(iii) The $+E$ spectra of the isomeric dinitrobenzenes are different (Table II), thus allowing differentiation of the isomers. This can also be achieved using either the positive or negative ion spectra,[20] but in these cases it is necessary to rely solely upon differing abundances of ions in the different spectra.

Conclusions

(1) $+E$ spectra derived from negative ions provide information analogous to that derived from conventional low resolution positive ion mass spectra.

(2) The $+E$ spectrum of a negative ion has the potential to be used to provide information concerning the structure of that negative ion.

Acknowledgment. We wish to thank the Australian Research Grants Committee for generous support under Grant C67/16756 and Dr. R. Graham Cooks for helpful discussion.

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Chemical Evolution. XXVI. Photochemistry of Methane, Nitrogen, and Water Mixtures as a Model for the Atmosphere of the Primitive Earth[1]

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Abstract: Methane-water vapor mixtures were irradiated using a low pressure mercury lamp and the reaction products were determined at intervals between 0.5 and 6 hr. Formaldehyde, acetaldehyde, and methanol were observed after 0.5 hr. The presence of ethylene glycol, ethanol, acetone, isopropyl alcohol, *tert*-butyl alcohol, methyl ethyl ketone, isobutyl alcohol, *tert*-amyl alcohol, and neopentyl alcohol was detected in small amounts after 2 hr and the yields increased after 4 and 6 hr irradiation times. Virtually the same product yields were obtained after irradiating a ~2:1 methane-water mixture as were obtained from a ~1:1:1 methane-nitrogen-water mixture demonstrating that nitrogen does not react under these conditions. Furthermore, no amino acids were detected when nitrogen was added to the reaction mixture. The reactions are initiated by the hydroxyl radicals formed by water photolysis. These hydroxyl radicals abstract a hydrogen atom from methane as the first step in the synthesis. The prebiological significance of these photochemically generated compounds is discussed.

Ultraviolet light from the sun offered the greatest potential as the energy source to drive chemical reactions on the primitive earth. It has been estimated that, in the absence of ozone, wavelengths less than 300 nm contributed 3400 cal cm^{-2} $year^{-1}$ and those less than 200 nm contributed 41 cal cm^{-2} $year^{-1}$ to the surface of the primitive earth.[2] The next most abundant energy sources, electrical discharges and shockwaves are estimated to have contributed 4 and 1.1 cal

Table I. Total Yield of Photoproducts In Static System (mol × 10^7)[a,b]

Products	1	2	3	4	5	6	7	8	9[c]	10[c,d]	11[c,e]
Irradiation time, hr	0.5	0.5	1	2	2	2	3	4	4	6	6
Formaldehyde	7.7	18.7	7.3	12.9	17.0	10.1	8.3	5.8	15.3	27.0	25.2
Methanol	6.1	8.7	6.1	1.1	2.7	0.8	2.7	2.3	0.9	2.3	2.4
Acetaldehyde	3.6	5.6	1.3	0	2.2	2.1	1.7	0.7	0.4	2.5	2.1
Ethylene glycol	0	0	3.7	2.9	8.5	1.9	0	11.3	3.6	7.3	10.3
Ethanol						1.9			3.9	13.5	8.7
Acetone						4.8			14.4	61.2	64.4
Isopropyl alcohol						~0.8			2.6	5.1	4.6
tert-Butyl alcohol						1.6			2.1	9.0	7.5
Methyl ethyl ketone						1.3			1.7	9.0	12.2
Isobutyl alcohol						<1.7			~2.3	6.8	5.2
tert-Amyl alcohol						0.8			3.9	6.3	6.2
Neopentyl alcohol						<1.7			~1.8	4.5	4.4

[a] Product was not determined for the blanks. See Experimental Section for detailed procedures. [b] Duplicate runs reported to give an indication of the reproducibility. [c] Benzene was detected in this run. However, its presence is believed to be due to the benzene in the vacuum pump oil. [d] Toluene was detected in this run. However, its presence is believed to be due to toluene in the vacuum pump oil. [e] A mixture of 223 Torr of methane and 200 Torr of nitrogen was used in place of the usual 423 Torr of methane.

cm^{-2} year^{-1}, respectively.[2] Because of the apparent abundance of uv light on the primitive earth we have been investigating the possible role of photochemical transformations in the synthesis of the biomolecules necessary for the origins of life.

