



Prebiotic Syntheses Under Shock in the Water – Formamide – Potassium Bicarbonate – Sodium Hydroxide System

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Abstract

Syntheses under shock in nitrogen bubbled samples of the water – formamide – bicarbonate – sodium hydroxide system at pH 8.63, 9.46 and 10.44 were performed in the stainless steel preservation capsules. The maximum temperature and pressure in the capsules reached 545 K and 12.5 GPa respectively. Using the LC-MS-MS analysis, the 21 synthesis products have been identified, including amines and polyamines, carboxamide, acetamide and urea derivatives, compounds containing aniline, pyrrolidine, pyrrole, imidazole, as well as alcohol groups. It was found that the Fischer-Tropsch-type syntheses with catalysis on the surface of the stainless steel of the conservation capsule associated with the adsorbed hydrogen cyanide reactions and transamidation processes play the main role in the shock syntheses. Formation reactions of all the above-mentioned compounds have been suggested. It was proposed that hydrogen cyanide, ammonia, isocyanic acid, aminonitrile, aminoacetonitrile, as well as adsorbed species $H_{(a)}$, $CH_{(a)}$, $CH_2_{(a)}$, $CHOH_{(a)}$, $NH_2_{(a)}$ and $H_2CNH_{(a)}$ are especially important for the formation of the products. A reduction reaction of adsorbed bicarbonate with hydrogen to formaldehyde has been first postulated. In the studied system also classical reactions take place – Wöhler's synthesis of urea and Butlerov's synthesis of methenamine. It was suggested that material of meteorites may be an effective catalyst in the Fischer-Tropsch-type syntheses at falling of the iron-nickel meteorites in the water – formamide regions on the early Earth. It was concluded that life could have originated due to the impact of meteorites on alkaline water-formamide lakes located near volcanoes on the early Earth.

Keywords Shock wave · Prebiotic Fischer-Tropsch-type syntheses · Heterogeneous catalysis · Formamide · Bicarbonate

Introduction

A strategic approach to solving the fundamental problem of the origin of life consists in ascertaining the conditions for the effective prebiotic synthesis of key organic compounds,

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many of which were discussed in the literature (see, for example, (Deamer and Weber 2010; Nakashima et al. 2018; Menor-Salván 2018; Orgel 2008; Powner and Sutherland 2011; Sutherland 2017) and references therein). The prebiotic conditions include energy sources, pressure, temperature, chemical composition of the atmosphere, the aquatic environment and minerals, methods of performing chemical reactions, etc. The impact of shock waves on homogeneous and heterogeneous systems in a closed reactor, simulating the collision of meteorites with the surface of the planet in the water areas, can be used as a source of energy and a way of implementing prebiotic syntheses.

To date, a number of experimental results of prebiotic syntheses under shock in various systems have been obtained. The shock heating of a prebiotic gas atmosphere (consisting of methane, ethane, ammonia and water) followed by rapid cooling was first used by Bar-Nun et al. (1970). As a result, four natural amino acids (glycine, alanine, valine and leucine) with a high yield by ammonia were obtained. Later, using experimental simulation of the shock action on the water-silicate system, the formation of the complex hydrocarbons (weighing up to 700 Da) was detected due to the proposed condensation of particles on the surface of silicate (Gerasimov et al. 2002). As a result of impact (at a speed up to 7.15 km/s) on ice containing a mixture of H₂O, NH₃, CO₂ and CH₃OH, some amine acids (glycine, DL-alanine, DL-alpha-aminobutyric acid, DL-norvaline, DL-alpha-aminoisobutyric acid and DL-isovaline) were synthesized (Martins et al. 2013). Nakazawa et al. (2005) obtained an important result: under the action of a shock wave (at impact velocity of up to 0.88 km/s) in the presence of iron and water, molecular nitrogen is effectively reduced to ammonia which suggests the possibility of the N₂ reduction by the meteorite iron in prebiotic conditions. Later, Furukawa et al. (2009) used an impact device, which created pressure up to 6 GPa, to simulate the conditions of prebiotic synthesis during a collision with meteorites. After exposure to a mixture of solid carbon, iron, nickel, water and molecular nitrogen, some fatty acids and amines were recorded as products. When ammonia was added to the mixture, glycine was found among the products. In continuation of the investigation, the authors (Suzuki et al. 2015) recently attempted to synthesize amino acids under the action of shock waves on the ammonium formate and ammonium carbonate solutions at up to 0.92 km/s impact velocity and up to 19 GPa pressure, but have received only very low yields of amino acids (glycine, alanine, beta-alanine, sarcosine) and aliphatic amines (methylamine, ethylamine, propylamine, butylamine). In the work of Kurosawa et al. (2013) the importance of mid-size (0.1–1 km in diameter) meteorite impacts to cyanide accumulation on the early Earth was demonstrated using both impact and laser experiments. Aerodynamic ablation and chemical reactions with the ambient atmosphere after oblique impacts were studied. A polycarbonate projectile and graphite were used as some analogs of meteoritic organic matter. It was found that a significant fraction (>0.1 mol%) of the vaporized carbon is converted to HCN and cyanide condensates which may have played an important role in the origin of life. Important series of shock experiments were performed to assess the feasibility of the delivery of organic compounds to the Earth through cometary impacts (Blank et al. 2001). Aqueous solutions containing near-saturation levels of amino acids (lysine, norvaline, aminobutyric acid, proline and phenylalanine) were sealed inside stainless steel capsules and shocked by ballistic impact with velocities of 0.5–1.9 km/s. Calculated maximum conditions experienced by the solutions ranged from 5.1–21 GPa and 412–870 K. In all experiments, a large fraction of the amino acids survived. Phenylalanine appeared to be the most reactive of the amino acids. The impact process results in peptide bond formation and new compounds included amino acid dimers and cyclic diketopiperazines. It

was concluded that impact pressure has a greater influence than temperature in determining reaction pathways and significant concentrations of organic material could survive a natural impact process. It should be noted that in the cited papers the mechanisms of prebiotic synthetic reactions were not considered in detail.

