

SYNTHESIS OF ORGANIC COMPOUNDS FROM CARBON MONOXIDE AND WATER BY UV PHOTOLYSIS

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Abstract. The photolysis of water vapor with carbon monoxide at 1849 Å yields alcohols, aldehydes and organic acids, with an overall quantum yield of 3.3×10^{-2} . This rather high quantum yield could have led to a contribution of $\sim 10^{11}$ organic molecules $\text{cm}^{-2} \text{sec}^{-1}$ to the pool of organic material on the primitive Earth. The reactions are initiated by the photolysis of water molecules and the resulting hydrogen atoms reduce the carbon monoxide to a variety of one and two carbon compounds. The organic molecules are dissolved in water and thus escape destruction by photolysis. Photolysis of water vapor with carbon dioxide did not yield organic compounds under these conditions.

Introduction

It is widely accepted now that organic synthesis in the Earth's primitive atmosphere was the opening step for the sequence of events which led to the emergence of life on Earth. Both geological evidence and the current theories on the formation of the solar system suggest that the primitive atmosphere could not have contained free oxygen, but not much more can be said with certainty about the atmospheric composition. Mainly because of the lack of geological evidence from the first $\sim 0.5 \times 10^9$ yr. of the Earth's history and the uncertain nature of the theories concerning the formation of the Earth from the solar nebula, i.e. the thermal history of the forming Earth (Reeves, 1974). The suggested compositions range from a hydrogen rich methane-ammonia atmosphere to a hydrogen free atmosphere composed of carbon monoxide, carbon dioxide and nitrogen (see for instance Kenyon and Steinman, 1969 and Van Trump and Miller, 1973). While a methane-ammonia atmosphere would have been favoured on a cold Earth, formed from a hydrogen rich solar nebula, a carbon monoxide-nitrogen atmosphere would have been outgassed from a hot Earth, formed from a hydrogen deficient nebula. Nevertheless, even a pure methane-ammonia atmosphere would have been enriched quite rapidly with carbon monoxide and nitrogen by the effect of a variety of energy sources upon it (Bar-Nun and Shaviv, 1975). UV radiation, lightning discharges and thunder shock-waves all cause the oxidation of hydrocarbons by water vapor into carbon monoxide. Thus,

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either carbon monoxide was an important atmospheric constituent from the very beginning, or became so during atmospheric evolution.

Organic synthesis of biomonomers from hydrocarbons-ammonia mixtures was studied very extensively both because of the ease of forming a large variety of biomonomers from such mixtures and because of the impact of Miller's (1955) pioneering experiment. The effort devoted to the study of synthesis in a carbon oxides atmosphere was less extensive and the variety of biomonomers formed was smaller. Part of these studies were not related to the Origin of Life problem and were performed before this problem was reopened by Oparin and Haldane (see e.g. Kenyon and Steinman, 1969). Thus, syntheses were performed by electrical discharges on CO-H₂O mixtures (Lob, 1904), CO-H₂ (Lob, 1906), CO-NH₃-H₂O (Lob, 1913), CO-NH₃ (Bessen, 1911), CO-H₂-N₂ (Briner and Hofer, 1940), CO-H₂-N₂-H₂O, CO-H₂-NH₃-H₂O, CO₂-H₂-N₂-H₂O (Abelson, 1957a, 1957b). Ionizing radiation was used by Calvin and coworkers on a CO₂-H₂-H₂O mixture (Garrison et al. 1951). Ultraviolet radiation was used by Getoff et al. (1960) and by Groth and Suess (1938) on CO₂-H₂O mixtures and recently by Hubbard and co-workers (Hubbard et al. 1970, 1971, 1973, 1975, 1976, Horowitz et al. 1972a, 1972b, 1974) on CO-H₂O, CO-CO₂-H₂O, CO₂-H₂O, CO₂-N₂ and CO-NH₃ mixtures. These latter studies were performed in the presence of substrata such as silica or alumina as catalysts, using UV radiation at $\lambda > 2500 \text{ \AA}$. In one case (Hubbard et al. 1971), the photolytic reactions in a CO-H₂O mixture were studied at $\lambda < 2000 \text{ \AA}$ in the gas-phase, without a catalyst. In these experiments however, the products remained in the gas-phase or were deposited on the walls, being therefore vulnerable to photolytic destruction and rendering the quantum yield measurements quite meaningless. It was felt therefore that the yields could be improved considerably if the products were to be absorbed in liquid water, thereby escaping destruction. The set-up of gas-phase photolysis which is followed by absorption in liquid water is a realistic simulation of conditions in the primitive atmosphere, provided that the photolysis takes place close to the cloud tops, as will be discussed below.