We concluded previously that any ammonia present on the primitive earth would have been photochemically converted to nitrogen and hydrogen in 10^5-10^6 years.[3] This is a relatively short time period if one considers that the age of the earth is 4.5×10^9 years. Hydrogen sulfide has been suggested as a possible uv absorbing species on the primitive earth;[4] however, it would have been photochemically destroyed even more rapidly than the ammonia.[3] Water vapor would have absorbed the bulk of the uv light in the atmosphere of primitive earth in the absence of ammonia and hydrogen sulfide. Its uv absorption begins below 200 nm and extends below 100 nm. Methane and nitrogen are likely to have been the two other most abundant gases in the primitive atmosphere. In this study we report the results of an investigation of the photochemical reactions of methane–water vapor and methane–water vapor–nitrogen mixtures.

Experimental Section

Materials. Distilled water was further purified by distillation in a Corning AG-16 still and was degassed by four freeze-pump-thaw cycles. Nitrogen (Matheson prepurified), methane (Matheson UHP), and helium (Matheson UHP) were used without further purification.

Analytical Procedures. Gas Chromatographic Analyses. F and M Models 400 and 5750 and Fisher Model 2400 equipped with a 6 ft × $^1/_{16}$ in. id Porapak Q column and flame ionization detectors were used. Compounds were identified by the coincidence of the retention time with a coinjected authentic sample. Ethanol, isopropyl alcohol, *tert*-butyl alcohol, methyl ethyl ketone, isobutyl alcohol, *tert*-amyl alcohol, and neopentyl alcohol were determined by the peak area as measured by the half-height width times height.

Mass Spectral Analyses. The samples were collected from the F and M 5750 chromatograph using a 3:1 splitter in a 400 ml evacuated flask. The flask was cooled to −196°, the helium carrier gas was pumped off, and the contents were then warmed and distilled into a 50 ml evacuated flask cooled to −196°. The contents of the 50 ml flask were then pumped into a Consolidated Electrodynamics Co. 20-130 mass spectrometer. The identity of the reaction products was established by direct comparison with authentic samples whose spectra were measured on the same instrument.

Colorimetric Analyses. Formaldehyde was determined by the chromotropic acid procedure using a Beckman DU spectrophotometer.[5] A limiting concentration of 1×10^{-5} M could be detected. Methanol, ethanol, acetaldehyde, and ethylene glycol did not interfere.

Methanol was determined by the procedure of Boos[6a] as modified for the presence of formaldehyde.[6b] A Beckman DU spectrophotometer was used to measure the absorption at 570 nm. A limiting concentration of 1×10^{-5} M could be detected.

Acetaldehyde was determined by the procedure of Stotz.[7] A limiting concentration of 2×10^{-5} M could be detected when the absorbance at 567 nm was measured on a Unicam SP 800 spectrophotometer. When both formaldehyde and methanol were present the absorption maximum shifted to the vicinity of 610 nm. Consequently it was not possible to precisely determine the amount of acetaldehyde by this procedure. Approximate acetaldehyde yields were obtained by comparison of the position of the absorption maximum with that of known mixtures of methanol, formaldehyde, and acetaldehyde.

Ethylene glycol was determined by the procedure of Sawicki et al.[8] The absorbance at 628 nm was measured on a Unicam SP 800 spectrophotometer. Methanol and ethanol did not interfere at a concentration of 1.7×10^{-4} M and acetaldehyde did not interfere at a concentration of 1×10^{-4} M. Formaldehyde gave the same color so the concentration of ethylene glycol was calculated by subtracting the concentration of formaldehyde from the experimentally determined concentration of ethylene glycol.

Acetone was determined by the procedure of Berntsson.[9] The absorption at 474 nm was measured against a reagent blank on a Unicam SP 800 spectrophotometer.

It was not possible to detect hydrogen peroxide,[10a] glyoxal,[10b] or biacetyl[10b] as reaction products.