It is essential that prebiotic syntheses in the water – formamide systems under shock have not yet been studied, although the key role of formamide (FA) in the origin of life is recognized by many researchers. Formamide can be a universal precursor of all major components of living organisms, including nucleic bases, nucleosides, nucleotides, amino acids, sugars, amino sugars and carboxy acids (see, for example, refs. (Ferus et al. 2014, 2015; Nakashima et al. 2018; Nguyen et al. 2015; Saladino et al. 2012, 2015; Šponer et al. 2016) and references therein). In the cited works, many ways of synthesizing these compounds were considered, but among these reaction pathways there are no means to synthesize biologically important compounds under shock action on the formamide-containing systems.

In the present work first results of our systematic investigation of syntheses reaction at shock action on the formamide-containing systems are presented. As is known, the difficult problem of formamide concentration in the conditions of early Earth can be solved taking into account thermoconvection in hydrothermal pores and the preference of geothermal volcanic scenarios over ocean-based scenarios, as well as allowing evidence that formamide-based reactions proceed successfully in the presence of substantial amounts of water (see refs. (Djokic et al. 2017; Mulkidjanian et al. 2012; Niether et al. 2016; Niether and Wiegand 2017; Saladino et al. 2018) and references therein). We believe that the most intense concentration of formamide occurred during the evaporation of water from water – formamide lakes due to the heat of nearby volcanoes. In this regard, to simulate the impact in geothermal conditions of early Earth, we chose water – formamide system with a rather high concentration of formamide (3 M).

The choice of pH values to mimic the conditions of prebiotic syntheses deserves special attention. As known, the early Earth's environment is controversial. According to estimates (Krissansen-Totton et al. 2018), ocean pH evolves monotonically from ~6.6 at 4.0 Ga to ~7.9 at the Proterozoic-Phanerozoic boundary. On the other hand, by analogy with modern alkaline lakes, Kempe and Degens (1985) argued for a pH 9–11 “soda ocean”. While analysis of the Archean marine sedimentary rocks make a Precambrian “soda ocean” unlikely, but nitrogen isotope evidence for alkaline lakes on late Archean continents (Stüeken et al. 2015). As these authors note, aqueous alteration of volcanic glass followed by evaporative concentration of ions should have led to the development of high alkalinity (pH ≥ 9). It is reasonably believed that alkaline lakes in the Archean could have been significant for the origin and early evolution of life (Stüeken et al. 2015). Considering Darwin's remark that life could have arisen in “warm little pond” (Darwin 1888), modeling of prebiotic syntheses in alkaline media of the Archean lakes (pH of 9 or higher) is of particular importance, which predetermined our choice of pH values for shock experiments.

Considering that bicarbonate could be present in prebiotic conditions, syntheses under shock by ballistic impact in the three samples of the water – formamide (3 M) – bicarbonate (0.2 M) – sodium hydroxide system bubbled by nitrogen at pH 8.63, 9.46 and 10.44 were fulfilled in the stainless steel preservation capsule. Using the LC-MS-MS analysis, the synthesis products have been identified and on this basis pathway of the products syntheses were proposed.

Materials and Methods

In the experiments distilled water prepared in a glass distillation apparatus, potassium bicarbonate (analytical grade), sodium hydroxide (analytical grade) and formamide (PanReac AppliChem, ultrapure, 99.5%) were used. According to the LC-MS-MS analysis data in the water – formamide solution only minor quantity of the $C_{17}H_{36}N_2O_2$ compound (known surfactant) was present.

For impact syntheses, an original steel design has been developed, the scale drawing of which is shown in Fig. 1. The preservation capsule with inner ring (in the center of the construction shown in Fig. 1) was made of the stainless steel of the (in Russian) 12X18H10T grade (Fe ~67%, Cr ~18%, Ni ~10%, State Standard 5949–75) which is an analog of the 321 steel (USA, ASTM Standard). The working volume of the capsule was 0.2 ml. All details of the capsule before experiments were thoroughly washed first with ethanol and then with distilled water.

The required pH values were created by introducing sodium hydroxide into the water – formamide – bicarbonate solutions, which were bubbled with high-purity nitrogen (99.996%) for about 30 min. After this, the solutions were placed in the preservation capsules, bubbled with high-purity nitrogen for about 10 min and then quickly screwed tight.

In the experiments, a light-gas gun with helium was used. Immediately after the completion of the shock experiment, each reactor was washed out and drilled from the side of the impact of the striker and the content of the reactor was taken for analysis into special vials with tight covers, which ensured their long-term storage in the refrigerator without any change in the content.

Samples were analyzed by a HPLC-MS method on an Agilent 1260 Infinity Binary System chromatograph coupled to an AB Sciex Triple TOF 5600 high-resolution mass spectrometer, equipped with a DuoSpray ionization source. Ionization of the sample components was carried out using the electrospray method through a TIS probe (nebulizer gas pressure of 55 psi, heater

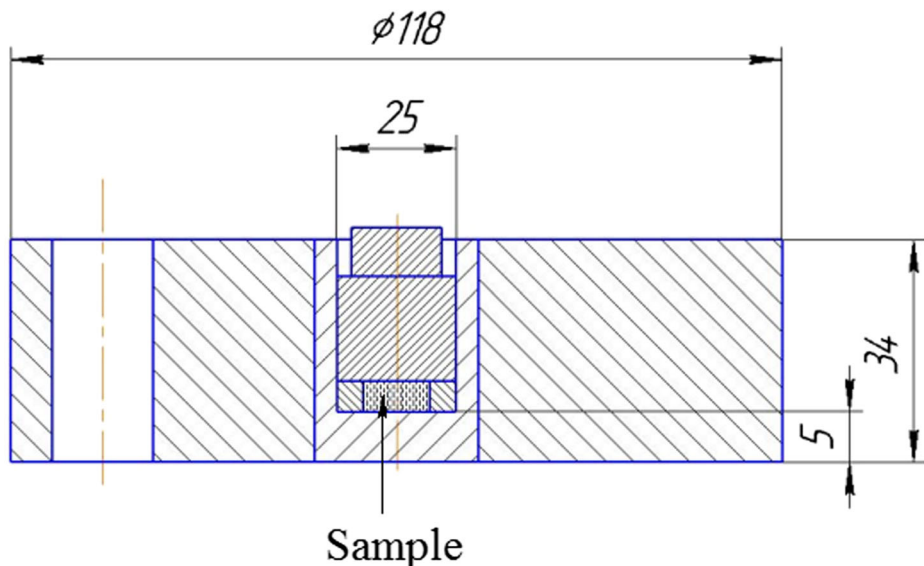


Fig. 1 The scale drawing of the steel design with the preservation capsule (in the center)

