ON THE SYNTHESIS OF SUBSTANCES IN WATER SATURATED WITH GASES OF A REDUCING ATMOSPHERE UNDER THE ACTION OF ULTRASONIC WAVES

1958

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

I. E. EL' PINER and A. V. SOKOL' SKAYA

ON THE SYNTHESIS OF SUBSTANCES IN WATER SATURATED WITH GASES OF A REDUCING ATMOSPHERE UNDER THE ACTION OF ULTRASONIC WAVES

(Presented by Academician A. I. Oparin, 19 XII 1957)

In the present communication data are presented showing that the propagation in water of ultrasonic waves of high intensity gives rise, even in the absence of oxygen, to chemical processes accompanied by the synthesis of a number of new substances.

According to the widely accepted so-called cavitation electrochemical theory ([1–3]), in the cavitation cavity, as a result of the occurrence of high electrical voltages, an electrical breakdown takes place ([4]), causing ionization of the water molecules present there in the vapor state. The ionized water particles decompose almost instantaneously into valence-unsaturated free radicals and atomic hydrogen ($H_2O \rightarrow H + OH$), as occurs when water is acted upon by ionizing radiation.

If, indeed, moving charges capable of ionizing water molecules arise in the cavitation cavity, then we are entitled to expect that molecules of the gas diffusing there may also undergo such a process. Proceeding from these considerations, one of us as early as 1950 ([5]) carried out special experiments which showed that in water saturated with gaseous hydrogen and molecular iodine, dissociation of iodine occurs under the action of ultrasonic waves. This process is apparently effected in the cavitation cavity, into which iodine molecules diffuse together with gaseous hydrogen. The ionization (or dissociation) of iodine is closely connected with the parallel ionization (or dissociation) of hydrogen. Later, the reduction of iodine in water saturated with hydrogen and molecular iodine under the action of ultrasonic waves was also observed by Henglein ([6]).

Recently we have succeeded in showing that, under the action of ultrasonic waves, other gases are also activated (dissociated) in water. Thus, for example, it was found that in the presence of hydrogen and nitrogen in water subjected to sonication, ammonia is formed.

Sonication of water in the presence of nitrogen and hydrogen was carried out in glass vessels at an ultrasonic-wave intensity of 6–7 W per 1 cm^2 of the radiating surface (oscillation frequency 380 and 750 kHz). The volume of distilled water

subjected to sonication was 10 ml. The water under study was first saturated simultaneously with gaseous nitrogen and hydrogen, carefully freed from oxygen impurities.

For fine purification of nitrogen from oxygen we used the method developed by L. M. Kantorovich and F. M. Rapoport ([7]), which consists essentially in passing the dehydrated and heated gas through a column containing a preparation consisting of copper deposited on silica gel. Purification of the hydrogen obtained in a Kipp apparatus was carried out by passing it through an alkaline solution of pyrogallol. As a result

after these manipulations, oxygen was not detected in the gas-saturated water by the polarographic method of analysis.

The quantitative content of ammonia in water before and after sonication was determined with Nessler' s reagent (see Table 1).

As can be seen from Table 1, the amount of ammonia formed increases with increasing sonication time. When water is saturated only with nitrogen, ammonia appears only after prolonged sonication (120 min) and in very small amounts. Very small amounts of ammonia are also detected upon prolonged sonication of water in the presence of oxygen and nitrogen, which is also in agreement with some literature data ([8]). In the presence of oxygen in water saturated with nitrogen, chiefly nitrogen oxides are formed under the action of ultrasonic waves.

It is important to note that the presence of carbon monoxide in a gas mixture of nitrogen and hydrogen does not prevent the formation of ammonia in the sonicated water. We obtained carbon monoxide by decomposing oxalic or formic acids with slight heating in the presence of sulfuric acid.

