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BRIEF COMMUNICATIONS

Hydrolysis of Acetylsalicylic Acid under the Conditions of Electrolysis

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Abstract—The hydrolysis of acetylsalicylic acid in the anolyte under the conditions of electrolysis was studied.

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Acetylsalicylic acid (ASA, Aspirin®) is one of the most popular drugs which, together with other drugs, gets into wastewater, and hampers operation of biological sewage treatment plants [1, 2]. It is known that the biological activity of ASA-containing aqueous solutions can be decreased by more than an order of magnitude by their electrooxidation [3]. However, it remains unknown whether ASA itself or its hydrolysis product, salicylic acid (SA), undergoes electrooxidation. To answer this question, we compared in this study the ASA anodic oxidation kinetics, on the one hand, and the ASA hydrolysis kinetics under electrolysis and without it, on the other hand.

EXPERIMENTAL

The ASA hydrolysis was studied in 0.1 N aqueous H_2SO_4 at room temperature. The ASA and SA anodic oxidation was carried out at 25°C in a two-electrode electrochemical cell with a membrane separating the anode and cathode chambers. A smooth platinum plate was used as anode. The current density was 10 mA cm^{-2}. The anolyte was analyzed by high-performance liquid chromatography (HPLC) and UV spectroscopy.

We found that, on keeping ASA in aqueous H_2SO_4 without electrolysis, the absorption band in its UV spectrum at 227 nm is shifted to 235 nm. This means that, under these conditions, ASA is hydrolyzed to form SA. This conclusion is consistent with Fig. 1 showing that, as the SA/ASA ratio in their mixtures increases, the absorption band at 227 cm^{-1} linearly shift to longer wavelengths. From this correlation, we determined the SA content of the ASA–SA mixtures in the course of ASA hydrolysis. We found that the ASA hydrolysis is relatively slow and a 90% degree of hydrolysis is reached only in 16 days (Fig. 2). The time dependence of the SA content of the reaction mixture

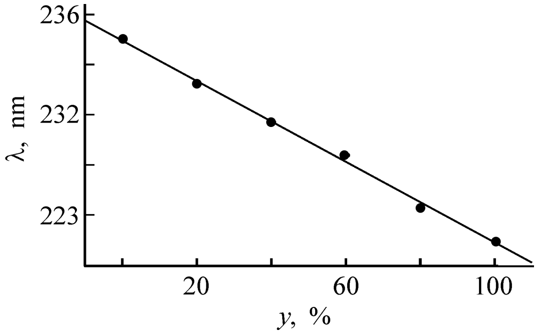


Fig. 1. Position of the maximum of the absorption band in the UV spectrum of ASA–SA solutions in 0.1 N H_2SO_4 vs. ASA content *y*.

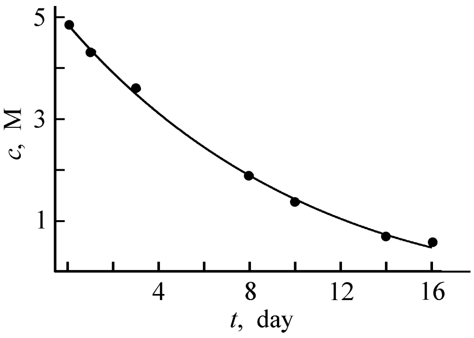
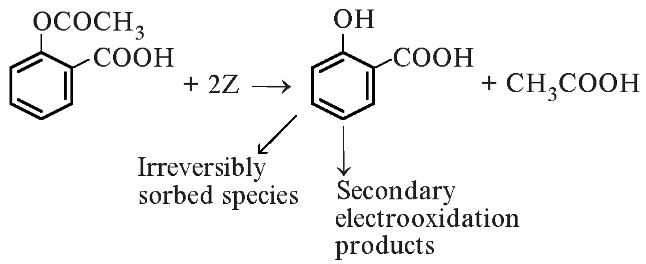


Fig. 2. Dependence of the ASA concentration *c* on hydrolysis time *t* in aqueous H_2SO_4.

showed that the ASA hydrolysis kinetics is described by a first-order rate equation with a rate constant of 0.0059 h^{-1}.

A chromatographic analysis of ASA solution subjected to electrolysis showed that the overall process of the ASA electrochemical conversion involves two successive stages. First, ASA is hydrolyzed to form SA and then, after accumulation of salicylic acid, the products of SA anodic oxidation appear in the anolyte. We found that, under the conditions of electrolysis, the rate of ASA hydrolysis is several times that under electroless conditions. Owing to the high rate of ASA hydrolysis under the conditions of electrolysis, the total ASA oxidation rate is comparable with that of the SA oxidation.

