SHORT COMMUNICATIONS

Formation of Ozone and Hydrogen Peroxide during an Electrical Discharge in the Solution–Gas System

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Abstract—Hydrogen peroxide formation is studied in an electrodeless electrochemical reaction, which occurs in a liquid during an interaction between water dissociation products and active species formed by an electrical discharge in the electrode/liquid gap. Data are obtained for the corona, spark, and arc discharges (at 0.05–0.1, 0.5, and >2 mA, respectively), separately for positive and negative voltages across the electrode placed over the liquid surface. Measurements are taken in oxygen, helium, and hydrogen environments, at atmospheric pressure and room temperature. Yield of ozone is determined under the same conditions of the electrical discharge between the electrode and the liquid surface. Hydrogen peroxide formation is shown to essentially depend on the electrical discharge regime, gas composition in the discharge gap, and the solution acidity. The ozone yield depends solely on the gas composition and the voltage polarity across the discharge gap.

Earlier [1], we have proposed a novel avenue of investigations concerning reactions that involve active species, which emerge during an electrical discharge in the electrode/liquid gap. Characterization of the basic products formed in simplest systems is one of the primary problems to be solved for this new class of reactions. The liquid (water)–gas system is one of such systems. In connection with this, we studied the formation of ozone and hydrogen peroxide during the corona, spark, and arc discharges (at 0.05–0.1, 0.5, and >2 mA, respectively) at different polarities of the voltage across the electrode placed over the liquid surface in the water–gas system. In accordance with [1], the discharge regions were distinguished in the degree of screening of the external field by the space charge formed during an electric discharge in the electrode/liquid gap.

To determine the hydrogen peroxide yield, we used titration by 0.01 N $KMnO_4$ solution in an acid medium. Prior to the titration, the analyzed solution was bubbled with air for no less than 5 min, in order to remove ozone dissolved in water [2, 3]. The degree of water deozonation was determined in a separate experiment, when the discharge was struck between two electrodes placed over the water surface. The ozone yield was measured using iodometry [3].

The reaction was carried out in a glass vessel plugged with a stopper. The examined solution's volume was 20 ml in all the experiments. The hermetically sealed reaction vessel had ports for electrodes and inlet/outlet connections for blowing-through a gas (oxygen, hydrogen, or helium) in whose atmosphere the reaction was to proceed.

Both electrodes were of platinum. The contact electrode was mounted on a glass insulator and placed in the liquid 10 mm beneath its surface. It was 0.3 mm in diameter. The diameter of discharge electrode (placed over the liquid surface) was 0.1, 0.3, and 1 mm for the corona, spark, and arc discharges, respectively. The electrode diameter was chosen from the condition of obtaining the most steady discharge of a given type. The discharge current was preset by a restricting resistor (1–10 MΩ), which was connected in series with the discharge gap, and by the voltage of the power source (8–10 kV). The discharge electrode was placed 2.5–3 mm from the liquid surface.

In the case of hydrogen peroxide formation, we measured its initial differential yield G_0 expressed in equivalents per Faraday (equiv/F). All in all, we obtained: (1) the dependence of the initial yield G_0 on the solution acidity at pH ranging from 1 to 13, (2) the dependence of G_0 on the current in the electrical discharge region and on the polarity of the discharge electrode voltage, and (3) dependence of G_0 on the gas composition in the spark gap. All measurements were carried out at atmospheric pressure and room temperature (20°C).

The dependence of G_0 on the solution acidity in an oxygen atmosphere was studied in detail for the spark discharge (at a current of 0.5 mA). The pH values were set by adding H_2SO_4 or NaOH into distilled water. The experimental results for the positive discharge-electrode voltage are presented in the figure. The yield is seen to be practically independent of the solution acidity for pH between 3 and 10; it equals 2.2 ± 0.4 equiv/F. The yield increases at pH < 3 and decreases at pH > 10; it is practically zero (less than 0.004 equiv/F) when pH equals 13.

After the reaction occurred, the solution acidity always increased. The highest change in pH was observed for a neutral solution: from pH 6 in the initial solution to pH 5 after a 1-h exposure. At pH < 3 and

G_0, equiv/F
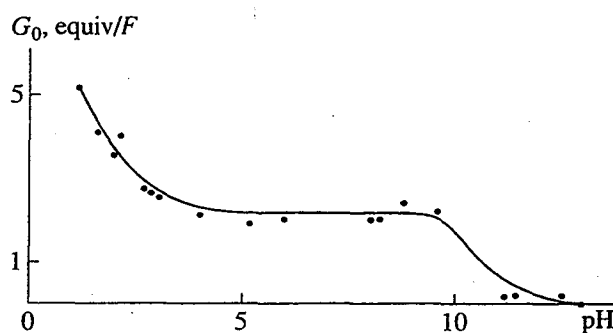
Dependence of the initial yield of hydrogen peroxide on the solution acidity at a positive polarity of the discharge-electrode voltage, at a current of 0.5 mA (the spark discharge).

pH > 10 no change in acidity was observed after a 1-h exposure to a current of 0.5 mA.

When the voltage polarity was reversed at a 0.5-mA current, the pH dependence of G_0 retained its character; however, the yield was approximately ten times as low, namely, 0.3 ± 0.1 equiv/F for pH between 3 and 10.

The current dependence of the differential yield in the oxygen atmosphere at pH 1.6 is presented in the table. We see that the yield reaches maximum in the spark discharge mode (at a current of 0.5 mA): 4.3 and 1.2 equiv/F at positive and negative polarities of the discharge-electrode voltage, respectively. When passing to the arc discharge mode, the yield drops and decreases monotonically with the current increase. The yields in the arc discharge mode are close to those obtained by Davies and Hickling [4] and by Pavlov [5] for the same discharge region at the same voltage polarity (1.1 equiv/F).