Ultraviolet Lamp. A low pressure mercury lamp was constructed by Engelhard-Hanovia, Newark, N.J., from 8 mm diameter Supersil quartz wound into a helical coil 6 in. long. The output at 184.9 nm was determined by the rate of photolysis of 1.84 Torr of ammonia in 750 Torr of argon in the 50 l. flask discussed below. The rate of ammonia loss was followed spectrophotometrically at 213 nm.[3] A lamp intensity of 1.86×10^{18} quanta sec^{-1} was calculated assuming that the quantum yield for ammonia photolysis is 0.25.[3]

Photolyses. Static System. A three-neck 50-l. round-bottomed flask was fitted through two necks with a mercury lamp and thermometer, respectively, and it was connected to a vacuum line through the third neck. The system was evacuated with a Cenco Hyvac 6 vacuum pump and a silicone oil diffusion pump. Pressures greater than 2 Torr were measured with a Baratron type 77 pressure meter and those less than 2 Torr with a Cenco Pirani gauge. The flask was evacuated to 5×10^{-3} Torr and 10 ml of water was distilled into the flask from the vacuum line. In runs 1-10 of Table I methane was then added to the flask until a pressure of 450 Torr was attained (27 Torr of water vapor and 423 Torr of methane). In run 11 methane was added until the pressure reached 250 Torr and then nitrogen was added until the pressure rose to 450 Torr. The contents of the flask were then maintained at 70-75° with steam to

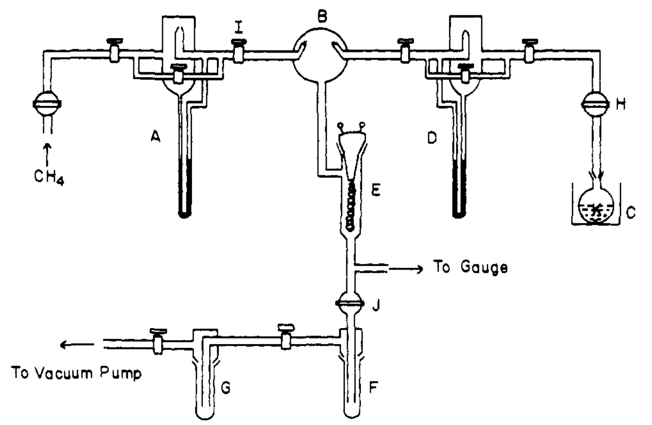


Figure 1. Flow system used for the photolysis of methane-water mixtures: A, D, silicone oil manometers; B, mixing chamber; C, constant temperature bath; E, ultraviolet lamp; F, G, pentane slush traps; H, I, J, stopcocks; K, water.

Table II. Total Yield of Photoproducts in Flow System (mol × 10^7)

	Amt of H_2O used, ml	Amt of CH_4 used, mol	Length of time, hr	Products		
				HCHO	CH_3CHO	CH_3OH
(1)	3.8	~0.25	3	4.3	1.3	
(2)	67	~0.33	4	4.0	10	1.3
(3)	29	~0.44	4	1.4	3.8	0
(4)	157	~0.5	3	105	1.3	13

vaporize all the water (240 Torr) during the course of the photolysis. At the end of the irradiation the contents of the flask were pumped into two traps which were maintained at −130° (pentane slush). In runs 1-5 and 7 and 8 the contents of both traps were warmed to room temperature and the combined contents analyzed colorimetrically for the presence of formaldehyde, methanol, acetaldehyde, and ethylene glycol (Table I). In runs 6 and 9-11 only the contents of the first trap were analyzed by first extraction with 2 ml of toluene (run 9) or 3 ml of *o*-xylene (runs 6, 10, and 11). Both the aqueous layer and the organic layer were subjected to GC, MS, and colorimetric analyses (Table I). The second trap which was adjacent to the vacuum pump contained only a small amount (ca. 0.5 ml) of liquid.

Flow System. The entire system (Figure 1) was evacuated to 2 × 10^{-3} Torr. The flow of methane through the system was controlled by stopcock I and tank regulator. The rate of flow of water vapor was controlled by the temperature of the constant temperature bath C used to warm the water in flask K. When the desired flow rates were obtained the lamp was turned on and the products and water were trapped at −130° (pentane slush) at F and G. At the end of the photolysis the contents of F and G were allowed to warm to room temperature, combined, and analyzed colorimetrically (Table II).