gas pressure of 55 psi, evaporator temperature of 550 °C). The analysis was carried out in the modes of the negative and positive ionization at ionization potentials of -4.5 and 5.5 kV respectively. Panoramic mass spectrometry data were recorded in TOFMS mode (signal accumulation time is 0.1 s, ion detection range is 50–2000 Da, declusterization potential is 100 eV, collision energy is 10 eV, collision energy variation is 0 eV). The registration of the MS-MS data was performed using an IDA (Information Dependent Acquisition) method (the intensity of isolated precursor ions is more than 500 cps, the signal accumulation time is 0.02 s, the number of isolated precursor ions per analysis cycle is 5, the ion detection range is 50–2000 Da, the declusterization potential is 100 eV, the collision energy is 35 eV, collision energy spread is 15 eV). Chromatographic separation of the sample components was carried out on an Agilent Zorbax Eclipse Pluse C18 column (100*2.1 mm, particle size is 3.5 μm) with an Agilent Eclipse Pluse C18 precolumn (2.1*12.5 mm, particle size is 5 μm). The column temperature was maintained at 40 °C. The mobile phase was formed from eluents A and B. The elution rate was 400 $\mu\text{l}/\text{min}$. When using a positive ionization mode, the 0.1% solution of formic acid in the 98:2 water-acetonitrile mixture was used as eluent A and the 0.1% solution of formic acid in the 98:2 acetonitrile-water mixture was used as eluent B. When a negative ionization mode was used, the 0.05% solution of formic acid in the 98:2 water-acetonitrile mixture was used as eluent A and the 0.01 M solution of ammonium formate in the acetonitrile-water mixture 95:5 was used as eluent B. Elution was carried out according to the following scheme: 0 min 99% A, 0.1 min 99% A, 25 min 1% A, 30 min 1% A, 30.5 min 99% A, 35 min 99% A, 35.5 min 1% A, 40 min 1% A, 40.5 min 99% A, and 47 min 99% A. The sample injected volume was 10 μl . The temperature of the samples in the autosampler was 4 °C. The data were processed in the PeakView (v.2.2, AB Sciex), MasterView (v.1.1, AB Sciex) software.

Results and Discussion

Conditions and results of the shock syntheses in the water – formamide (3 M) – potassium bicarbonate (0.2 M) – sodium hydroxide system at tree pH values (Samples 1–3) are given in Table 1. On the basis of data on impact speeds, material and parameters of the striker and capsule, according to a special program (Gavrilov et al. 1982), dependences of temperature and pressure in the solutions on the time after impact have been calculated. An example of such dependencies for Sample 1 at impact speed $V=585$ m/s is shown in Fig. 2. As can be seen from Fig. 2, for Sample 1 the temperature and pressure reached maximum at 545 K and 12.5 GPa, respectively, through 0.7 μs after the impact and remained at ~ 460 K and ~ 1.8 GPa, respectively, through 3 μs after the impact. The calculated maximum temperatures and pressures for Samples 2 and 3 are also given in Table 1.

The LC-MS chromatograms as extracted-ion chromatograms (XIC) for the Samples 1–3 with blanks are given in Fig. 3 (corresponding ion masses, together with the retention times, are presented in ESM). According to the LC-MS-MS analysis of the products of the impact synthesis in the three samples studied the formulas of the 21 compounds were established (see Table 1). As follows from Table 1, Samples 1 and 2 are similar by the number of synthesized compounds and exceed Sample 3. Moreover, the relative intensity of the signals in the LS-MS spectra for the same compounds in Sample 2 is slightly higher than in Sample 1 (the relative intensities of such signals can be compared correctly only for identical compounds). It can be concluded that the most effective shock syntheses in the studied system proceed at pH ~ 9 .

Table 1 Conditions and results of the shock syntheses in water – formamide – potassium bicarbonate – sodium hydroxide system bubbled by nitrogen (according to the LC-MS-MS analysis, relative intensities of the LS-MS spectrum signals are given in parentheses)

Sample No	Sample composition	Shock condition	Products of the shock synthesis
1	3.0 M FA, 0.2 M KHCO ₃ , pH 8.63	$V = 585$ m/s, $T_{\max} = 545$ K, $P_{\max} = 12.5$ GPa	C ₆ H ₁₅ N 1 (136), C ₆ H ₁₂ N ₄ 2 (10385), C ₈ H ₁₃ N 4 (89), C ₈ H ₁₁ NO 6 (1015), C ₆ H ₁₂ N ₂ O 7 (328), C ₇ H ₁₄ N ₂ O 8 (490), C ₁₀ H ₂₀ N ₂ O 11 (620), C ₁₂ H ₂₄ N ₂ O 13 (318), C ₉ H ₁₆ N ₂ O 14 (274), C ₁₅ H ₁₆ N ₂ O 15 (337), C ₅ H ₈ N ₂ 16 (375), C ₈ H ₁₄ N ₂ 18 (509), C ₁₁ H ₁₈ N ₂ O ₂ 21 (253)
2	3.0 M FA, 0.2 M KHCO ₃ , pH 9.46	$V = 530$ m/s, $T_{\max} = 500$ K, $P_{\max} = 10.8$ GPa	C ₆ H ₁₂ N ₄ 2 (24115), C ₈ H ₁₁ N 5 (424), C ₈ H ₁₁ NO 6 (586), C ₇ H ₁₄ N ₂ O 8 (357), C ₈ H ₁₆ N ₂ O 9 (1039), C ₉ H ₁₈ N ₂ O 10 (2737), C ₁₀ H ₂₀ N ₂ O 11 (2274), C ₁₁ H ₂₂ N ₂ O 12 (1245), C ₁₂ H ₂₄ N ₂ O 13 (798), C ₇ H ₁₂ N ₂ 17 (875), C ₈ H ₁₄ N ₂ 18 (2382), C ₉ H ₁₆ N ₂ 19 (703), C ₁₀ H ₁₈ N ₂ 20 (565)
3	3.0 M FA, 0.2 M KHCO ₃ , pH 10.44	$V = 563$ m/s, $T_{\max} = 520$ K, $P_{\max} = 11.8$ GPa	C ₁₀ H ₂₆ N ₄ 3 (359), C ₈ H ₁₁ N 5 (771), C ₈ H ₁₁ NO 6 (666), C ₈ H ₁₆ N ₂ O 9 (913), C ₆ H ₁₈ N ₂ O 10 (1556), C ₁₀ H ₂₀ N ₂ O 11 (1137), C ₁₁ H ₂₂ N ₂ O 12 (407), C ₇ H ₁₂ N ₂ 17 (635)

