GLYCINE AND ALANINE SYNTHESIS FROM
FORMALDEHYDE AND HYDROXYLAMINE IN THE FIELD OF
ULTRASOUND WAVES

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Abstract. High intensity ultrasound waves coupled with other form of energy obviously were initiators of pre-biochemical reactions; these reactions occurred in the water masses of the primordial Earth.

Essential biological substances like formaldehyde, ammonia, hydrocyanic acid, and amino acids compounds similar to carbohydrates by their properties were synthesized in the field of ultrasound waves in model experiments.

The main partners of these reactions are water and gases of reductive atmosphere: hydrogen, carbon monoxide, methane, nitrogen and argon.

Formation of amino acids takes place in aqueous solutions of formaldehyde and hydroxylamine. The sonication yielded alanine and glycine, $2.0 \times 10^{-7}$ and $1.8 \times 10^{-7}$ molecules per 100 eV respectively.

Our experimental data allows us to consider that ultrasound waves of high capacity can initiate and activate primary chemical reactions and these reactions took place in the hydrosphere of the Earth. We were able to carry out synthesis of essential biological substances in aqueous solutions in the field of ultrasound waves. Ideas about the role of the cavitation in the initiation of chemical processes prompted the development of these studies. The cavitations are formed under ultrasonic irradiation (sonication) of aqueous solutions. Under definite conditions in places of rarefaction, breaks are formed in the sonicated solution with the formation of small cavities. The bubbles are rapidly collapsed in places of compression. The presence of different gases in the water facilitates the formation of cavitation to a considerable extent (microscopic gas bubbles make the breaking of liquid easier).

Molecules of water or of solute gases which diffuse into the cavitation bubble undergo dissociation, leading to the initiation of chemical reactions (oxidation, reduction and others) (Elpiner, 1973). The molecules of water split into free hydroxyl radicals and hydrogen atoms (Prudhomme and Grabar, 1949). The cleavage of water takes place in presence of inert gases (argon, krypton), too.

It likely to assume that cavitation can occur when acoustic or ultrasonic vibration reach definite intensity under natural conditions as well as in the laboratory. According to the calculations made by Gasarian at El'piner's request (El'piner, 1973), during strong seaquakes removal of the seabottom can produce acoustic vibrations with pressure in the wave exceeding the hydrostatic pressure, that must be followed by cavitation. Cavitation may also accompany submarine explosions or the eruption of submarine volcanoes or can be caused by the influence of surface waves of the ocean (Anbar, 1968). All this supports our ideas about direct role of water masses and gaseous substances present in water in the abiogenic synthesis of organic substances on the Earth.

Under laboratory conditions, water saturated with carbon monoxide will form
formaldehyde in the field of ultrasonic waves. Reaction yield increases when the water is saturated with carbon monoxide and hydrogen. When the water is saturated with three components – carbon monoxide, hydrogen and molecular nitrogen, the yield of the formaldehyde decreases and hydrocyanic acid and ammonia are found in the system (El'piner and Sokolskaya, 1958). Formaldehyde is also formed in the sonication of aqueous solution of methane in the absence of other gases (El'piner and Sokolskaya, 1971). This is significant because formaldehyde is an initial substance in model experiments for the synthesis of biologically active compounds – like amino acids, heterocyclic compounds (imidazole) and aldehydes with structure similar to carbohydrates (Sokolskaya, 1975).

After the sonication of aqueous solution of formaldehyde and hydroxylamine with frequency 850 kHz and intensity 10-12 W/cm² substances which reacted positively with ninhydrin were found. In these sonification experiments 10 ml of 2.5 % aqueous solution of formaldehyde in the presence of 0.2 % hydroxylamine were used. (The solution was saturated with argon.) Upon sonication, the solution was passed through the column with KY-2(H⁺). The column was washed with the water, and subsequently, with ammonia. Ammonia fraction was dried in a vacuum and was separated on a paper chromatogram (solvent: butanol, acetic acid, water 4 : 1 : 5). The chromatogram showed a number of compounds revealed by ninhydrin. For quantitative estimation of these compounds, all the ninhydrin reaction – stained patches were eluted with water and the solution density was estimated by spectrophotometer at $\lambda = 570$ nm. The amount of ninhydrin-positive substances ranges from 17 to 20 μg (estimation for glycine).

Amino acids such as glycine, alanine and glutamic acid were among the products having positive reaction with ninhydrin. Their presence was determined by means of separation of the acidic hydrolysate of ammoniac fraction KY-2(H⁺) in presence of markers of different amino acids.

For further identification of amino acids the location regions of amino acids determined in parallel pre-developed chromatogram were eluted by water. The water eluates were distilled in the presence of ninhydrin. In the distillates of the glycine region eluates formaldehyde was determined with chromotrope acid; in alanine region distillate acetaldehyde was determined with 4-oxydiphenyl (Braunstein and Bychkov, 1943). When the aqueous solution of formaldehyde and hydroxylamine was sonicated the yield of alanine was 1.9-3.7 μg, and the yield of glycine was 2.2-2.5 μg (Table I). A formaldehyde solution (2.5 %, 10 ml) in the presence of 0.2 % hydroxylamine saturated with argon was used as one control solution. This control solution was not sonicated, but was subjected to all the procedures involving the addition of the above substance from the beginning to the end of the test. In addition, a 10 ml of 2.5 % formaldehyde aqueous solution saturated with argon and a 10 ml of 0.2 % hydroxylamine aqueous solution saturated with argon were sonicated separately with a subsequent test.

A compound with carbonyl group was found among the reaction products in sonicated solutions of formaldehyde and hydroxylamine in the fractions passed through KY-2(H⁺) resin. This compound reacts with anilin in the presence of phthalic acid (pink colour); with AgNO₃ ammoniacal solution (black-brown colour); with diphenylamine in the presence of orthophosphoric acid (blue colour).