One further comment regarding the atmospheric partial pressure of carbon monoxide should be made, in view of the reaction: $\text{CO} + \text{OH}^- \rightleftharpoons \text{HCOO}^-$. Van Trump and Miller (1973), after a kinetic study of this reaction, suggest two limiting cases: One in which all the carbon monoxide was present initially in the atmosphere and its partial pressure was determined either by the rate of the formate producing reaction (in a cold ocean) or by the rate of oceanic mixing (in a hot ocean). In the second and more realistic case, the rate of gradual outgassing of carbon monoxide and the rate of its conversion to formate would balance at a certain steady state of carbon monoxide partial pressure. Their range of estimated steady state levels might be improved by taking into account the gradual accumulation of water in the oceans and of additional carbon monoxide removal mechanisms, such as oxidation to carbon dioxide and reactions of the sort which is discussed below. The complexity of this problem is indeed very large, as shown for instance by Bortner et al. (1972) for the case of carbon monoxide in the Earth's contemporary atmosphere. Nevertheless, it is clear that a very large carbon monoxide

partial pressure can not be expected to exist in the primitive atmosphere for extended periods. Rather, 10^{-1} to 10^{-4} atm. would be a more likely value.

Experimental

The carbon monoxide photolysis experiments were performed in a cylindrical Spectrosil quartz vessel, 30 cm long and 3 cm wide. After thorough cleaning of the vessel and its outgassing at 10^{-6} torr for an hour, 1 ml of triple distilled water was introduced into it. The water was degassed by four freezing and thawing cycles at a vacuum of 2×10^{-5} torr. Carbon monoxide ('Matheson Purity' — 99.99%) or carbon dioxide (Matheson — 'Coleman Instrument' purity — 99.99%) was then introduced into the vessel which, after vigorous shaking, was equilibrated at 40°C for 30 min, before irradiation. All pressures were measured by mechanical gauges and the system was completely free of mercury vapor. Irradiation by a Thermal Syndicate low pressure mercury lamp having a flux of 1.8×10^{18} photons min^{-1} at 1849 Å, was done either through the end of a horizontal vessel or through the side of a vertical vessel. In the experiments with a vertical vessel, the lamp was placed about 10 cm above the liquid water, which was therefore not irradiated. In the horizontal experiments, the vessel was slightly tilted, so that the liquid water accumulated at the far end of the 30 cm long vessel and was not irradiated. In both cases, a film of water droplets was formed on the walls in cold areas which were always far from the lamp and thus were not irradiated.

A Corning type 9–54 filter was used in some experiments, to cut off radiation at wavelengths shorter than 2000 Å. Actinometry of the lamp was done according to the method of Leighton and Forbes (1930), using a Corning, type 9–54, filter for monitoring the lamp's output below and above 2000 Å. A flux of 1.8×10^{18} photons min^{-1} was found for $\lambda < 2000$ Å and a flux ten times larger for $\lambda > 2000$ Å. The lamp was placed 0.5 cm away from the irradiation vessel and the light was not collimated. In this setup, quantum yields could be calculated only in experiments with a vertical vessel.

After irradiation, the vessel was shaken vigorously and an aliquote of the solution was injected into a Packard-Becker model 417 gas chromatograph for analysis. The various products were identified by their retention times on a Porapak-QS column, by comparison with those of known compounds. The limit of detection by the GC flame ionization detector was ~ 1 n mole. Formaldehyde was also analyzed by a spectrophotometric method, using chromotropic acid (Feigel, 1960) and carbonyl compounds by precipitate formation with 2, 4-DNP (Vogel, 1957).