The structures of all the synthesized compounds shown in Scheme 1 were identified by analyzing their decay products in the LC-MS-MS experiments according to the well-known rules (Gross 2004). Decay ways of the 21 compounds reconstructed under these rules are presented in ESM. It should be noted that all products were recorded only in positive ionization and in negative ionization products were not found. Identification of the four compounds was confirmed by literature data (see refs. in ESM). The structures of the majority of the compounds represented in Scheme 1 are identified quite definitely and correspond to a single synthesis logic which is discussed below. However, in the case of the compound **21**, the structure of a radical $R = C_6H_{11}O$ cannot be determined precisely, it is likely that $C_6H_{11}O$ is a cyclohexanol radical.

As can be seen from Scheme 1, the identified products of the shock syntheses include amines (**1**, **4**) and polyamines (**2**, **3**), aniline derivatives (**5**, **6**), derivatives of carboxamide (**7–9**) and acetamide (**10–13**) containing pyrrolidine substituents (**7–13**), pyrrole (**14**) and imidazole (**16–21**) derivatives, methylaniline containing urea (**15**) as well as compounds containing alcohol groups (**6**, **14**, **21**). The presence of several homologous series (**7–9**, **10–13**, **16–20**) among the detected compounds is noteworthy. The fact of formation of homologous series is a characteristic feature of Fischer-Tropsch syntheses and occurrence of mentioned homologous series in our case can be most rationally explained by realization of the Fischer-Tropsch-type syntheses with heterogeneous catalysis on the surface of the stainless steel preservation capsule. The following three circumstances are in favor of this hypothesis. First, the rather high temperatures calculated by us for the studied experimental conditions of the impact

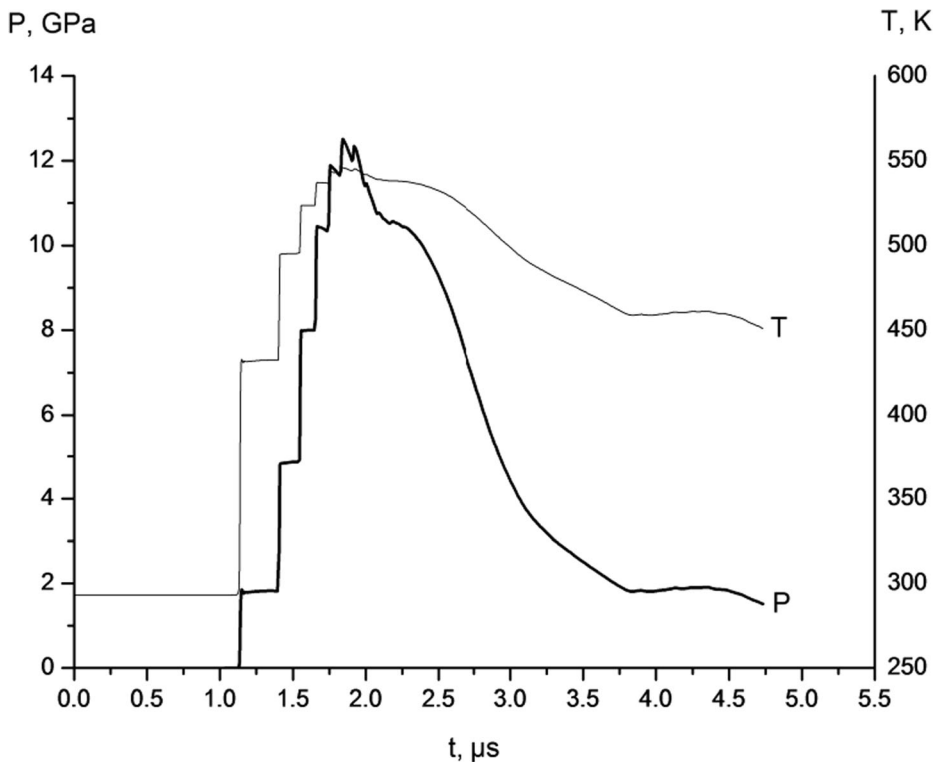
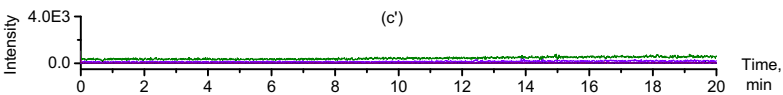
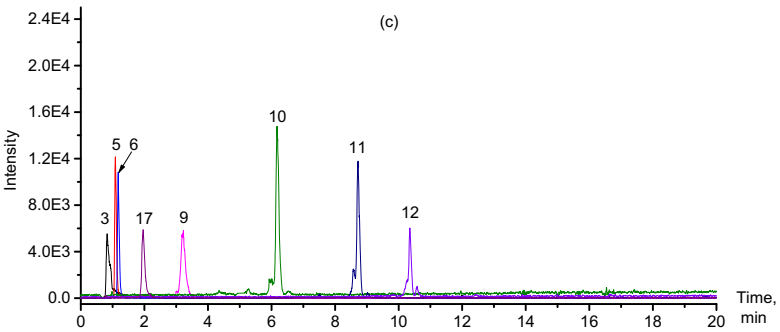
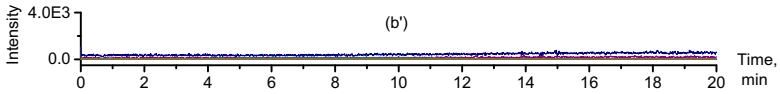
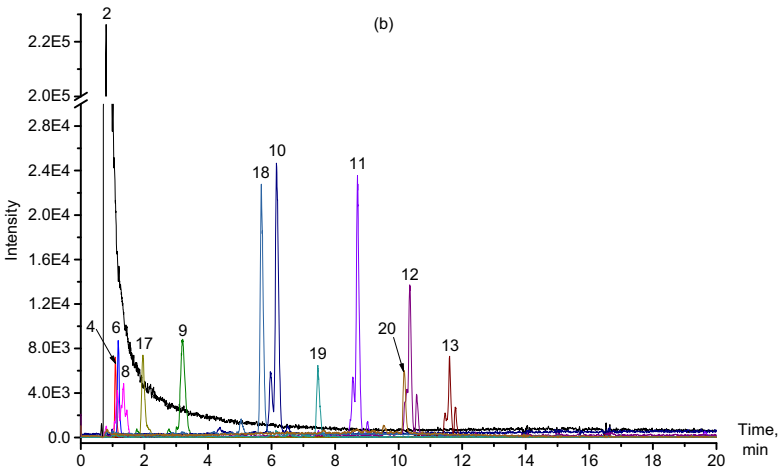
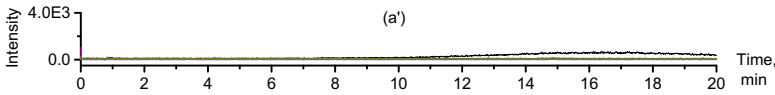
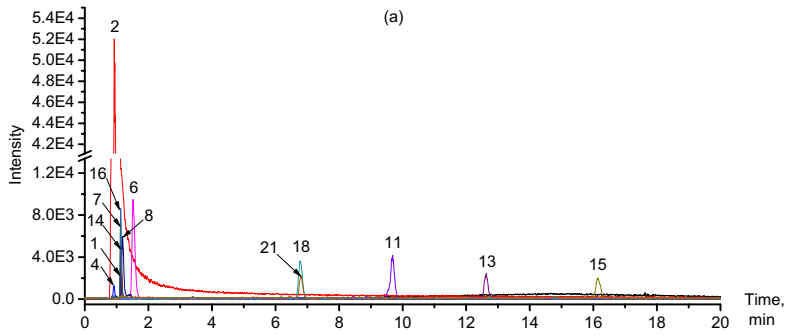


