

Amino acid formation induced by high-power laser in CO₂/CO–N₂–H₂O gas mixtures

Svatopluk Civiš^a, Libor Juha^{b,*}, Dagmar Babánková^{a,e}, Josef Cvačka^c,
Ota Frank^d, Jan Jehlička^d, Božena Králiková^b, Josef Krása^b, Pavel Kubát^{a,e},
Alexandr Muck^c, Miroslav Pfeifer^b, Jiří Skála^b, Jiří Ullschmied^e

^a J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague 8, Czech Republic

^b Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 18221 Prague 8, Czech Republic

^c Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 16610 Prague 6, Czech Republic

^d Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University in Prague, Albertov 6, 12843 Prague 2, Czech Republic

^e Institute of Plasma Physics, Academy of Sciences of the Czech Republic, Za Slovankou 3, 18221 Prague 8, Czech Republic

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Abstract

In a mixture of molecular gases with compositions (CO₂–N₂–H₂O and CO–N₂–H₂O) and total pressure close to that of the Earth's early atmospheres, a centimeter-sized plasma was created by focusing a single 85-J, 450-ps near-infrared laser pulse in a center of 15-L gas cell. Chemical consequences of the laser-produced plasma generation in such a mixture were investigated using high-performance liquid chromatography with mass-spectrometric detection (HPLC/MS). Amino acids were identified in the reaction mixture containing CO₂ as well as in that one based on CO, both exposed to 10 laser shots.

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1. Introduction

The boom of experimental studies in prebiotic synthesis of bioorganic compounds began with Miller's famous experiment [1,2] fifty years ago. Numerous organic compounds were formed with high yields from a mixture of CH₄–NH₃–H₂O–H₂, mimicking strongly reducing early Earth's atmosphere, initiated by an electric spark [1,2]. The situation became more complicated because of further development of the theories of the Earth's primitive atmosphere [3]. In the newly suggested, mildly reducing mixtures a spark discharge induced a formation of only a low quantity of organic compounds [4]. Therefore other techniques, e.g., a radiolysis with XUV synchrotron radiation [5], were tested for an initiation of chemical

reactions in the mixtures, containing CO₂ as a main source of carbon. Recently, weighty arguments were presented [6] in support of large amounts of CO in the primitive atmosphere. The CO-dominant atmosphere has already been exposed to 2.5–3.0 MeV protons [6], XUV synchrotron radiation [7], magnetoplasma dynamic arc-jet [8,9], and spark discharge [8]. A formation of amino acids [7,8] and RNA bases [6,9] were reported. However, the electric spark almost failed to produce amino acids [8].

We exposed CO₂–N₂–H₂O and CO–N₂–H₂O mixtures to a large-scale laser spark, modeling a chemical action of high-energy-density events (i.e., lightning [10], impact of an extraterrestrial body [11], etc.) in primitive atmospheres containing a large portion of carbon dioxide or monoxide. An HPLC/MS search for four selected amino acids was carried out after running ten laser sparks induced by a high-power laser system in the mixture. The results of this search are reported in this Letter.

* Corresponding author. Fax: +420-2-868-90265.

E-mail address: juha@fzu.cz (L. Juha).

2. Experimental

Laser-induced dielectric breakdown (LIDB) in the molecular gases was achieved with an iodine photodissociation high-power laser system, working at a fundamental frequency ($\lambda = 1.3152 \mu\text{m}$). Single 400-ps laser pulses were extracted from the Prague Asterix Laser System (PALS) [12] behind 4th amplifier. Each pulse carries an energy of $(97 \pm 36) \text{ J}$. One pulse per twenty minutes is delivered by the laser system. The laser beam was focused in the gas cell by a plano-convex lens with focal length and diameter of 25 and 15 cm, respectively. Pulse energy losses at the focusing lens and cell window do not exceed 15%. Details and scales of the experimental layout can be seen in Fig. 1. The emission spectra of the LIDB plasma were measured with optical multi-channel analyzer OVA-284-V2.0 (ZWG-Berlin, Germany).

The glass absorption cell (Fig. 1a) and all glass instruments (pipettes etc.) were cleaned by concentrated HNO_3 , then by deionized water (delivered from Milli-Q Gradient A10; Millipore) and baked in an oven at a temperature of $500 \text{ }^\circ\text{C}$. The cell was evacuated overnight

using oil-free pump (10^{-3} Torr) and a liquid nitrogen trap located at the entrance of the cell to protect the cell against an organic contamination, and then filled by the mixture of $\text{CO}_x\text{-N}_2$ (1:1; CO , CO_2 – Linde 99%, N_2 – Messer 99.996%) to atmospheric pressure and by 10 mL of deionized water. The gaseous mixture was, after irradiation, bubbled into 10 mL of deionized water. When all the gas was pumped out (pressure about 1 Torr), the cell was opened, the water was collected, and the cell was washed with 5 mL of deionized water again. All samples were put together, and the volume was reduced in a vacuum evaporator to 2 mL. Then 500 μL of 6 M HCl (Lachema, p.a.) was added, and this mixture was heated at $110 \text{ }^\circ\text{C}$ for 24 h and dried under vacuum.

