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Study of the photoinduced formose reaction by flash and stationary photolysis

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The chemical condensation of formaldehyde into more complex aldehydes (glycolaldehyde and glyceraldehyde) and monosaccharides (glucose, lyxose, erythrose and erythrulose) under UV irradiation was found to proceed in acidic aqueous solutions in the absence of catalysts and initial primers.

The chemical condensation of formaldehyde (the formose reaction) occurs in the presence of inorganic bases acting as catalysts to form a complex mixture of carbohydrates.[1–3] The formose reaction is an autocatalytic process since the necessary condition for the reaction to proceed is the presence of an initiating primer in the form of at least several molecules of monosaccharides.[2] Namely this feature of the formose reaction has recently attracted special attention. The reaction, due to its autocatalytic character and a possibility to produce the monosaccharide ribose, could serve as one of the major ways of chemical evolution on the prebiotic Earth.[4]

The most active primer for the formose reaction is glycolaldehyde. In the presence of even small amounts of glycolaldehyde in the initial solution, the formaldehyde consumption starts without an induction period. In the course of the reaction, the glycolaldehyde concentration increases, and its following reactions result in the formation of a broad spectrum of carbohydrates. A possible mechanism of the primer formation on the prebiotic Earth might be based on the light-induced transformations of formaldehyde.[5,6] The aim of this work was to study the influence of UV irradiation on the formose reaction, first of all, at its initial stage.

The photochemistry of formaldehyde plays an important role in the chemistry of atmosphere, and the photochemical properties of formaldehyde in the gas phase were studied in detail.[7,8] In aqueous solution, formaldehyde exists mainly in the hydrated form of methylene glycol, $CH_2(OH)_2$. Since the hydrated form of formaldehyde is a very weak chromophore, the mechanism of formaldehyde photolysis in aqueous solutions is poorly understood. Nevertheless, at high formaldehyde concentrations, one can achieve the optical densities of solutions of about 0.1–0.5 units per centimeter in the wavelength range 250–350 nm (Figure 1), which allows the use of laser flash photolysis (LFP)[9] for the investigation of the reaction mechanism. The goal of this study was to identify intermediates and products formed in the photolysis of aqueous formaldehyde solutions. To avoid the influence of the regular formose reaction on the proceeding of photochemical reaction, all of the experiments were carried out in acidic solutions and in the absence of catalysts, *i.e.*, under conditions when the regular formose reaction does not occur.

Table 1 Changes in the concentrations of the initial compound (formaldehyde) and the reaction products and in pH in an irradiated aqueous formaldehyde solution.

Compound	Irradiation time/h					
	0	4	8	18	24	28
Formaldehyde, mol dm^{-3}	11.8	10.7	8.0	5.5	2.9	1.7
pH	3.18	2.12	1.92	1.83	1.79	1.74
Formic acid, mol dm^{-3}	–	0.32	0.80	1.22	1.46	1.84
Glycolaldehyde, mol dm^{-3}	–	0.074	0.105	0.115	0.100	0.110
Glyceraldehyde, mmol dm^{-3}	–	2	4	8	6	6
Glucose, mmol dm^{-3}	–	2.0	4.3	5.6	7.7	5.7
Lyxose, mmol dm^{-3}	–	–	–	1.1	1.7	1.8
Erythrose, mmol dm^{-3}	–	–	–	0.8	1.1	1.2
Erythrulose, mmol dm^{-3}	–	–	–	1.8	2.4	2.2

The transient absorption spectrum observed 1 μs after the laser pulse irradiation (λ = 308 nm) of a deaerated aqueous 10.4 M formaldehyde solution (pH 3.2) is shown in Figure 2. At all wavelengths the signal decays with the same rate, and, thus, can be attributed to the same intermediate. Under argon, the signal decay obeys a second-order rate law, at the absorption maximum at 380 nm the decay is characterised by $k_1/\varepsilon_{380} = (1.3\pm0.2)\times10^6$ cm s^{-1}, where k_1 is the second-order rate constant, and ε_{380} is the absorption coefficient of the intermediate. Under oxygen, the initial intensity of the transient absorption signal does not change,