Results and Discussion

The experimental results are summarized in Table 1. Clearly, the photolysis at 1849 Å of carbon monoxide-water mixtures yields a rather surprising variety of products. No organic products are observed when irradiation is done only at 2537 Å and likewise when carbon dioxide replaces the carbon monoxide. Although in the latter case some carbon

TABLE I
Results of carbon oxides-water photolysis

Run	vessel's position ^a	CO torr	CO ₂ torr	time of irradiation hrs	irradiation at λ , μ	precipitate	Products μ M ^c						total yield (d) of organics μ M C ₁ /hr
							HCHO	CH ₃ CHO	CH ₃ OH	HCOOH(d) + CH ₃ CH ₂ OH	CH ₃ COOH	CO	
2	horizontal	300	—	43	1849 2537	yellow	2.3	0.8	30.0	1.0	8.4	1.2	
4	vertical	300	—	46	1849 2537	yellow-brown	5.1	0.5	17.0	7.8	9.5	1.2	
3	horizontal	300	—	65	2537	—	<10 ⁻³	—	—	—	—	—	
5	vertical	300	—	47	2537	—	<10 ⁻³	—	—	—	—	—	
6	vertical	300	220	65	1849 2537	dark yellow	<10 ⁻³	—	0.4	2.8	33.0	1.1	
8	vertical	—	340	188	1849 2537	—	—	—	—	—	—	2.4 0.01	

^aIrradiation was done either from the end of a horizontal vessel or through the side of a vertical vessel. The temperature of the reaction vessel was maintained at 40 °C, leading to a water vapor pressure of 55 torr.

^bIn some experiments a filter for $\lambda < 2000 \text{ \AA}$ was inserted between the irradiating lamp and the vessel.

^cThe values listed are an average of two identical experiments.

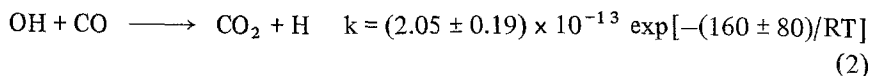
^dFormic acid and ethanol could not be separated on the GC column. Therefore their yields were calculated by using an average sensitivity in the GC detector and in the calculation of the total yield as C₁, their combined yield was multiplied by 1.5.

monoxide is being formed. The distribution of products from carbon monoxide alone and from a mixture of carbon monoxide and dioxide is quite different. In all the experiments with carbon monoxide, a yellow or yellow-brown solid was deposited on the wall adjacent to the irradiation lamp. This substance could not be dissolved in water or acetone and was dissolved only in concentrated sulphuric acid. Upon addition of 2 ml. of concentrated sulphuric acid to 0.5 ml of the solution (for the analysis of formaldehyde) a yellow-brown color developed. As this color interfered with the quantitative analysis of formaldehyde, known quantities of formaldehyde were added to the solution and its original content was obtained by extrapolation. The nature of the solid was not investigated at this stage. However, since the solid is present also when aldehydes are absent from among the reaction products, it seems that aldehydes are not involved in the formation of the solid, which is therefore not a sugar. A possible candidate might be a carbon suboxide polymer. Obviously, more experimental work, which is now in progress, is necessary before complete characterization of this chemical system can be achieved. Nevertheless, some preliminary conclusions can be already drawn at this stage. The absence of organic products after irradiation at 2537 Å suggests that surface catalysis by the quartz walls is rather inefficient, in agreement with the results of Hubbard and co-workers. In the study of surface catalyzed reactions at $\lambda > 2500$ Å, Hubbard uses substrata with very large surface areas and such an area was not available in the present experiments. The experimental results also do not contradict the results of Van Trump and Miller, where OH⁻ ions were found to catalyze the conversion of carbon monoxide to formate. As they suggested, water alone does not seem to catalyze this reaction.

Since carbon monoxide does not absorb at 1849 Å, the reaction should be initiated by the photolytic dissociation of water molecules into H and OH radicals (Calvert and Pitts, 1966), and the reduction of carbon monoxide starts with an attack by a hydrogen atom:



The photolysis of carbon dioxide alone, with water, did not yield any organic products nor the yellow solid. Only a very small conversion to carbon monoxide was observed, about two orders of magnitude lower than for organics from carbon monoxide. This result is reasonable, since carbon monoxide is readily oxidized to carbon dioxide by OH radicals, through the following reaction:



(Davis et al. 1974. The rate constant is in cm³ molec⁻¹ s⁻¹ and the activation energy in cal.). Thus, both H and OH compete for the carbon monoxide, in reactions (1) and (2) respectively. As will be shown later, the experimental pressure regime was similar to the atmospheric pressure at the water photolysis layer and therefore, the relative rates of the two reactions in the experiments are similar to the atmospheric ones. In the presence of a small amount of carbon monoxide, most of it will be oxidized back to carbon dioxide by the OH radicals, while in the presence of a large amount of carbon monoxide, the OH radicals will be exhausted by the reaction with carbon monoxide and the rest of the

carbon monoxide will be available for reactions with hydrogen atoms, to form organic molecules.

