\text{Ca}(\text{OH})_2]$ produced by the hydrolysis reaction. When the CaC_2 cartridge was heated and operated at 160°C , the $\text{Ca}(\text{OH})_2$ was maintained in an anhydrous condition and the analytical method became reproducible and quantitative. The system was calibrated by adding known amounts of water vapor (1 to 2 μmole increments) and determining the amount of acetylene produced.

Several 15-minute reaction runs were made; Table I shows the results of water determination of four successive experiments under the same nominal conditions (1 torr H₂ pressure, 1 torr CO pressure). The continuous decrease in water production probably reflects a decreasing transmittance of Lyman- α by the LiF windows with a corresponding decrease in H(²P) atom concentration.

TABLE I

WATER PRODUCTION
(μ moles/15 min)

1.	0.80
2.	0.78
3.	0.55
4.	0.38

Ave. 0.63 ± 0.18 μ moles
water for 15-min run

After the water production was quantitatively determined, the organic components were then qualitatively and quantitatively determined in the second analytical procedure by adding a 6-ft Carbo-Wax column to the flame ionization detector system and referring peak areas to the known acetylene peak area which was calibrated against water. The elution times of all of the expected CH and CHO compounds were determined for the 6-ft Carbo-Wax column with the column operating at 100°C. Elution times were determined for methane, ethane, ethylene, acetylene, propylene, formaldehyde, acetaldehyde, ethylene oxide, glyoxal, acetone, methanol, and ethanol.

The total organic fraction was about 30 mole %, water accounting for the 70 mole %. The amounts of reaction products are given in Table II. As previously mentioned, methane and ethane were major components of blank runs, and these are not listed as reaction products. In addition to compounds listed in Table II, those positively identified as being present in the 3% were ethane and acetylene. Compounds possibly present included propylene, acetaldehyde, acetone, ethanol, and formic acid.

TABLE II

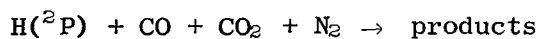
REACTION PRODUCTS

Compound	Mole %
Water	70
Ethylene	15
Glyoxal	5
Formaldehyde	5
Methanol	2
Other Organics	3

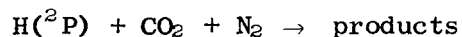
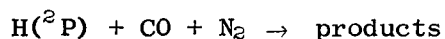
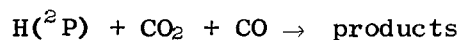
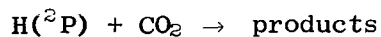
Of thirteen peaks (excluding methane) exhibited by the chromatographs, five were fully identified as single components, four were not fully resolved and might have consisted of two or more of the oxygenated compounds, and four peaks were not identified.

Future Work

The reaction

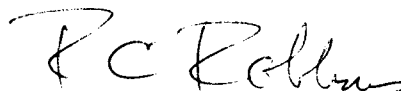


is currently being studied. The interferences are such that the reactions



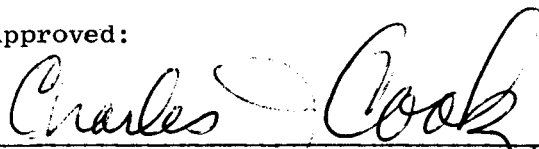
will be investigated as to product yield and identity.

Attempts will be made to learn more about the reaction rates by using a number of smaller volume reactors with these reactions and by using dilute reactant mixtures, 1.0% CO in argon and 100 ppm CO in argon.



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