Fig. 2 The calculated dependences of temperature and pressure on the time after impact for Sample 1 in the water – formamide (3 M) – potassium bicarbonate (0.2 M) – sodium hydroxide system at pH 8.63

syntheses promote the well-known reactions of thermal decomposition of formamide to hydrogen cyanide, ammonia, carbon monoxide, molecular hydrogen and isocyanic acid in the following reactions (see, for example, refs. (Ferus et al. 2015; Nguyen et al. 2011, 2015) and references therein):

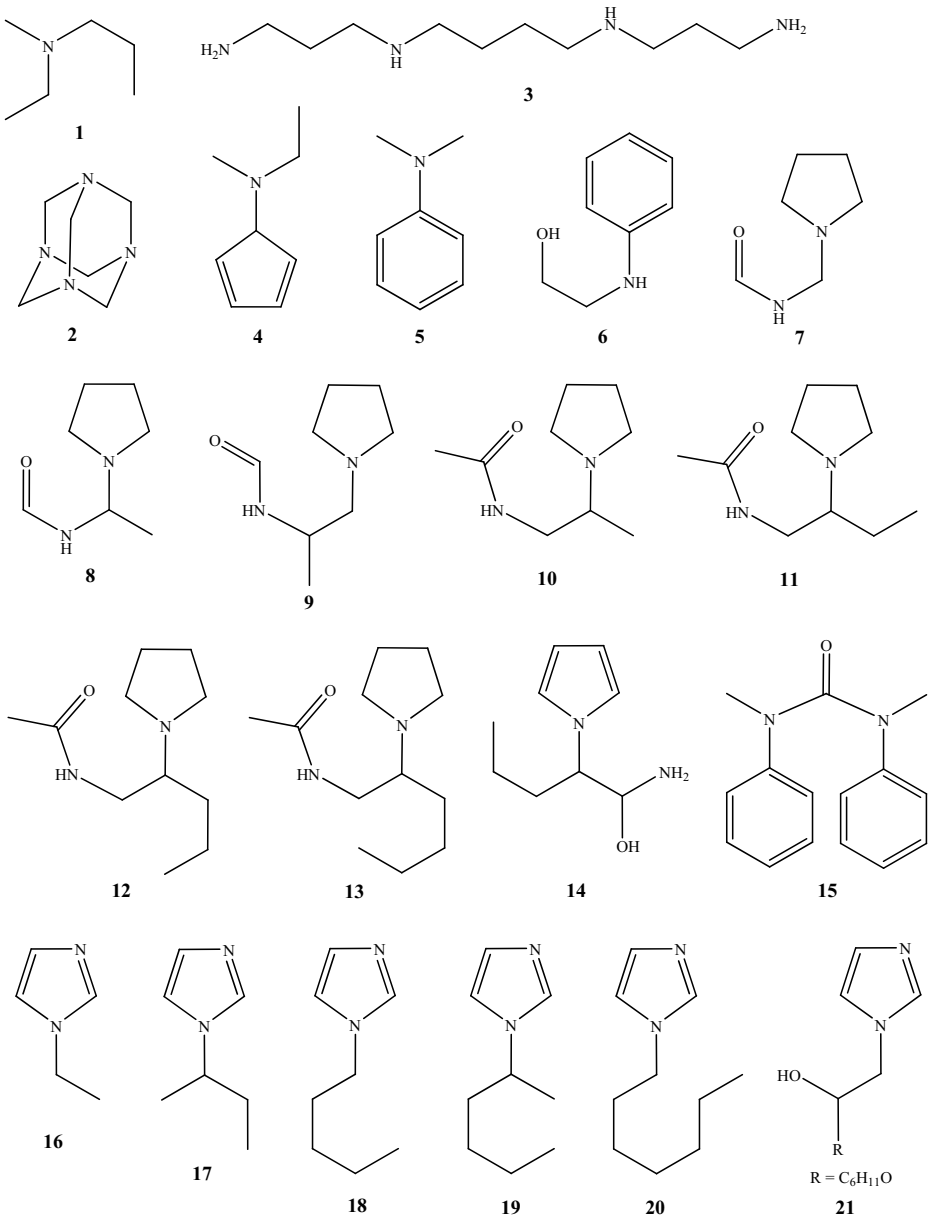


According to the results of calculations (Nguyen et al. 2011) the energy barriers of reactions (1)–(3) lie within 73–78 kcal/mol. Although process (1) is energetically most preferable, reaction (3) is accompanied by the formation of molecular hydrogen with high reducing ability in the Fischer-Tropsch-type syntheses. Secondly, iron is an effective catalyst in the Fischer-Tropsch-type syntheses in the presence of hydrogen, carbon monoxide and ammonia (van de Loosdrecht et al. 2013; von Henkel 2012). Thirdly, high pressure, calculated by us in the conservation capsule at the shock experiments, promote the effective adsorption of hydrogen and carbon monoxide on the surface of stainless steel, even in the presence of water.



◀ **Fig. 3** XIC of the ions with definite m/z for the Sample 1 (a), Sample 2 (b) and Sample 3 (c) with corresponding blanks (a', b' and c') (Samples 2 and 3 were examined at the same time, and Sample 1 before them for 8 months)

In addition, the possibility of hydrogenation of adsorbed hydrogen cyanide by metal catalysts, estimated through quantum chemical computation by Hsiao et al. (2016), as well as transamidation processes, reviewed by Lanigan and Sheppard (2018), should be taken into account.



Scheme 1 The structures of the synthesized compounds

The hypothesis about realizing the Fischer-Tropsch-type syntheses associated with the adsorbed hydrogen cyanide reactions and transamidation processes in the studied systems allows us to uniformly explain the formation of all 21 detected synthesis products, taking into account the following literary data:

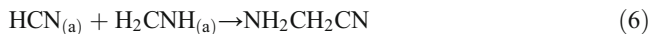