Results and Discussion

Product Analysis. Gaseous mixtures of methane and water vapor were photolyzed with a low pressure mercury lamp at 70–75° in a 50-l. round-bottomed flask. The flask was initially evacuated to 5 × 10^{-3} Torr and 10 ml of water (240 Torr at 72.5°) and 423 Torr of methane were added and the flask was heated to 70–75° to assure that all the water was vaporized. A spiral low pressure mercury lamp emitting 10^{18} quanta sec^{-1} at 184.9 nm was used as the light source. No mercury gauges or mercury diffusion pumps were used in the pumping system so that there would be no possibility of mercury sensitized reactions.

The system was designed so that the water vapor absorbed 95–100% of the light. In this way the primary photoproducts would be observed after short irradiation times while the subsequent photolyses of these photoproducts would be observed after longer irradiation times (Table I). The addition of nitrogen to the reaction flask resulted in essentially no change in the relative amounts of the reaction products (Table I, compare runs 10 and 11) so nitrogen was omitted from the other runs. The failure to detect ninhydrin positive compound in run 11 either before or after acid hydrolysis further suggested that the nitrogen was not reacting.[11] A few experiments were also performed in the flow system shown in Figure 1.

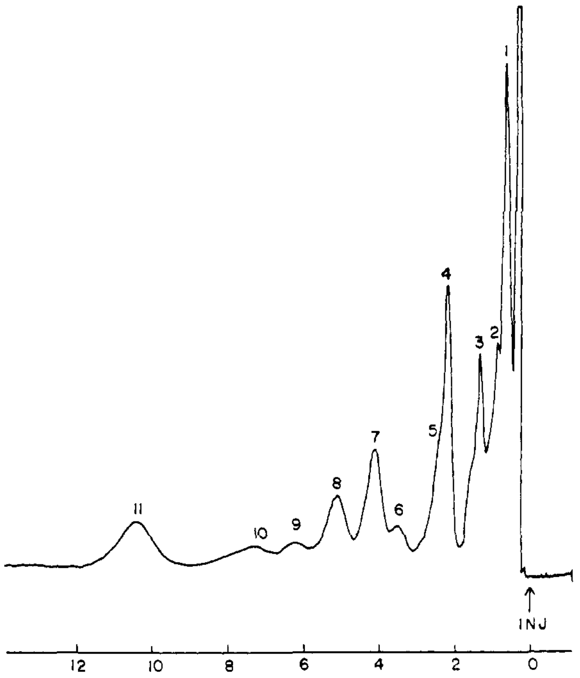


Figure 2. Gas chromatographic trace of 1 μl of the aqueous layer from run 10 on the F and M 400 gas chromatograph. The products were identified as (1) formaldehyde, (2) methanol, (3) ethanol, (4) acetone, (5) isopropyl alcohol, (6) unknown; (7) *tert*-butyl alcohol, (8) methyl ethyl ketone, (9) unknown, (10) isobutyl alcohol, and (11) *tert*-amyl alcohol. A 6 ft × 1/16 in. id Porapak Q column was used with a helium flow rate of 25 ml min^{-1}, hydrogen flow rate of 30 ml min^{-1}, and air flow rate of 300 ml min^{-1}. The column temperature was 162°, and the injection port and detector were 250°.

A dozen alcohols, aldehydes and ketones were identified as reaction products in the static system (Table I). A GC trace of the 6 hr reaction mixture is shown in Figure 2. These compounds were identified first by comparison of GC retention times with those of authentic coinjected samples and then either by a specific color test or by mass spectrum. The yields were determined either by the area under the GC trace or by visible spectral analyses of a derivative. In many of the runs the products were analyzed only by a specific color test. The presence of substantial quantities of acetone was not suspected initially so no test was made for acetone. Some of the same reaction products were observed in the flow system as were found in the static system (Table II).

Three major water soluble products could not be identified (peaks 6 and 9 in Figure 2 and one at longer retention time) and two major *o*-xylene soluble compounds were not identified. One of these *o*-xylene soluble compounds exhibits a retention time less than benzene and the second has a retention time between that of toluene and *o*-xylene. The following compounds were not formed in sufficient amounts to be detected by GC: *n*-propyl alcohol, acetic acid, tetrahydrofuran, *sec*-butyl alcohol, 3-methyl-2-butanone, *n*-butyl alcohol, allyl alcohol, phenylacetylene, and styrene. The limit of detection of these compounds is about 10^{-7} mol. In addition, color tests for hydrogen peroxide, biacetyl and glyoxal were negative.

