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HYDROGEN PEROXIDE FORMATION ON THE ADSORPTION OF ACIDS BY ACTIVATED CHARCOAL

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According to Naray Szabo (1) the process taking place on an oxygen carbon electrode runs as follows:

$$C_xO + H_2O = C_x + 2OH' + 2\oplus; \quad (1)$$

C_xO is an oxygen atom adsorbed by the charcoal. In the case of an acid solution one may write

$$C_xO + 2H^{\cdot} = C_x + H_2O + 2\oplus.$$

However, it was long since stated in literature that hydrogen peroxide, too, was apt to form during the cathodic reduction of oxygen on various electrodes. Berl (2) suggested the use of porous carbon electrodes for an industrial production of hydrogen peroxide. Schematically this process may be represented as follows:

$$C_xO_2 + 2H^{\cdot} = C_x + H_2O_2 + 2\oplus. \quad (2)$$

It was found in our laboratory by P. Dolin and P. Spiridonov that as a result of this reaction hydrogen peroxide appears in galvanic cells with air depolarization.

Proceeding from the relation established by Frumkin between adsorption processes and electrochemical processes, we were able to show in one of the works performed at this laboratory (3) that with small amounts of oxygen adsorbed on charcoal the process of anion adsorption is expressed quantitatively by the following equation:

$$C_xO + 2H^{\cdot} + 2A' = H_2O + C_x + 2A' + 2\oplus \quad (3)$$

the anions being attracted by the positive charges of the charcoal. In connexion with the electrochemical theory of adsorption it was of interest to establish whether the process of anion adsorption might be attended by the formation of hydrogen peroxide. If so, the adsorption process should run according to the following scheme:

$$C_xO_2 + 2H^{\cdot} + 2A' = C_x + 2A' + H_2O_2 + 2\oplus. \quad (4)$$

A series of experiments was started in order to find out the conditions under which the formation of hydrogen peroxide would take place.

Experiments with adsorption were carried on as follows (4): 0.5 g of charcoal were poured into an ampulla. Then 10 cm³ of a H_2SO_4 solution were added into it. Oxygen was passed through the solution and the latter was then

strained through a glass filter placed in the apparatus. Titration with alkali served to determine the amount of adsorbed anions, while the quantity of hydrogen peroxide formed was determined by titration with a permanganate solution. Qualitatively the formation of H_2O_2 was proved by means of bichromate. The results of the experiments are referred to in Table 1.

Table 1

Final concentration of the solution in g. equ./l	Amount of the adsorbed acid in milliequ. per 1 g of charcoal	Amount of H_2O_2 formed in milliequ. per 1 g of charcoal	Amount of H_2O_2 in % of the total amount of adsorbed acid
0.00015	0.18	0.0016	1
0.0029	0.24	0.012	5
0.0197	0.32	0.038	11.9
0.059	0.448	0.060	13.0
0.134	0.60	0.086	14.3
0.814	1.12	0.16	14.3
3.14	1.35	0.228	16.8

From these data it is obvious that with increasing concentration of H_2SO_4 grows also the yield of peroxide. It may be remarked here that charcoal is at the same time a catalyst in respect to the decomposition of H_2O_2. Therefore the determination of H_2O_2 should be made soon after the start of the experiment.

After 10 min. the yield of hydrogen peroxide with reference to the amount of adsorbed acid is at its maximum. 1 hour after the start of the experiment the concentration of hydrogen peroxide will decrease 2 times.

Further investigations have shown that an essential condition for hydrogen peroxide to form is the presence of oxygen in gaseous state. If indeed the coal, after it has been in contact with oxygen, is placed in water and the whole system saturated with nitrogen, then the pouring in of an outgased solution of the acid will no longer bring about the formation of hydrogen peroxide in significant quantities. In this case the amount of hydrogen peroxide formed will not surpass 0.003 milliequivalents per 1 g of coal when the final concentration of the acid is 0.357. This is about thirty times less than if the adsorption is carried on in the presence of air. At the same time the difference in the amount of adsorbed acid is not beyond 15—20%, when the results of experiments carried on in nitrogen and in air are compared.