- 1) As it is known, three mechanisms of the Fischer-Tropsch-type syntheses over iron catalyst were proposed (see, for example, (van de Loosdrecht et al. 2013)): the carbide mechanism, the enol mechanism and the CO insertion mechanism. The carbide mechanism (Fischer and Tropsch 1926) proposes that CO dissociates before the carbon atom is partially hydrogenated to $\text{CH}_{n(a)}$ species ($n=0-3$ and index (a) means adsorption on active site on the catalyst surface). It is shown (van de Loosdrecht et al. 2013) that activation energies for direct CO dissociation on the Fe(100) surface are 103–110 kJ/mol and activation energies for hydrogenation to $\text{CH}_{n(a)}$ species ($n=0-3$) on atomically flat surfaces are in the range of 50–100 kJ/mol; this implies a favorable $\text{CH}_{n(a)}$ species ($n=0-3$) formation under the conditions of our shock experiments. The enol mechanism (Storch et al. 1951) assumes that CO is partially hydrogenated to a $\text{CHOH}_{(a)}$ species (oxymethylene) which then may react as the monomer in our shock experiments introducing alcohol group.
- 2) In the DFT investigation of the adsorption and hydrogenation of hydrogen cyanide on the W(111) catalyst (Hsiao et al. 2016), it was found that maximum adsorption energy of HCN on the W(111) surface is -49.8 kcal/mol. Before forming an key imine intermediate $\text{H}_2\text{CNH}_{(a)}$ two adsorbed hydrogen atoms $\text{H}_{(a)}$ react with the nitrogen and then carbon atoms of $\text{HCN}_{(a)}$ in the first and second hydrogenation steps with calculated barriers of 37.4 and 16.3 kcal/mol respectively. In addition, the $\text{H}_2\text{CNH}_{(a)}$ intermediate decomposes into the $\text{CH}_{2(a)}$ and $\text{NH}_{(a)}$ particles with barrier of 27.5 kcal/mol. Similar processes with rather low activation barriers can occur on the surface of the iron catalyst providing the reactive intermediates for our impact syntheses.
- 3) As it is well known, “formamides are inherently more reactive towards transamidation and will readily undergo transamidation at high temperatures, in the absence of reagents or catalysts” (Lanigan and Sheppard 2018).

Given the presence in the H_2 , CO, NH_3 and HCN containing systems the above considered $\text{H}_{(a)}$, $\text{CH}_{(a)}$, $\text{CH}_{2(a)}$, $\text{CHOH}_{(a)}$, $\text{NH}_{(a)}$, $\text{NH}_{2(a)}$ and $\text{H}_2\text{CNH}_{(a)}$ species, the formation of almost all the products of the shock synthesis can be uniformly explained. In addition, considering the rather large number of acetamide derivatives (10–13) as products of transamidation processes, the acetamide formation can be most easily explained by the following reaction:



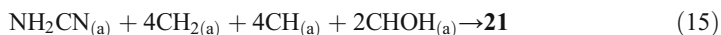
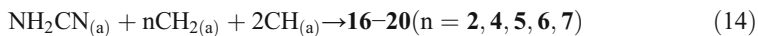
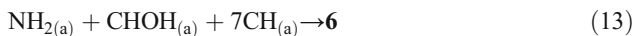
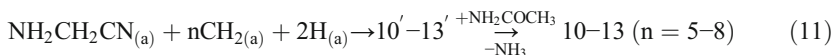
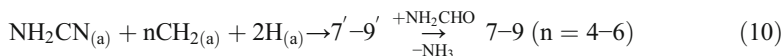
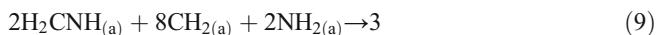
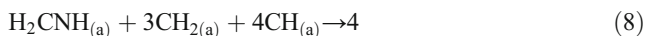
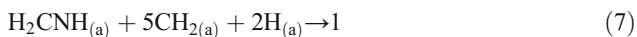
Taking into account the formation in the shock syntheses of a large number of compounds (7–14) in which two nitrogen atoms are connected by one or two methylene groups, it is possible to suggest ways of their syntheses through two nitriles (aminonitrile (cyanamide) and aminoacetonitrile):





This assumption agrees well with the fact that nitriles actively accumulate during the Fischer-Tropsch-type syntheses in the $\text{H}_2/\text{CO}/\text{NH}_3$ system (von Henkel 2012), but the exact mechanisms of the nitriles formation had not yet been established.

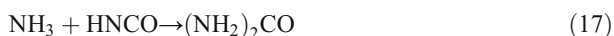
Considering the above reactive species, reactions (4)–(6) and transamidation processes (for compounds 7–13), the formation reactions of 19 synthesized compounds can be represented in the following generalized form (without consideration of possible intermediates):



Of course, the actual formation reactions of the 19 compounds considered may include a wide variety of intermediate products, but for a more detailed discussion of them further research is needed. We note only that formation of a large number of the pyrrolidine derivatives (7–13) as products of the Fischer-Tropsch-type synthesis is well consistent with the accumulation of pyrrolidines in the carbon monoxide – steam – ammonia system (Kölbel and Trapper 1966).

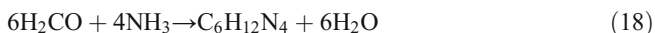
It should be noted that the impact on chemical systems can lead to a significant population of higher vibrational states of molecules, anharmonicity of vibrations, up to the breaking of chemical bonds (see (Kay 2017) and references therein). The question of whether it is sufficient to consider only the above reactions on the metal surface of the conservation capsule or a possibility of the shock-induced radical reactions in solution should also be taken into account, remains open and requires further research, including quantum-chemical calculations.

Formation reactions of 1,3-dimethyl-1,3-diphenylurea (**15**) and hexamethylenetetramine (urotropine or methenamine, **2**) deserve special attention. These reactions proceed unambiguously. The compound **15** is clearly the product of the transamidation reaction of N-methylaniline with urea. Obviously, urea is formed as a result of the interaction of ammonia (from reaction (2)) with isocyanic acid obtained by process (3) according to quantum chemical computation data (Nguyen et al. 2011), which results in the urea formation in accordance with the mechanism of the classic Wöhler's reaction proposed by Tsipis and Karipidis (2003):



According to the quantum chemical calculations by Tsipis and Karipidis (2003), the most energetically economic path of the rate-determining step of the Wöhler's reaction includes the addition of NH_3 to the $\text{C}=\text{N}$ double bond of isocyanic acid, directly giving urea. Thus, in our shock experiments a variant of the Wöhler's synthesis of urea is evidently realized.

We emphasize that the methenamine ($\text{C}_6\text{H}_{12}\text{N}_4$ **2**) formation in the studied system indicates the presence of formaldehyde, which interacts with ammonia, formed in process (2), giving **2** by the reaction (18) discovered by Butlerov (1860):



Note that at impact on all other studied by us water – formamide systems, which do not contain bicarbonate, methenamine is not formed. This indicates the reduction of bicarbonate with hydrogen to formaldehyde under present experimental conditions in Samples 1 and 2 (at pH 8.63 and 9.46).

According to our assumption, the mechanism of reduction of bicarbonate (or carbonate) to formaldehyde with hydrogen can include the interaction between the adsorbed species on the surface of the stainless steel, just as it was established for the process of the nitrate reducing with hydrogen using the stainless steel catalytic effect (Truche et al. 2013). The proposed processes include two similar stages, providing the reduction of the carbon atom and the dissociation of the hydroxide ion or water molecule from bicarbonate or carbonate.



Details of the mechanism would be established using quantum chemical computations in the future.

It is assumed (see (Ogorodnikov 1984) and references therein) that the methenamine formation begins with the accumulation of methanolamine ($\text{NH}_2\text{CH}_2\text{OH}$) or methylenimine (H_2CNH) according to reaction (21):



The methylenimine can also be formed in the Fischer-Tropsch-type synthesis described above. However, further stages of the methenamine synthesis include the participation of formaldehyde which can also be formed in the Fischer-Tropsch synthesis but quickly decomposes with 100% selectivity to CO and H_2 on the surface of the catalyst (van de Loosdrecht et al. 2013). However, the reduction of bicarbonate (or carbonate) by hydrogen makes it possible to accumulate in the solution a sufficient amount of formaldehyde which is necessary for the synthesis of a significant amount of methenamine (see Table 1). It should be noted that acid hydrolysis of hexamine has been shown to yield of amino acids (Fox and Windsor 1970).

The presence of signs of the formaldehyde formation in the impact products is of fundamental importance since in such conditions vital sugars may be obtained by the Butlerov's reaction (formose reaction) (Butlerow 1861). However, it should be noted that the problem of the synthesis of sugars as well as nucleotides critically considered by Schwartz (1995) is very difficult. Sugars were not detected in the products of the present shock experiments. This is possible because the formed formaldehyde reacts much more rapidly with nitrogen-containing compounds than enter into the formose reaction. It is possible that changing the concentration ratio formamide/bicarbonate in favor of the latter will result in sugars under the shock action on the water – formaldehyde – bicarbonate system with addition components. This assumption should be checked in further shock experiments with the above considered and more complex systems.