Figure 3 shows the dependence of the SA and ASA concentrations in the anolyte (M) on the electrolysis time. It is seen that the electrochemical conversion of ASA appreciably decelerates with time. It is believed [4] that this effect is caused by the fact that the SA formed by the ASA hydrolysis is irreversibly sorbed on the platinum surface and, as a result, the platinum surface becomes less accessible to ASA adsorption and its subsequent hydrolysis. Assuming that ASA hydrolysis occurs on two neighboring surface platinum atoms of the electrode, we can suggest that the ASA hydrolysis rate is proportional to the product of the ASA concentration in solution by the $(1 - \theta)^2$ factor, where θ is the fraction of platinum surface covered by irreversibly sorbed SA molecules. If the rate of the irreversible sorption of SA is proportional both to its concentration in the anolyte and to the free anode surface area $1 - \theta$, we can formulate a system of equations describing the ASA hydrolysis kinetics under the conditions of electrolysis. These equations take into account that, on the one hand, SA partially inactivates the platinum surface via its irreversible sorption, and, on the other hand, it is itself subject to anodic oxidation. The overall process of the electrochemical conversion of ASA on Pt anode can be represented by the following scheme (Z is an active center):



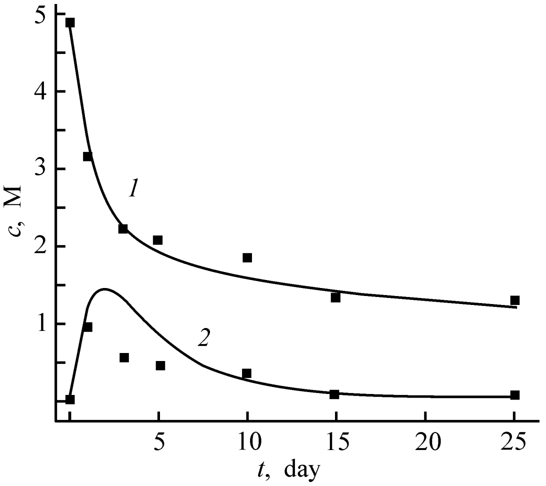


Fig. 3. Dependence of (*1*) ASA and (*2*) SA concentrations *c* in the anolyte (0.1 M H_2SO_4) on the electrolysis time *t*.

The kinetics of the processes in this scheme are described by the following equations:

$$dc_1/dt = -k_1 c_1 (1 - \theta)^2,$$

$$d\theta/dt = k_2 c_2 (1 - \theta),$$

$$dc_2/dt = k_1 c_1 (1 - \theta)^2 - k_3 c_2,$$

where c_1 and c_2 are, respectively, the ASA and SA concentrations in a time t after starting the electrolysis and k_1, k_2, and k_3 are, respectively, the rate constants of SAA hydrolysis, accumulation of irreversibly sorbed SA species, and SA oxidation.

The quantity k_3 was taken to be 0.37 h^{-1} as reported in [5]; k_1 and k_2 (0.4 and 0.17 h^{-1}, respectively) were determined from our experimental data by least-squares fitting. Figure 3 shows that the ASA hydrolysis kinetics is fairly well described by the system of the above rate equations.

Our experiments showed that the rate constant of ASA hydrolysis under the conditions of electrolysis exceeds that in the absence of current by a factor of 42. Taking into account that hydrogen peroxide promotes the ASA hydrolysis [6], we can suggest that the acceleration of ASA hydrolysis under the conditions of electrolysis is caused by adsorbed oxygen species containing O–O bonds.

In the course of ASA hydrolysis under the conditions of electrolysis, the electric current is consumed only for generation of catalytically active oxygen adsorbed on the platinum surface. Therefore, we can suggest that, at a lower current density, the SA oxidation rate will decrease and ASA hydrolysis will become the main process. This assumption was completely confirmed by our experiments. We found that, with the current density decreasing to 0.5 mA cm^{-2}, the SA oxidation is virtually suppressed and the ASA hydrolysis becomes essentially the only process.

CONCLUSIONS

(1) Acetylsalicylic acid is not subjected to direct anodic oxidation on platinum electrode.

(2) The hydrolysis rate of acetylsalicylic acid under the conditoins of electrolysis in acidic solutions in the range of oxygen evolution potentials exceeds that in the absence of current by an order of magnitude. This phenomenon can be used to accelerate the hydrolysis of acetylsalicylic acid and other esters.

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