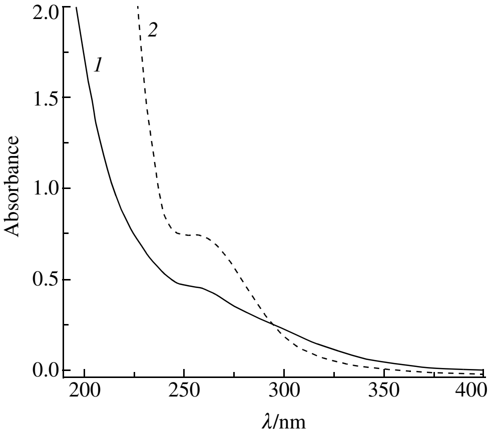

Figure 1 Absorption spectra of an aqueous 12.6 M formaldehyde solution: (*1*) before irradiation; (*2*) after irradiation for 4 h followed by dilution by a factor of 10.

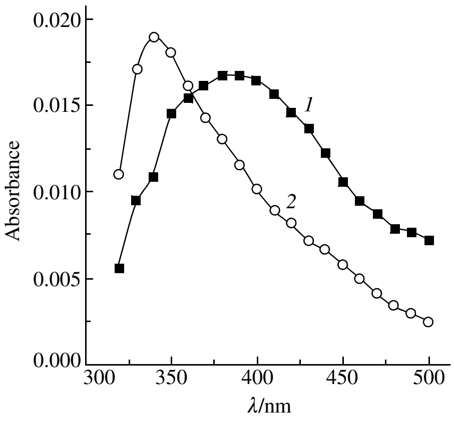

Figure 2 Transient absorption spectra obtained 1 μs after pulse photolysis: (*1*) 10.4 M formaldehyde solution in water; (*2*) same solution preirradiated for 4 h and then diluted by a factor of 15.

while the decay significantly accelerates and becomes exponential (Figure 3). The rate constant of the oxygen quenching, $k_2 = (6.1\pm0.8)\times10^9$ dm^3 mol^{-1} s^{-1}, was determined from the dependence of the decay rate on oxygen concentration. Thus, the observed intermediate with the absorption maximum at 380 nm is the formaldehyde triplet state. Unfortunately, the quenching mechanism remains unknown: whether the reaction between the triplet formaldehyde and oxygen is electron transfer yielding a formaldehyde cation radical and superoxide, or the triplet energy transfer from formaldehyde to oxygen takes place, resulting in the singlet oxygen formation. Nevertheless, taking into account that by the completion of quenching (about 1 μs with a dissolved oxygen concentration of 1 mM) practically no residual absorp-tion is observed at all wavelengths, one can presume that the triplet energy transfer is a more probable quenching mechanism. Thus, the primary reactions taking place in the direct 308 nm photolysis of aqueous formaldehyde solution can be described by the following scheme:

$$\mathrm{HCHO + H_2O \longleftrightarrow CH_2(OH)_2} \quad (1)$$

$$\mathrm{HCHO \xrightarrow{h\nu} {}^{T}HCHO^*} \quad (2)$$

$$\mathrm{2\,{}^{T}HCHO^* \xrightarrow{k_1} 2HCHO} \quad (3)$$

$$\mathrm{{}^{T}HCHO^* + O_2 \xrightarrow{k_2} HCHO + {}^{S}O_2} \quad (4)$$

$$\mathrm{{}^{T}HCHO^* + CH_2(OH)_2 \xrightarrow{k_3} {}^{\cdot}CH_2OH + {}^{\cdot}CH(OH)_2} \quad (5)$$

Note that under our experimental conditions the decay of the triplet formaldehyde signal remains bimolecular at the highest concentrations of the initial solution (up to 12 M) and the lowest intensities of laser flashes (down to 7 mJ per pulse). From that one can conclude that the rate constant k_3 of reaction (5) does not exceed 10^4 dm^3 mol^{-1} s^{-1}.