The somewhat unexpected formation of spermine ($\text{C}_{10}\text{H}_{26}\text{N}_4$ 3) at pH 10.44 instead of methenamine ($\text{C}_6\text{H}_{12}\text{N}_4$ 2) at pH 8.63 and 9.46 can be explained by the lower rate of the formaldehyde formation by the reaction (20) as compared to the reaction (19) taking into account that at pH > 10 and high temperatures the carbonate form dominates over bicarbonate. This hypothesis will be verified in the mentioned quantum-chemical computations.

It should be emphasized that many of the intermediates presented in above equations (including HCN, $(\text{NH}_2)_2\text{CO}$, H_2CO , H_2CNH , NH_2CN , $\text{NH}_2\text{CH}_2\text{CN}$) play an important role in other models of prebiotic syntheses presented in the literature (see, for example, (Cleaves II 2008; Fiore and Strazewski 2016; Islam and Powner 2017; Nakashima et al. 2018; Noe et al. 2013; Saladino et al. 2012; Sutherland 2017) and references therein). Especially important is the formation of many imidazole derivatives in the present shock syntheses because imidazole catalyzes prebiotic peptide syntheses (Rabinowitz and Hampai 1985; Sawai and Orgel 1975; Serov et al. 2016). All these circumstances confirm universality of formamide in the origin of life.

The fact that the most effective syntheses in the studied systems are realized at pH ~9 probably indicates that the real prebiotic syntheses on our planet could occur in a similar alkaline medium that is present in many hydrothermal systems, in particular on Kamchatka (Kompanichenko et al. 2015).

As known, the role of the Fisher-Tropsch catalysis in solar nebula chemistry has been noted in the literature (see (Studier et al. 1968; Kress and Tielens 2001) and references therein). It is well known the catalytic effect of meteorites on neat formamide in the absence or in the presence of proton or heavy ion irradiation resulting in the synthesis of many prebiotic

compounds (Ferus et al. 2015; Saladino et al. 2013, 2015, 2016, 2018). The key role of meteorites in the formation of prebiotic molecules in a formamide – water environment was revealed (Rotelli et al. 2016). In this work, it was shown that carbonaceous chondrites catalyze the synthesis of natural nucleobases, carboxylic acids and amino acids from mixtures of formamide with water or seawater at 140 °C. However, to the best of our knowledge, the possibility of the Fisher-Tropsch-type syntheses under shock when the iron-nickel meteorites as heterogeneous catalysts fall in the water – formamide fields on the early Earth has not yet been taken into account. Meanwhile, such water – formamide systems with a high content of formamide, formed under action of radioactive minerals, could well exist on the early Earth bypassing the so-called “water paradox” (see (Adam et al. 2018) and references therein). Thus the present shock experiments with the water – formamide systems in the stainless steel preservation capsule to some extent simulate the processes taking place at falling of the meteorites into the water – formamide regions on the prebiotic Earth. We believe that the results of these experiments expand our understanding possible formamide-mediated prebiotic chemistry.

It should be emphasized that heterogeneous catalysis can be very important for prebiotic syntheses but the role of this catalysis remains underestimated. For the origin of life, heterogeneous catalysis under the action of meteorites may play no less important role than the generation of radicals by UV light.

The already obtained results of the study of the fairly simple system testify to the enormous synthetic potential of impact on the water – formamide systems. Even more impressive results were obtained by us using shock action on such systems with the addition of a number of components that could be present in prebiotic conditions. To interpret these experimental data, quantum-chemical computations of the reaction paths on the surface of heterogeneous catalysts are necessary with primarily modeling key reactions (5), (6), (19) and (20) taking into account the adsorption of water molecules. The results of these investigations are scheduled to be reported in the future.

Summary and Conclusions

In the present study, according to the results of the shock action on the water – formamide – bicarbonate system, 21 compounds have been identified, including amines and polyamines, carboxamide, acetamide and urea derivatives, compounds containing aniline, pyrrolidine, pyrrole, imidazole, as well as alcohol groups. In addition, the formation of another four compounds – formaldehyde and methylenimine (the precursors of methenamine), urea and acetamide (the precursors of the aforementioned derivatives) – was established. Formation reactions of all the above-mentioned compounds have been proposed. In these reactions the Fischer-Tropsch-type syntheses with catalysis on the surface of the stainless steel of the conservation capsule associated with the adsorbed hydrogen cyanide reactions and transamidation processes are played the main role. It was shown that hydrogen cyanide, ammonia, isocyanic acid, aminonitrile, aminoacetonitrile, as well as adsorbed species $H_{(a)}$, $CH_{(a)}$, $CH_{2(a)}$, $CHOH_{(a)}$, $NH_{2(a)}$ and $H_2CNH_{(a)}$ are especially important for the formation of the products. A reduction reaction of bicarbonate with hydrogen to formaldehyde on the surface of stainless steel has been first proposed. It is noteworthy that in the studied systems, classical reactions take place – Wöhler’s synthesis of urea and Butlerov’s synthesis of methenamine. Some of the proposed reaction paths and mechanisms require confirmation by quantum-chemical computations in the future.

It should be emphasized that many of the precursors in the syntheses during impact in the water – formamide – bicarbonate system discussed in this work play an important role in other models of prebiotic syntheses presented in the literature which confirms the formamide universality in the origin of life. Comparison of the effectiveness of the present shock syntheses indicates that they are more productive at pH ~9.

In general, we can conclude that heterogeneous catalysis can play a significant role in prebiotic syntheses. The obtained results suggest that the material of meteorites may be an effective catalyst in the Fischer-Tropsch-type syntheses at falling of the iron-nickel meteorites in the water – formamide regions on the early Earth. In prebiotic syntheses, heterogeneous catalysis under the action of meteorites may play no less important role than the generation of radicals by UV light. In the development of Darwin's idea that life could have arisen in "warm little pond" (Darwin 1888), taking into account the results of the present study, we assume that life could have originated due to the impact of meteorites on alkaline water-formamide lakes located near volcanoes on the early Earth. Further research is needed to confirm this hypothesis.

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