Rates of Production

The overall quantum yield for the incorporation of carbon from carbon monoxide into organic molecules can be obtained from the number of molecules produced and the number of photons absorbed by the water vapor. From the last column on Table 1, the total yield of organics as C_1 was $1.2 \mu\text{M h}^{-1}$ for run 4. At 40°C , the water vapor pressure was 55 torr (CRC – Handbook of Chemistry and Physics, 1967) which, with an absorption coefficient of $1 \text{ atm}^{-1} \text{ cm}^{-1}$ (Calvert and Pitts, 1966), absorbed 20% of the lamp's flux of 1.08×10^{20} photons h^{-1} . Thus, the quantum yield for C_1 incorporation into organic molecules is 3.3×10^{-2} .

The quantum yield reported here is likely to be an upper limit, since not all the organic molecules which were produced in the gas-phase were immediately dissolved in the liquid phase. The rate at which the organic molecules entered the liquid phase is not known, but is certainly not infinite compared to their rate of production. Therefore, some of the products were photolyzed in the gas phase, thus lowering the quantum yield if the photolysis products were carbon monoxide or dioxide and probably also affecting the product distribution. This situation is, however, quite similar to the situation in the atmosphere, where the photolysis occurs mainly above the cloud tops and the products are dissolved in the water droplets of the clouds only later.

Although the quantum yield was obtained by irradiation with the 1849 Å mercury resonance line, it is reasonable to assume that a similar value would have been obtained with a lamp having a continuous spectrum. This assumption is based upon the quantum yield of unity for the photolytic decomposition of water into $\text{H}(^2\text{S}_{1/2})$ and $\text{OH}(^2\pi)$ at all wavelengths longer than 1356 Å (Calvert and Pitts, 1966). A high pressure xenon arc will be used in the next series of experiments, in order to clarify this point.

The contributions to organic synthesis by the surface catalyzed reactions and the gas-phase reactions can now be evaluated. The quantum yield which was obtained for the gas-phase reactions is ~ 3000 times larger than the overall quantum yield of $\sim 10^{-5}$, which was obtained by Hubbard et al. (1973) for the surface catalyzed reactions at $\lambda > 2500 \text{ Å}$. A flux of 1.11×10^{15} photons $\text{cm}^{-2} \text{ s}^{-1}$ at $\lambda < 2900 \text{ Å}$ is currently reaching the upper atmosphere of the Earth (CRC – Handbook of Chemistry and Physics, 1975). Since it is assumed that the solar constant has increased by 40 percent over geological time (Sagan and Mullen, 1972), the flux at $\lambda < 2900 \text{ Å}$ was only 7.9×10^{14} photons $\text{cm}^{-2} \text{ s}^{-1}$. A limit of 2900 Å was determined from the sharp decrease in yields at $\lambda > 2800 \text{ Å}$ which was reported by Hubbard et al. (1973).

The flux which was available for water photolysis up to its absorption limit at 2000 Å (Calvert and Pitts, 1966), depended upon the atmospheric composition at that time. As mentioned earlier, a reasonable composition in the case of outgassing from a hot interior is nitrogen, carbon monoxide, carbon dioxide and sulphur dioxide. This is similar to the composition of volcanic emanations (Holland, 1963), with the water soluble gases being

heavily depleted from the atmosphere. Reasonable values for the mixing ratios of carbon dioxide and sulphur dioxide in the atmosphere could be their contemporary values, which are determined by the buffer capacity of the oceans for these gases. Thus, the mixing ratio of carbon dioxide would have been about 3×10^{-4} and that of sulphur dioxide $0-10^{-6}$ (McElroy, 1976). As mentioned earlier, the mixing ratio of carbon monoxide was probably between 10^{-1} and 10^{-4} . If the sulphur dioxide mixing ratio was near 10^{-6} , its high absorption at $\lambda < 2000 \text{ \AA}$ and between 2400 and 3000 \AA (Calvert and Pitts, 1966) would have led to a complete blocking of the radiation in these regions. In this case, both the gas-phase and the surface catalyzed reactions could not be operative. For these reactions to take place, the sulphur dioxide mixing ratio should have been 10^{-8} or less, which is well within the contemporary range of $0-10^{-6}$ (McElroy, 1976). Absorption by carbon monoxide at $\lambda < 1700 \text{ \AA}$ (Calvert and Pitts, 1966) would block only a minor fraction of the solar flux, which decreases very steeply in this region. Absorption by carbon dioxide would move this limit to 1800 \AA (Calvert and Pitts, 1966).