The formation of gas bubbles in the solution was observed during steady irradiation. One can assume that the gases are CO, CH_4, CO_2, H_2, and minor amounts of ethane and ethylene, as was shown earlier.[6]

A sample placed in a quartz cell was irradiated for several hours with full light from a DRSh-500 high-pressure mercury lamp. Then, the irradiated solution was treated with dinitrophenylhydrazine,[10] and monosaccharides were analysed by HPLC after derivatization. The formaldehyde concentrations were determined optically by the reaction with chromotropic acid.[11] Table 1 shows the product yields for different irradiation times. The concentrations of glycolaldehyde and glyceraldehyde grow up only at the initial stage of the irradiation, and then remain almost constant. These intermediate products participate in secondary photochemical reactions yielding more complex monosaccharides. A significant decrease in pH of the irradiated solution was also observed. The acid analysis performed with the use of a Nucleosil SA ion-exchange column, has shown that formic and acetic acids in the ratio of ~15:1 are accumulating in the solution.

The formation of methanol or ethanol was not detected in the solution. Thus, the Cannizzaro reaction

$$\mathrm{R{-}CHO + CH_2(OH)_2 \longrightarrow R{-}CH_2OH + HCOOH},$$

which usually accompanies the Butlerov reaction and results in the formation of formic acid and an alcohol, does not occur in our case. The acid formation could probably proceed *via* a radical mechanism.

Note that the optical properties of the solution significantly changed in the course of irradiation. The products, which absorb much stronger than the initial formaldehyde solution, are formed already at the early stage of the photolysis. Figure 1 shows the absorption spectrum of the solution irradiated for 4 h and then diluted with water by a factor of 10. The product has a maximum at 260 nm, at this wavelength its absorption is about 15 times stronger than that of the initial solution. Apparently, under these conditions, the main contribution to the photolysis will be given by the light absorption of this product rather than by that of formaldehyde. Indeed, the transient absorption spectrum observed in the flash photolysis of the pre-irradiated sample differs from the spectrum recorded with the fresh formaldehyde solution (Figure 2). The spectrum becomes narrower, and its maximum shifts to 340 nm. Oxygen quenches this intermediate with the rate constant $k_4 = (8\pm2)\times10^8$ dm^3 mol^{-1} s^{-1}. Most likely, this short-lived intermediate should be attributed to the triplet state of a photoactive product formed in the photolysis.

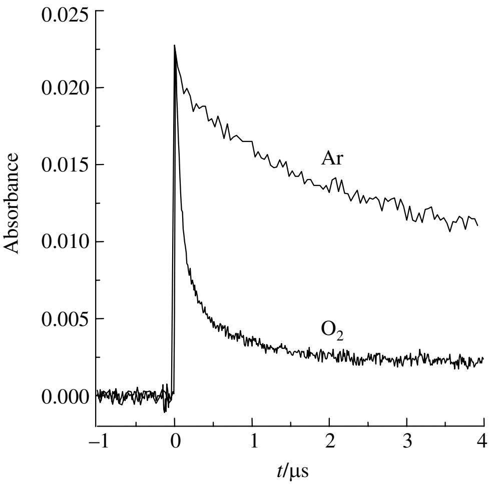

Figure 3 Transient absorption kinetics observed at 380 nm in the photolysis of an aqueous 10.4 M formaldehyde solution under argon and oxygen.

The influence of oxygen on the photochemical reaction was studied by performing the photolysis of a 12.6 M formaldehyde solution with bubbling argon or oxygen followed by the analysis of the irradiated samples. Under oxygen, both formaldehyde consumption and product formation decreased by a factor of 2–3. This result additionally testifies that the reaction under study occurs *via* the formation of triplet states of formaldehyde and photoactive photolysis products, and that the oxygen quenching evidently proceeds through triplet energy transfer.

Thus, the chemical condensation of formaldehyde into more complex monosaccharides can proceed under UV irradiation even in acidic solutions without catalysts and initial primers. At the initial stage of irradiation, the photolysis proceeds through the formation of a fomaldehyde triplet state, the subsequent reactions of the latter result in the formation of photoactive products. Under further irradiation, the primary products absorb the majority of light, and the formation of complex carbohydrates (glucose, lyxose, erythrose and erythrulose) seems to be the result of these secondary photochemical processes.

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