Derivatization of the sample with dansylchloride for HPLC analysis of amino acids is described in detail in [13]. The solid sample extracted from the cell, $1 \times 10^{-4} \text{ mol}$ dansylchloride (Sigma-Aldrich, 99%) and $3 \times 10^{-4} \text{ mol}$ Na_2CO_3 (Lachema, reagent grade) were dissolved in 500 μL of water/acetonitrile/acetone mixture (1:1:3). Acetonitrile was Chromasolv-gradient grade purchased from Riedel de Haen. The system reacted in the dark at a laboratory temperature for 24 h. The resulting solu-

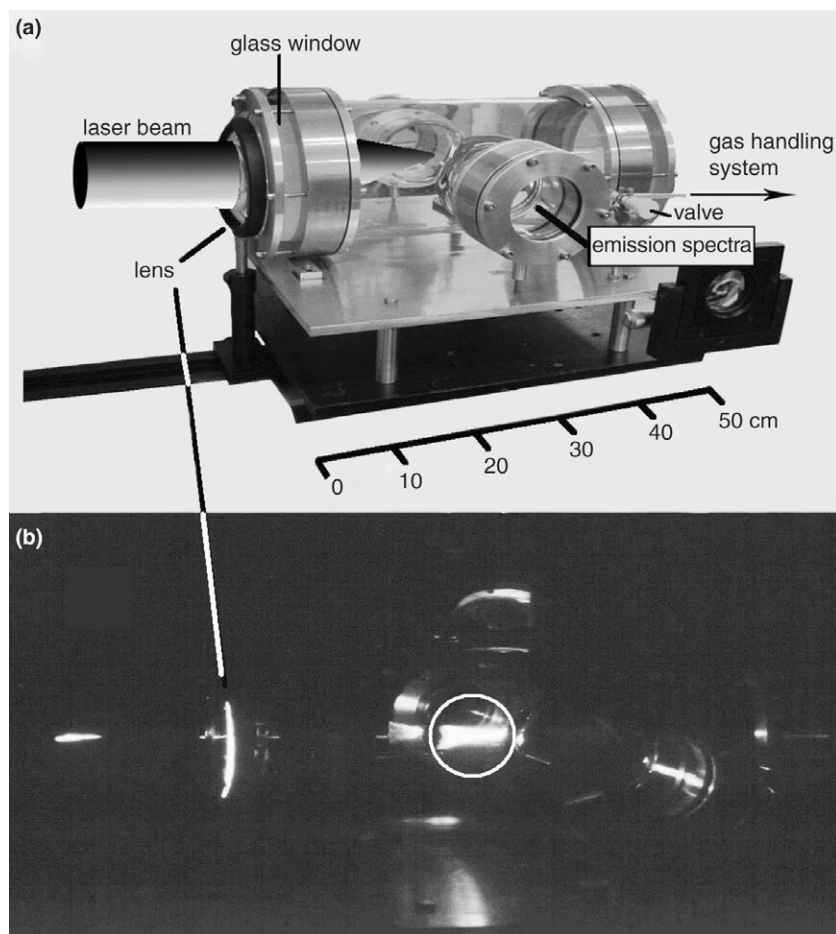


Fig. 1. (a) The layout used for focusing of the PALS beam in the gas mixture. (b) Time-integrated photograph of a plasma created in the cell by a single, 85-J laser pulse focused in the $\text{CO}_2\text{-N}_2\text{-H}_2\text{O}$ mixture; the laser spark is circled.

tion was acidified by KHSO_4 (1M; Lachema, reagent grade) to pH 2–3. Then it was extracted three times into 0.5 mL of dichloromethane (Lachema, p.a.), and the residual salts were removed three times by 2 mL of de-ionized water. Finally, the solution was dried in the stream of N_2 (Messer, 99.996%) and the evaporation residue was dissolved in methanol (Riedel de Haen, Chromasolv-gradient grade; 50 μL). The standards of amino acids (glycine, alanine, serine, and asparagine; all Sigma-Aldrich) were prepared for the analysis in a similar way.