Although the water vapor-carbon monoxide reactions are discussed here in order to show that biomonomers could be produced even if the atmosphere was partly oxidized and lacked molecular hydrogen from the very beginning, it is worth mentioning that a completely reduced methane-ammonia atmosphere should have passed through a nitrogen-carbon monoxide-water vapor stage (Shaviv and Bar-Nun, 1975). In this case, large scale water photolysis in the troposphere could not have taken place until the atmosphere was completely cleared up of the products of methane and ammonia photolysis, as some of these species absorb strongly at $\lambda < 2000 \text{ \AA}$.

Coming back to the partially oxidized atmosphere and assuming a sulphur dioxide mixing ratio lower than 10^{-8} , the flux which was available for water photolysis, between 1800 and 2000 \AA , would have been $5.87 \times 10^{12} \text{ photons cm}^{-2} \text{ s}^{-1}$ (CRC — Handbook of Chemistry and Physics, 1975; Sagan and Mullen, 1972). The ratio of fluxes: $\phi(\lambda 1800-2900 \text{ \AA})/\phi(\lambda 1800-2000 \text{ \AA})$ would have been 134. With the quantum yield of the gas-phase reactions being about 3000 times larger than the quantum yield of the surface catalyzed reactions, it seems that the contribution to organic synthesis by the gas-phase reactions could have been about 20 times larger than the contribution by the surface catalyzed reactions.

From the solar flux of $5.87 \times 10^{12} \text{ photons cm}^{-2} \text{ s}^{-1}$ between 1800 and 2000 \AA and the experimentally obtained quantum yield of $\sim 3 \times 10^{-2}$, the rate of production of alcohols, aldehydes and acids with one and two carbon atoms in the primitive atmosphere would have been $\sim 1.8 \times 10^{11} \text{ molecules cm}^{-2} \text{ s}^{-1}$. This rate of production is comparable to the rate of $\sim 10^{10} \text{ molecules cm}^{-2} \text{ s}^{-1}$ calculated for the production of amino acids by thunder shock-waves in a hydrocarbon-ammonia atmosphere (Bar-Nun et al. 1970). The question now arises as to where the production of these molecules takes place, since a proximity to the clouds is essential for their survival. From the altitude dependant water content of the contemporary atmosphere (U.S. Standard Atmosphere, 1976), it is apparent that the larger part of the solar flux at $\lambda < 2000 \text{ \AA}$ would be absorbed by the water vapor around an altitude of 10 km. At this altitude, the atmospheric pressure is around 0.25 bar, which is similar to the pressure of 300 torr at which the present experiments

were carried out. This altitude is well within the range of the cloud tops, and therefore the produced molecules could dissolve in the water droplets of the clouds and rain down on the surface. The fraction of molecules which were shielded from further photolysis depended therefore on the cloud coverage of the primitive Earth. If the contemporary cloud coverage of 50% was maintained during that era, this much of the organic molecules could survive. The atmospheric lapse rate at that time was most likely different from the contemporary one, because of the different atmospheric composition. This, however, should not have affected the rates of production but only shifted the cloud tops, and the water photolysis layer above them, to a different altitude.

In concluding the discussion on the rates of formation of biomonomers by the photolysis of water vapor and carbon monoxide, it should be stressed again that we have no geological evidence of any kind for the atmospheric composition more than 3.76 b.y. ago. We do know, however, that before 3.76 b.y. ago enough carbon dioxide was present in the atmosphere to form carbonate deposits, such as those found in the Isukasia formation in Greenland (Moorbath et al., 1973; Perry and Ahmad, 1977). Therefore, the estimated rates of formation are necessarily only indicative of the possible contribution of such processes to the pool of organic matter on the primitive Earth.

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