INFLUENCE OF CERTAIN ORGANIC COMPOUNDS ON THE CATHODIC IMPLANTATION OF ALKALI METALS

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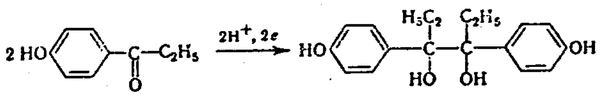
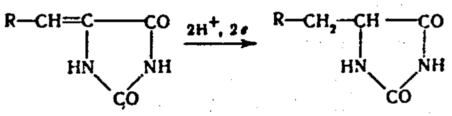
The authors investigate the cathodic implantation of sodium in tin and lead from 0.5 N $NaClO_4$ solution in dimethylformamide at −1.3 to −2.0 V (nhe) in the presence of p-hydroxypropiophenone, indolalhydantoin, and benzalhydantoin. A relation is established between the processes of electroreduction of organic compounds and cathodic implantation of alkali metals. From the data one can infer that one route for the reduction of the compounds in question is their interaction with the products of cathodic implantation of alkali metals.

Many processes of electrosynthesis of organic compounds take place in solutions containing alkali metal ions. Under such conditions there is a real possibility of occurrence of an electrochemical reaction of implantation of alkali metal ions in the electrode and their accumulation in the surface layer [1]. Cathodic implantation of alkali metals during reduction of organic compounds cannot be regarded as merely a side reaction, because implantation can lead to the formation of chemically active intermetallic compounds on the cathode, capable of interacting, for example, with water [2]. We must expect these products to react with the organic compounds also. In particular, it has been suggested [3] that the reduced efficiency of the process of electroreduction of p-hydroxypropiophenone on a tin cathode is due to implantation of alkali metal. It is therefore of interest to elucidate the role of the product of cathodic implantation during the electroreduction of organic compounds and the relations between the processes of implantation and electroreduction.

We have investigated cathodic implantation in the presence of p-hydroxypropiophenone, benzalhydantoin, and indolalhydantoin The schemes of cathodic reduction of these compounds are as follows:

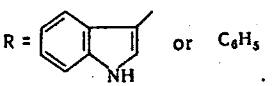


(1)



(2)

where



These compounds were chosen because in alkaline solutions they are electroreduced at fairly negative potentials [4, 5], i.e., in conditions in which alkali metals can be implanted. Their reduction products are of interest for medicine and also in a number of branches of the national economy. As cathodes in these

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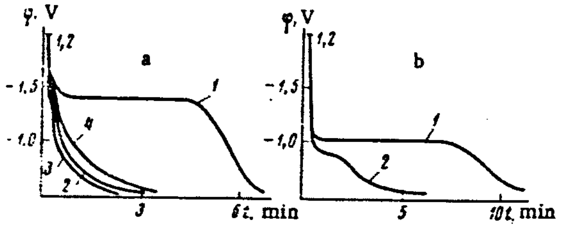

Fig. 1

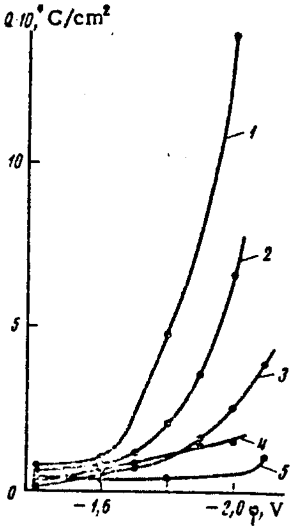

Fig. 2

Fig. 1. Anodic chronopotentiograms for tin (a) and lead (b) in 0.5 N $NaClO_4$ in dimethylformamide (base electrolyte): preliminary cathodic polarization at $\varphi_c = -2.0$ V, time 3 min (a, b), anode current density $i_a = 1.45 \cdot 10^{-5}$ (a) or $3.6 \cdot 10^{-5}$ A/cm² (b). 1) Base electrolyte (a, b); 2) base electrolyte + 0.4 mole/liter n-hydroxypropiophenone (a) and 0.32 mole/liter benzalhydantoin (b); 3) 0.32 mole/liter benzalhydantoin (a); 4) base electrolyte + 0.44 mole/liter indolalhydantoin (a).

Fig. 2. Quantity of sodium detected on tin electrode vs cathodic polarization potential. Time of preliminary cathodic polarization 3 min; anode current density $i_a = 1.45 \cdot 10^{-5}$ A/cm². 1) 0.5 N $NaClO_4$ in dimethylformamide (base electrolyte); 2) base electrolyte + 0.2 mole/liter pinacone of p-hydroxypropiophenone; 3) base electrolyte + 0.44 mole/liter of indolalhydantoin; 4) base electrolyte + 0.4 mole/liter of p-hydroxypropiophenone; 5) base electrolyte + 0.32 mole/liter of benzalhydantoin.

processes, the most often-used metals are tin and lead. The laws of cathodic implantation in these metals from aqueous and nonaqueous solutions in the absence of reducable organic compounds have been investigated previously.