The HPLC was performed on Finnigan LC/MS system, consisting of vacuum membrane degasser SCM 1000, quaternary gradient pump P 4000, autosampler AS 3000, spectrophotometric diode array detector UV 6000 LP (all Thermo Separation Product, Inc., USA) and ion-trap mass spectrometric detector LCQ (Finnigan Corp., USA). The system was controlled by a personal computer with Xcalibur software (Finnigan Corp., USA) and SN 4000 control unit (Thermo Separation Product, Inc., USA). The Adsorbosphere HS column (250 \times 4.6 mm, 5 μm) together with the Adsorbosphere HS pre-column (7.5 \times 4.6 mm, 5 μm ; both from Alltech, thermostated at 30 $^\circ\text{C}$) was used for separation of the samples prepared by the procedure described above and standard amino acids in acetonitrile/water mobile phase (linear gradient elution: from 1% to 100% acetonitrile in 30 min, then neat acetonitrile from 30 to 40 min). The flow rate was 0.5 mL/min; 5 μL of methanolic solution was injected. The mass spectrometer worked in a full-scan mode ($m/z = 50\text{--}1000$ range). Individual dansylated (Dns) amino acids, alanine (retention time of 17.1 min), glycine (15.3 min), serine (13.6 min), and asparagine (24.8 min) were identified based on their mass spectra and by a comparison of retention times of unknowns and standards.

During the experimental campaign held at the PALS facility several blank experiments were performed in the cell. All the procedures described above were carried out, only the laser beam was not sent into the cell. No measurable production of amino acids was found.

3. Results and discussion

The centimeter-sized plasma, which is shown in Fig. 1b, was produced by 85-J pulse of near-infrared-laser radiation focused into the gas cell. According to the optical spectra shown in Fig. 2a, the LIDB plasma contains excited carbon and nitrogen ions, atoms and molecules, and CN as well. The spectrum shown in Fig. 2a is very similar to a spectrum (Fig. 2b of graphite-ablation plume expanding into low-pressure nitrogen, generated by a conventional excimer laser [14]. Broadening of emission lines in Fig. 2a is due to the atmospheric pressure of the $\text{CO}_2\text{--N}_2\text{--H}_2\text{O}$ mixture. The

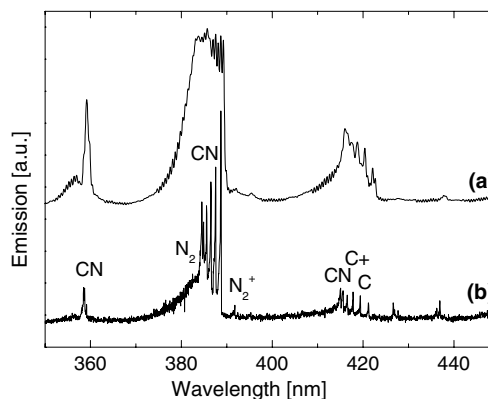


Fig. 2. Comparison of emission spectra (a) measured in this work from the plasma produced by a laser-induced dielectric breakdown in the $\text{CO}_2\text{--N}_2\text{--H}_2\text{O}$ mixture with (b) that of the plasma formed by KrF excimer laser ablation of graphite under nitrogen (nitrogen pressure: 20 Pa, laser fluence: 5 J/cm^2 , distance: 1 mm from the target [14]).

similarity of both spectra supports a possibility to simulate chemical processes initiated by a high-energy-density event in a model atmosphere utilizing an ablation plume formed from carbonaceous solids [15].

Chemical consequences of LIDB in the $\text{CO}_2/\text{CO--N}_2\text{--H}_2\text{O}$ mixtures were evaluated with HPLC/MS. Prior to the analysis, products were hydrolyzed and subsequently derivatized with dansylchloride. Dansylchloride is known to react with amino acids forming corresponding sulfonamides quantitatively. Such Dns-amino acids are easy to separate in reversed-phase HPLC systems and give a high flux of pseudomolecular ions $[\text{M}+\text{H}]^+$ by atmospheric pressure chemical ionization. The HPLC trace shown in Fig. 3a clearly indicates the presence of alanine among the products formed in the $\text{CO}_2\text{--N}_2\text{--H}_2\text{O}$ mixture exposed to LIDB plasma, because the peak of Dns-Ala at 17.1 min dominates over other peaks in the chromatogram. To visualize other dansylated amino acids, reconstructed chromatograms were calculated for ions at $m/z = M_{\text{AA}} + 234.1$. As an example, reconstructed chromatogram at $m/z = 309.1$ (Dns-Gly) is shown in Fig. 3b. Retention time of 15.3 min found in Fig. 3b is in a good agreement with the retention time of dansylated glycine standard. Glycine, alanine, serine and asparagine were found in the material prepared from the irradiated $\text{CO}_2\text{--N}_2\text{--H}_2\text{O}$ mixture by this method. Only alanine was identified among the products formed due to LIDB in the $\text{CO--N}_2\text{--H}_2\text{O}$ mixture.