Three control experiments were performed in the static system to establish that the reaction products were not artifacts. In one of the controls 10 ml of water was added to each trap, the trap was cooled with liquid nitrogen, and the vacuum system was pumped for 4 hr to determine if any of the reaction products were organic compounds present in the vacuum system. In the second control all the usual reactants were added but no uv light was used. In the third control uv light was used but helium was substituted for methane. A hydrocarbon, probably isopentane, was isolated from the above controls. Obviously it is derived from the vacuum system. This compound was also found with the reaction products in the normal photolyses runs. A small amount of benzene was also observed in the second control.

The yields of the simpler compounds such as formaldehyde, methanol, and acetaldehyde appear to remain essentially constant while the yields of the more complex molecules such as acetone, isopropyl alcohol, and *tert*-butyl alcohol increase with prolonged irradiation time. These data demonstrate that a steady state concentration of the initial photoproducts is formed. Photoexcitation of these primary products results in the formation of more complex molecules. The steady state concentrations of acetone, isopropyl alcohol, and *tert*-butyl alcohol may have been reached at the end of 6 hr, although this is not certain because no longer term irradiations were performed. Presumably even higher molecular weight compounds would be obtained if the photolysis were allowed to proceed for several days.

The quantum yield for formaldehyde formation is 2×10^{-4} after 0.5 hr and 0.4×10^{-4} after 6 hr. The decrease in quantum yield with time indicates the approach to a photostationary state. The chemical yields of the other compounds are comparable to that of formaldehyde so the quantum yield for their synthesis is also about 10^{-4}. Since over 12 products have been detected the combined quantum yield for all products is approximately 10^{-3}.

Reaction Pathway. The initial photochemical step in our system must be the dissociation of water vapor into hydrogen atoms and hydroxyl radicals (reaction 1) (Table III).[12] This reaction proceeds with a quantum yield of 0.34 at 184.9 nm.[13] The hydroxyl radical then reacts with methane to yield methyl radicals (reaction 2). The combination (reaction 6) or disproportionation (reaction 5) of the hydroxyl radicals is not considered likely because of their low steady state concentration relative to methane. Our failure to observe hydrogen peroxide as a product in the flow system is consistent with this conclusion.[14] Dimerization of the hydrogen atoms (reaction 4) is a more likely reaction because of their slow rate of reaction with methane (reaction 3). The dimerization of methyl radicals (reaction 7) or the combination of methyl radicals and hydroxyl radicals (reaction 8) are major reactions because there are no alternative radical molecule reaction pathways at the early stages of the photolysis. For example, the reaction of methyl radicals with methane is not productive while the reaction of methyl radicals with water vapor is energetically unfavored.[15]

Methanol and ethane would be expected to be the primary photoproducts in our system. However, these substances must undergo rapid hydrogen abstraction with hydroxyl radicals (reactions 9 and 10) followed by combination with hydroxyl radicals to yield formaldehyde and ethanol, respectively. Further reaction of ethanol with hydroxyl radicals would yield acetaldehyde. This would explain why formaldehyde and acetaldehyde are formed at short irradiation times. The direct photolyses of methanol to formaldehyde and ethanol to acetaldehyde are also possible reaction pathways at higher methanol and ethanol concentrations.[16]

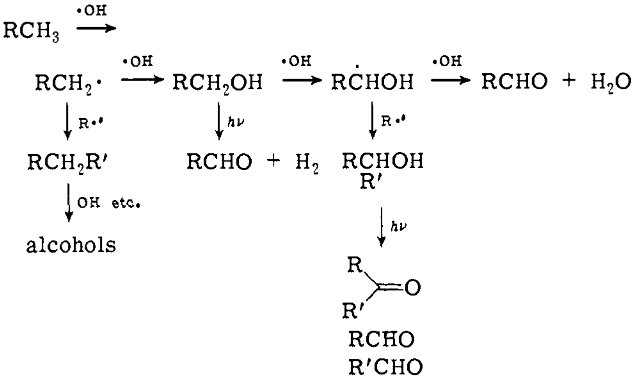
Table III. Rate Constants for Possible Reactions (at 300°K)