When the discharge-electrode polarity is negative in the arc discharge mode, the yield also decreases with the current increase. However, the current dependence of the yield could not be obtained in a wide current range in this discharge mode, because the electrode starts to melt at a current as low as 10 mA. Neverthe-

Dependence of the initial yield of hydrogen peroxide in water on the current (on the electrical discharge region) for electrical discharge in the oxygen atmosphere. Solution pH 1.6

Current, mA	Yield (in equiv/F) for the electrode polarity		Discharge mode
	(+)	(−)	
0.05	<0.04	−	Corona discharge
0.1	−	<0.04	
0.5	4.32	1.22	Spark discharge
5	3.14	0.23	Arc discharge
10	2.82	0.13	
15	2.24	−	
40	1.54	−	
50	1.3	−	
60	1.14	−	

less, the table shows that the yield reduces significantly when the current increases. The yield is much less than unity at a current of 10 mA, which agrees with the data of [4, 5], where no hydrogen peroxide formation was observed in the arc discharge mode at the negative polarity of the discharge-electrode voltage.

In the corona discharge mode, the yield of hydrogen peroxide drops practically to zero, no matter what the polarity of the discharge-electrode voltage.

In the hydrogen and helium atmospheres, the yield of hydrogen peroxide decreases. For a neutral solution (pH 6) at a current of 0.5 mA and positive polarity of the discharge-electrode voltage, $G_0 = 1.13$ equiv/F for a hydrogen medium, and $G_0 = 1.18$ equiv/F for a helium atmosphere. When the polarity is reversed, the yield drops abruptly to less than 0.2 equiv/F.

In the spark discharge mode, at a current of 0.5 mA and the positive polarity of the discharge-electrode voltage, the hydrogen peroxide yield depends but weakly on the presence of chlorine ions in the liquid (0.02 M NaCl solution in a 0.05 M H_2SO_4 solution). The yield was 4 and 0.4 equiv/F for the positive and negative polarities, respectively.

Measurements of the ozone yield in the electrodeless reaction showed that at a fixed geometry of the experiment, the yield does not depend on the discharge type and the solution acidity at pH between 1.3 and 14. When the discharge-electrode voltage is positive, the yield is 100, 6, and 0.15 mol/F for oxygen, helium, and hydrogen, respectively, whereas under negative polarity it is 30, 3, and 0.3 mol/F. The error of these values does not exceed 10%.

The closest analogy to the process under study is the glow-discharge electrolysis (GDE). We showed in [1] that GDE is a particular case of the electrodeless reaction, specifically, it is a reaction in the arc discharge mode. Data on GDE, in particular on the hydrogen peroxide formation during GDE, accompanied so far have been analyzed by Hickling and Ingram [6, 7]. GDE was carried out at a gas pressure of 6.7–13.3 kPa, which is lower than the atmospheric pressure, at positive (relative to the liquid) potential at the discharge electrode, at a current of 20–100 mA.

The quantity of hydrogen peroxide formed during GDE per unit charge passed through the circuit was shown to be independent of the current and weakly dependent on the interelectrode distance, dissipated power, the electrodes' shape and size, and the gas pressure and composition [4]. Hence, it was concluded that the reactions proceeded mainly in the liquid phase.

According to [4–8], the hydrogen peroxide formation does not depend significantly on the nature of gas over the electrolyte. Nevertheless, the yield tends to increase in air and the oxygen atmosphere, compared with that in nitrogen, and to slightly decrease in the hydrogen atmosphere. The differential yield G_0 at the initial instant was 1.1 equiv/F in a 0.05 M solution of sulfuric acid and 1.8 equiv/F in a 0.05 M solution of

sodium bicarbonate [6, 7]. In the latter electrolyte, G_0 increased when the electrolyte concentration was increased up to the limiting value.

Chlorine ions present in the electrolyte decreased the hydrogen peroxide yield during GDE, and in a 0.02 M NaCl solution in sulfuric acid its formation was completely inhibited. No hydrogen peroxide was detected in strongly alkaline media, which, according to [6], was caused by the HO_2^- ions discharging at the anode.

Neutral salt solutions would become acidic after treatment in the GDE regime, which may evidence the discharge of hydroxyl ions [6, 7]. When the polarity of the voltage supply was reversed ("minus" on the discharge electrode, relative to the liquid), no hydrogen peroxide formed in a 0.05 M solution of sulfuric acid [8].

A comparison of the above data from the cited papers with those obtained by us shows that our results on the arc discharge are in agreement with the GDE data. However, in other discharge modes, regularities of the H_2O_2 formation significantly differ from GDE. These differences are as follows:

(1) The hydrogen peroxide yield depends significantly on the type of the electrical discharge. The maximum yield is observed in the spark discharge regime (in the case of GDE, the yield depends weakly on the current in the arc discharge mode).

(2) The hydrogen peroxide yield strongly depends on the gas composition in the discharge gap (with GDE, the yield is practically independent of the gas composition).

(3) The yield is noticeable when the discharge-electrode voltage is negative (with GDE, the yield is practically zero).

(4) In the corona discharge mode, practically no hydrogen peroxide forms, irrespective of the polarity,

which evidences the existence of other interaction channels for the active particles. In the case of GDE, no analogue of this phenomenon was ever observed.

(5) In the spark discharge mode, chlorine ions affect but weakly the hydrogen peroxide formation.

(6) The ozone yield does not depend on the discharge mode, it changes only when the voltage polarity is changed.

These distinctions point to mechanisms of the electrodeless reactions other than GDE.

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