The formation of organic molecules from mixtures of low-molecular gases (their composition was related to a cometary impact on early Earth) initiated by the LIDB plasma, has already been reported [16]. Nd:YAG laser, emitting 200 mJ in 15-ns pulse [16] at high repetition rate (i.e., 10 Hz), was used. No organic molecules were produced due to the accumulation of many laser pulses in CO_2 -rich mixture, while in a fully reducing (CH_4 -rich) mixture they were synthesized up to C_6 .

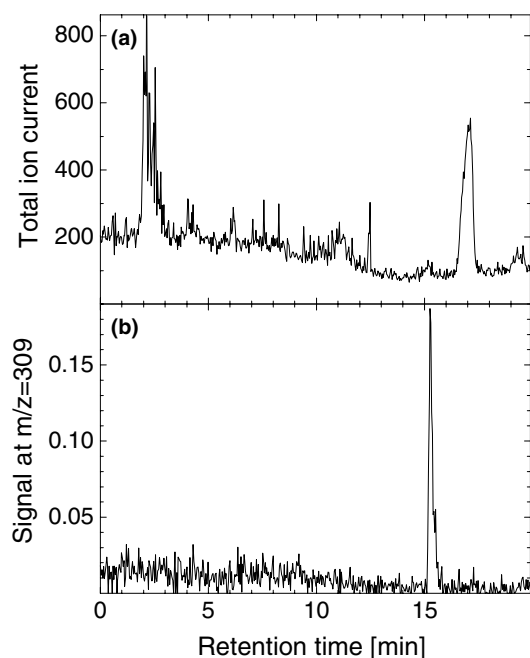


Fig. 3. HPLC/MS trace of a mixture containing various organic compounds synthesized by running ten laser sparks in the $\text{CO}_2\text{-N}_2\text{-H}_2\text{O}$ mixture, when (a) total ion current is detected and (b) chromatogram is reconstructed at $m/z = 309$ ($[\text{M}+\text{H}]^+$), which corresponds to dansylated glycine ions.

As opposed to the experiments described above [16], in this work we irradiate a reaction mixture with shorter pulses of higher energy, i.e., the LIDB threshold is approached at much larger diameter of the focused laser beam. Hence, the LIDB plasma is formed in a much larger volume. It was satisfactorily proven (see Fig. 3) that a measurable amount of amino acids was produced by a few 85-J, 400-ps pulses. This result is strongly encouraging for the study of those chemical phenomena at the PALS facility with only one single pulse because there is a reserve in a pulse energy (which can be increased up to 700 J) as well as detection limits of the chemical analytical methods. Such a single-shot experiment would bring the laser-driven model near the real, individual high-energy-density events in planetary atmospheres. The single shot technique is also able to protect produced organic molecules against their decomposition by energetic photons (i.e., UV/VUV radiation) and highly reactive species generated in repeated laser-plasma runs. Degradation and modification of larger molecules by LIDB plasma have been reported in numerous papers, see for e.g., [17] and [18], respectively.

The high pulse energy and the relatively short pulse duration result in the observed large volume (see Fig. 1b) of the laser spark. According to the data presented in [19,20] the intensity breakdown threshold might be localized in a vicinity of $2 \times 10^{10} \text{ W/cm}^2$ for our laser and gas mixture. The focused PALS beam, used in the present work, reaches that intensity level when its

diameter drops to 3.0 cm. The 10 cm^2 breakdown area seems to be a realistic estimation with respect to a picture of the expanded plasma in Fig. 1b.

In conclusion, several amino acids were found by HPLC/MS in the $\text{CO}_2\text{-N}_2\text{-H}_2\text{O}$ and $\text{CO-N}_2\text{-H}_2\text{O}$ mixtures, each exposed to ten 85-J pulses of focused near-infrared-laser radiation. A spark discharge running in $\text{CO-N}_2\text{-H}_2\text{O}$ mixture for eight hours (total energy input in the mixture was of 160 kJ) is not able to produce alanine [8] and focusing of many low-energy laser pulses in $\text{CO}_2\text{-N}_2\text{-H}_2\text{O}$ mixture does not produce organic molecules [16]. A large-scale, relatively hot dense LIDB plasma, delivering to the irradiated system a substantial amount of energy within a few shots, is responsible for an appearance of the organic molecules in the mixture of simple inorganic gases irradiated with the high-power laser system. The initial experiments, described here, represent the first step towards the study of chemical changes caused by the LIDB plasma produced by a single laser shot delivered from the PALS facility.

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