Reaction	k, l. mol^{-1} sec^{-1}	Ref
(1) $H_2O \xrightarrow{h\nu} H + OH$	Quantum yield = 0.34	*a*
(2) $CH_4 + OH \rightarrow CH_3 + HOH$	6.95×10^6	*b*
(3) $CH_4 + H \rightarrow CH_3 + H_2$	1×10^2	*c*
(4) $H + H \xrightarrow{M} H_2$	1.1×10^{10}	*d*
(5) $OH + OH \rightarrow H_2O + O$	1.6×10^9	*b*
(6) $OH + OH \xrightarrow{M} HOOH$	2.3×10^4	*e*
(7) $CH_3 + CH_3 \xrightarrow{M} CH_3CH_3$	2.6×10^{10}	*f*
(8) $CH_3 + OH \rightarrow CH_3OH$	2×10^9	*g*
(9) $CH_3CH_3 + OH \rightarrow CH_3CH_2 + HOH$	1.6×10^8	*b*
(10) $CH_3OH + OH \rightarrow CH_2OH + HOH$		*h*
(11) $CH_3OH \xrightarrow{h\nu} CH_2O + H_2$		*i*
(12) $CH_3OH \xrightarrow{h\nu} CH_2OH + H$		*i*

[a] N. Getoff and G. O. Schenck, *Photochem. Photobiol.*, 8, 167 (1968). [b] W. E. Wilson, *J. Phys. Chem. Ref. Data*, 1, 535 (1972). [c] R. Fristrom and A. A. Westerberg, "Flame Structure", McGraw-Hill, New York, N.Y., 1965, p 364. [d] J. K. Thomas, *J. Phys. Chem.*, 67, 2593 (1963); H. A. Schwarz, *ibid.*, 67, 2827 (1963). [e] This value was calculated from the third-order rate constant suggested by W. E. Wilson, *J. Phys. Chem. Ref. Data*, 1, 535 (1972). It was assumed for ease of calculation that methane and water had the same efficiency as a third body. The total concentration of methane and water in our system was 0.0338 mol l.$^{-1}$. [f] N. Basco, D. G. L. James, and R. D. Suart, *Int. J. Chem. Kinet.*, 2, 215 (1970). [g] R. I. Greenburg and J. Heicklen, *Int. J. Chem. Kinet.*, 4, 417 (1972). [h] Gas phase rate constant is not available. [i] Quantum yields are not available. Reaction 11 accounts for about 20% of the products and reaction 12 about 75%. J. Hagege, S. Leach, and C. Vermeil, *J. Chim. Phys., Phys.-Chim. Biol.*, 62, 736 (1965); R. P. Porter and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, 81, 2307 (1959).

Continued photolysis of these primary photoproducts would be expected to result in some of the more complex compounds observed in this research. The generalized reaction pathway is outlined in Scheme I and was derived by considering hydroxyl radicals as the main chain initiating species in these free radical reactions. In addition, it is assumed that the photochemical conversion of alcohols to aldehydes and ketones also contributes significantly to the observed reaction products.[17] The photochemical fragmentation of some of the larger molecules contributes to the steady state concentration of the lower molecular weight products. For example, acetone, methane, and hydrogen are the principal photoproducts of *tert*-butyl alcohol[18] and acetaldehyde is one of the major photoproducts of isopropyl alcohol.[17] Obviously the maximum molecular weight of the compounds produced in this system will be governed by the relative rates of the photosynthesis and photodecomposition reactions. No attempt was made to determine the maximum molecular weight compound.