Table 1

Synthesis of ammonia in the field of ultrasonic waves

Sonication duration, min	Amount of ammonia formed, γ per 1 ml of water	Amount of ammonia formed, γ per 1 ml of water	Amount of ammonia formed, γ per 1 ml of water	Amount of ammonia formed, γ per 1 ml of water	Amount of ammonia formed, γ per 1 ml of water
	with H_2	with N_2	with H_2+N_2	with H_2+N_2+CO	with air
50	–	–	0.85	–	–
60	0	0	1.26	–	0.04
120	–	0.62	2.6	–	–
180	–	–	8.7	–	0.62
180	–	–	–	7.8	–
180	–	–	–	7.1	–
180	–	–	–	8.5*	–

Sonication duration, min	Amount of ammonia formed, γ per 1 ml of water	Amount of ammonia formed, γ per 1 ml of water	Amount of ammonia formed, γ per 1 ml of water	Amount of ammonia formed, γ per 1 ml of water	Amount of ammonia formed, γ per 1 ml of water
180	–	–	9.0**	6.5**	–
360	–	–	12.5	–	–

* Sonication was carried out in 0.1 N HCl.
** Sonication was carried out in 1% succinic acid.

It was further found that when carbon monoxide is added to a gas mixture of N_2 and H_2, hydrocyanic acid is formed in the sonicated water (in addition to ammonia); for its determination we used Guignard' s method ([9]), based on the reaction of conversion of picric acid into purpuric acid in the presence of hydrocyanic-acid vapors.

Repeated studies showed that in sonicated water (exposure 3 hours) in the presence of N_2, CO, and H_2, from 1 to 10 γ of HCN is detected. Hydrocyanic acid was not detected in water sonicated in the presence of oxygen or of nitrogen alone, or of a gas mixture of N_2 and H_2.

The synthesis of hydrocyanic acid in the field of ultrasonic waves is also effected when, in the gas mixture used, carbon monoxide is replaced by methane, i.e., in the presence of N_2, H_2, and CH_4.

Table 2

Synthesis of formaldehyde in the field of ultrasonic waves

Sonication duration, min	Amount of formalde-hyde formed, γ (10^{-6} g) per 1 ml of water	Amount of formalde-hyde formed, γ (10^{-6} g) per 1 ml of water	Amount of formalde-hyde formed, γ (10^{-6} g) per 1 ml of water	Amount of formalde-hyde formed, γ (10^{-6} g) per 1 ml of water	Amount of formalde-hyde formed, γ (10^{-6} g) per 1 ml of water
	with H_2	with H_2+CO	with H_2+CO+N_2	with air	with CO
0	–	–	0	0	0
60	–	5.6	1.8	–	4.0
120	0.2	16.0	6.0	0.4	6.4
180	–	24	15.0	0.1	7.4
180	–	26.4	–	–	–

Subsequently we were able to establish that formaldehyde is formed in sonicated

water if hydrogen and carbon monoxide are present in this water. The method we used for determining formaldehyde is based on the reaction of the latter with phenylhydrazine and an alkaline solution of $K_3Fe(CN)_6$ [10]. The amount of formaldehyde formed was determined with an SF-4 spectrophotometer at λ 520 mμ.

As can be seen from Table 2, in 180 min, in water sonicated in the presence of H_2 and CO, 26 γ of formaldehyde is formed per 1 ml of water; in the presence of air in the sonicated water, formaldehyde is almost not detected. Formaldehyde is also formed under the action of ultrasonic waves in the presence of H_2, CO, and N_2. Under these conditions, NH_3 is synthesized simultaneously with formaldehyde.

and HCN, the amount of which increases with increasing duration of sonication. The appearance of these products may ensure the further synthesis of biologically important substances, as occurs under the influence of electrical discharges or ultraviolet radiation [11,12].

The data we have obtained make it possible to express certain considerations that acoustic and ultra-acoustic oscillations, along with other physical agents (ultraviolet rays, electrical discharges, and radioactive decay), could have served as a source of energy for the synthesis of the basic products that provided the material for the construction of living organisms in the initial period of our planet' s existence. Such a conception fully accords with A. I. Oparin' s theory [13] of the origin of life on Earth. A quantitative estimate of the acoustic energy that arose, and continues to arise to this day, under natural conditions (electrical discharges, waterfalls, seaquakes, etc.) is of the utmost importance.

Received21 XI 1957

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Note: Figure translations are in progress. See original paper for figures.

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