The evidence furnished by these experiments is that the formation of hydrogen peroxide is possible only at the expense of freshly adsorbed oxygen. Such oxygen, however, that has long been present on the coal surface is bound with it too firmly and can no longer react and form hydrogen peroxide. Ths fixation of the latter goes probably through the break up of O_2 molecules into atoms. When firmly bound oxygen reacts in the process of anion adsorption, water is formed. It was proved by special experiments that the formation of H_2O_2 is not connected with the autooxidation of carbon, which at room temperature leads to the formation of CO_2. When the adsorption of the acid is complete, the formation of H_2O_2 comes to an end, too, although the process of autooxidation continues at the same rate.

It is interesting to compare our data with those previously obtained at the same laboratory by Bruns and Piloyan ([5]). Those authors have shown that when adsorption of anions takes place on charcoal, additional quantities of gaseous oxygen are adsorbed, but the amount of adsorbed oxygen is not equivalent to that of adsorbed acid and it grows more rapidly with the increasing concentration of the acid than does the adsorption of anions*.

* In other words, the store of adsorbed oxygen on charcoal decreases in the process of adsorption of the acid. This is probably because of the repulsive interaction between the atoms of oxygen and anions in the double layer.

The results of the experiments by Bruns and Piloyan are shown in Table 2. In the 4th column are given the amounts of H_2O_2 that should form if the whole of the adsorbed oxygen reacted according to scheme (4).

Table 2

Concentration of the solution	Adsorption of O_2 in cm^3 per 1 g of charcoal	Adsorption of H_2SO_4 in milliequ. per 1 g of charcoal	Amount of H_2O_2 formed in milliequ. as calculated from the adsorption of O_2	Amount of H_2O_2 in % of the total amount of adsorbed acid
0.043	0.35	0.40	0.0315	8
0.142	0.92	0.50	0.083	14
0.327	1.15	0.60	0.103	17
0.731	1.22	0.80	0.120	15
1.27	1.48	0.86	0.133	15.4

If the experiments referred to in Tables 1 and 2 were not made with the same coal and are not therefore strictly comparable, nevertheless it may possibly be inferred from them that practically the whole of the oxygen adsorbed from the gaseous phase in the process of anion adsorption is used in the formation of hydrogen peroxide.

From the results obtained it will be apparent that there are two different forms of bound oxygen on the surface of the coal. This conclusion is also apt to arise from the data obtained for the cathodic polarization of an oxygen carbon electrode.

In order to establish the condition for hydrogen peroxide to form on the electrode, we made experiments in which a very pure ashless activated coal (prepared from phenol-formaldehyde resin) was subjected to cathodic polarization at various current densities during some specified intervals. The amount of hydrogen peroxide thus formed was then estimated. These experiments have shown that in the presence of oxygen an increase in the current density from 6.5×10^{-5} A to 130×10^{-5} A per 0.1 g of coal leads to an increase in the yield of oxygen peroxide from 10 to 47% with reference to the current.

If the current density goes further up, the yield of hydrogen peroxide goes down. The rate of hydrogen peroxide formation grows at first with the increase of the current density, but eventually a constant value is reached. Upon the composition of the solution the yield of hydrogen peroxide is but little dependent.

It is worth while to compare these data with those obtained on the polarization of coal in an atmosphere of an inert gas. In the latter case the store of adsorbed oxygen on the coal was periodically replenished at the intervals when there was no polarization in order to secure the passage of the current. In that way it was found that with equal electric quantities let through, the amount of hydrogen peroxide formed in the atmosphere of an inert gas is only 5—10% of that formed in the atmosphere of oxygen. This evidence also leads to the conclusion that only freshly adsorbed oxygen takes part in the formation of hydrogen peroxide. Oxygen that has long been on the surface of the coal reacts with the formation of water. Small quantities of H_2O_2 in an atmosphere of nitrogen may be accounted for by an incomplete removal of oxygen under the conditions of the experiment.

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