Scheme I



Prebiotic Significance. Although it is generally agreed that there was little or no oxygen in the atmosphere of the primitive earth[2,19] there is no agreement as to which particular compounds were present in the primitive atmosphere. It has been suggested from thermodynamic considerations that carbon was present as methane as long as a pressure of hydrogen greater than 10^{-4} atm was present.[20] However, others note that carbon dioxide is one of the principal gases emitted from contemporary volcanoes and they suggest that carbon was present mainly as carbon dioxide or carbon monoxide.[21] It is generally accepted that there was little gaseous ammonia in the primitive atmosphere because of its water solubility[22] and rapid photolysis.[3,21b] Whether there was sufficient ammonia or ammonium ion on the primitive earth for it to have had a significant role in prebiotic synthesis is still a subject of discussion.[3,19]

In our view a mixture of nitrogen, water vapor, and methane is a reasonable model for the primitive atmosphere. The nitrogen could have been formed by ammonia photolysis and the methane was slowly formed by the reaction of hydrogen with the volcanically outgassed carbon dioxide and carbon monoxide. Obviously the composition of the primitive atmosphere was constantly changing and at some time may have had larger amounts of carbon dioxide and carbon monoxide than methane. We restricted our investigation to the simpler methane-water-nitrogen model in the present study.

Water vapor would have been the principal uv absorbing compound in a methane-water-nitrogen atmosphere. Since the sun's emission is decreasing by about 50% per 10 nm in the vicinity of 200 nm there would have been relatively little light absorption by methane because the onset of its absorption is at 145 nm. It has been suggested that methane would have been photolyzed by the 121.6 nm Lyman α emission from the sun.[23b] However, all the potential constituents of the primitive atmosphere, including water, absorb at 121.6 nm thereby attenuating the light absorbed by methane. Since the bulk of the solar radiation which could effectively photolyze water is in the 200-175 nm range,[19b] we simulated that light with a low pressure mercury lamp with a principal short wavelength emission at 184.9 nm. The lamp also has longer wavelength emissions at 253.7 and 312.5 nm.

Our results demonstrate that alcohols, aldehydes, and ketones are the more likely products of the photolysis of a methane-water-nitrogen atmosphere. Some of the unidentified compounds in the *o*-xylene extract of the photolysate may be hydrocarbons; however, these are not predominant. Therefore, it appears very unlikely that the primitive earth was ever covered by a 1-10 m thick oil slick which was proposed as being formed as a result of methane photolysis.[23c] The formation of water soluble aldehydes, ketones, and alcohols, which enriched the organic content of the primitive ocean, appears to be a more reasonable model of prebiotic events.

Our results suggest that aldehydes would have been very effectively synthesized on the primitive earth by photolysis of an atmosphere which contained methane and water. The photochemical synthesis of formaldehyde from methane and water on siliceous surfaces has been reported.[24] The other proposed prebiotic aldehyde syntheses utilize γ-rays or electrical discharges,[25,26] energy sources which were not as prevalent as uv light on the primitive earth.[2] From the quantum yield of 10^{-4} for formaldehyde synthesis and the solar flux of 1.2×10^{13} quanta cm^{-2} sec^{-1} in the 175-200 nm region (summed from Table III of reference 19b) a formaldehyde synthesis rate of 3.8×10^{16} molecules cm^{-2} year^{-1} or 6×10^{-8} mol cm^{-2} year^{-1} can be calculated. Since the earth's area is 5.2×10^{18} cm^2 the rate of formaldehyde synthesis would have been about 10^{11} mol year^{-1}. The overall yield of organics would have been at least ten times greater than the formaldehyde yield.

It is tempting to calculate the yield of organics that could have accumulated on early earth after 10^6 or 10^9 years; however, such a calculation does not consider possible degradation reactions. The aldehydes and ketones formed in this study would have been susceptible to photolysis by 250-350 nm light. The photodecomposition of aldehydes and ketones is a very efficient process with quantum yields of 0.5-1 (reaction 13).[30] Furthermore, the light energy from the sun is 100 times greater at 250-350 nm than it is in the 200-175 nm range utilized for aldehyde and ketone synthesis.[2]

$$\mathrm{RCHO} \xrightarrow{h\nu} \mathrm{RCO} + \mathrm{HCO} + \mathrm{R} + \mathrm{H} \qquad (13a)$$

$$\text{or}$$

$$\mathrm{RH} + \mathrm{CO} \qquad (13b)$$

The photolysis of formaldehyde could have served as a source of hot hydrogen atoms on the primitive earth. It has been suggested that hot hydrogen atoms, formed in the presence of ammonia, initiated the synthesis of amino acids on the primitive earth.[27]

Formaldehyde could have been protected from photodecomposition by dissolution in water where it exists almost completely as the stable hydrate, methylene glycol,[31a] a compound which does not absorb light in the 250-350 nm region. However, some gaseous formaldehyde is always in equilibrium with the dissolved methylene glycol so that formaldehyde photolysis would always have been taking place.[31b] Hydration may have slowed the rate of formaldehyde photolysis but it would not have prevented it. Higher molecular weight aldehydes are hydrated to a much smaller extent than formaldehyde so protective effect of water would have been much less. Hydration would have resulted in a higher steady state concentration of formaldehyde than other aldehydes and ketones in the primitive ocean.

Another mechanism for the stabilization of aldehydes and ketones may have been by chemical reaction with cyanide[32] or self-condensation to sugars.[33] The equilibrium constant for cyanohydrin formation from cyanide and formaldehyde is 5×10^5 so that cyanohydrin formation would be favored in the presence of cyanide.[32] The photochemical synthesis of formaldehyde may have proceeded at a sufficiently rapid rate to counterbalance the observed decomposition of sugars in mild alkali.[33] Furthermore, the suggestion that the concentrations of formaldehyde present in the primitive ocean were higher than those of the other aldehydes because of formaldehyde hydration may explain why the sugars were apparently formed exclusively from formaldehyde. It is not clear if the 0.1-0.01 *M* steady state concentration of formaldehyde required for sugar formation would have accumulated as a result of photochemical synthesis.[34]

The aldehydes (or the corresponding alcohols) which are the direct Strecker Synthesis precursors to glycine, alanine, and serine were formed photochemically in this study (formaldehyde, acetaldehyde, and ethylene glycol, respectively).[35] In addition acetone and 2-butanone have been reported to give low yields of valine and isoleucine, respectively, when mixed with cyanide and ammonia.[36] However, for these syntheses to have been operative we must assume the presence of ammonia. Yet the photochemical aldehyde synthesis is based on the assumption that water and not ammonia is the principal uv absorbing component of the primitive atmosphere. Two ways out of this dilemma come to mind: (1) assume the initial formation of a stable cyanohydrin which reacts at some later date with the ammonia which was formed by the hydrolysis of cyanide; (2) assume the rate of diffusion of ammonia gas out of water is slower than its rate of photolysis. Ammonia would have been present in solution for amino acid synthesis yet absent in the vapor phase because of its rapid photolysis. Ammonia would still have been subject to rapid photodestruction so that this model would only have been valid for a short time on the geological time scale.

Finally, it should be noted that some of the starting materials and photoproducts in our work have been detected in interstellar space.[37] For example, water, methanol, formaldehyde, and acetaldehyde have been identified. Although our laboratory synthesis of aldehydes, ketones, and alcohols was carried out under conditions which differ appreciably from those in the interstellar medium, our results provide some support for the hypothesis that the interstellar molecules were formed photochemically.[37]

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Photodetachment of Electrons from Phenoxides and Thiophenoxide

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Abstract: The relative cross section for the gas phase photodetachment of electrons has been determined for several substituted phenoxides and thiophenoxide in the wavelength region 300-530 nm (4.13-2.34 eV). An ion cyclotron resonance spectrometer was used to generate, trap, and detect the negative ions and a 1000-W xenon arc lamp with a grating monochromator was employed as the light source. The following quantities were determined: $EA(o\text{-}CH_3C_6H_4O\cdot) \approx EA(C_6H_5O\cdot) \leq 2.36 \pm 0.06$ eV, $EA(o\text{-}ClC_6H_4O\cdot) \leq 2.58 \pm 0.08$ eV, $EA(C_6H_5S\cdot) \leq 2.47 \pm 0.06$ eV. It is suggested that a short wavelength portion of the photodetachment spectrum is the result of electronic excitation of the negative ions, followed by autodetachment.

Recent photodetachment experiments have indicated that complex molecular ions can exhibit unusual behavior. This appears to be particularly true for delocalized systems, such as $C_5H_5^-$ and $C_4H_4N^-$.[3,4] The photodetachment cross section of an anion can provide information about a variety of molecular properties. The threshold yields a vertical electron detachment energy, which in favorable cases also represents the electron affinity of the corresponding radical. Abrupt changes in the photodetachment cross section can arise from transitions to excited states,[5] thus, transition

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