Cathodic implantation was investigated by a chronopotentiometric method. Cathodic polarization of the electrode was effected in potentiostatic conditions (with a P-5827 potentiostat). Anodic chronopotentiograms were recorded with a KPS-4 potentiometer or an ÉNO-1 oscillograph. The organic compounds were purified by repeated recrystallization to constant melting point.

To eliminate parallel emission of hydrogen and chemical reaction of the implantation product with water, implantation in the presence of organic compounds was mainly studied in nonaqueous solutions. The dimethylformamide which was used to prepare the nonaqueous solutions was first dried over potassium hydroxide and then twice redistilled in a vacuum. The reference electrode was a calomel half cell. All potentials are referred to a normal hydrogen electrode.

As the cathode we used tin rods 1-2 mm in diameter made by drawing fused tin into glass capillaries. The working surface of the electrode (0.2-0.4 cm²) was freed from the glass.

Figure 1 shows the anodic chronopotentiograms recorded after preliminary cathodic polarization of the electrode. In the presence of an organic compound, the quantity of alkali metal detectable on the electrode after cathodic polarization is less than when no organic compound is present.

The influence of organic compounds on the quantity of alkali metal depends on the potential at which implantation takes place (Fig. 2). The effect sharply rises near potentials of −1.6 to −1.7 V, i.e., at the optimum potentials for reduction of the organic compounds in question [4, 5]. We must emphasize that it is in this potential range that there is a sharp rise in the quantity of alkali metal on the electrode in the

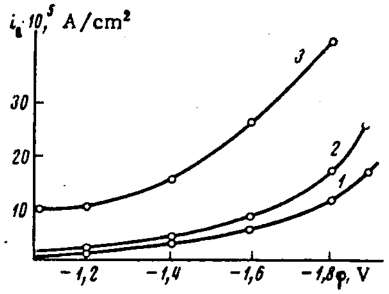

Fig. 3

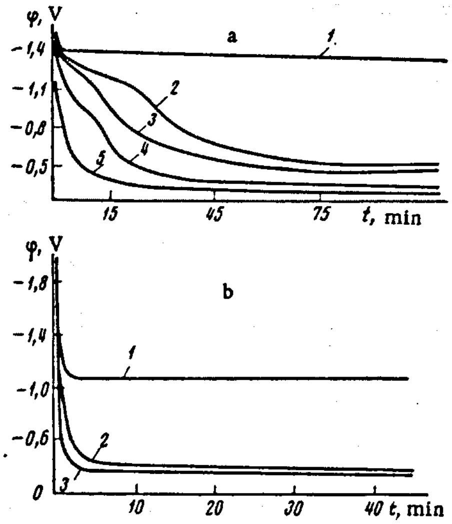

Fig. 4

Fig. 3. Polarization curves for tin electrode. 1) 0.5 N $NaClO_4$ in dimethylformamide (base electrolyte); 2) base electrolyte +0.44 mole/liter indolalhydantoin; 3) base electrolyte +0.4 mole/liter p-hydroxypropiophenone.

Fig. 4. Time dependences of potentials of tin (a) and lead (b) electrodes after cathode polarization is switched off. Preliminary cathodic polarization at $\varphi_C = -2.0$ V (a, b) for 120 min (a) or 60 min (b). 1) 0.5 N $NaClO_4$ in dimethylformamide (base electrolyte) (a, b); 2) base electrolyte +0.2 mole/liter pinacone of p-hydroxypropiophenone (a) and 0.4 mole/liter p-hydroxypropiophenone (b); 3) base electrolyte + 0.32 mole/liter benzylhydantoin (a, b); 4) base electrolyte + 0.32 mole/liter benzalhydantoin (a); 5) base electrolyte + 0.4 mole/liter p-hydroxypropiophenone (a).

absence of organic compounds. The graphs are qualitatively the same for both lead and tin.

A decrease in the amount of alkali metal on the electrode in the presence of organic compounds can occur either because of the competing electrochemical process of reduction of these compounds or because of their direct interaction with the products of cathodic implantation. That these compounds are reduced in these conditions is shown by the increase of cathode current in their presence (Fig. 3) and by data on preparative electroreduction [4, 5].

To elucidate the role of the products of cathode implantation in the process of reduction we investigated the interaction of the intermetallides with the organic compounds in the absence of cathodic polarization. In each experiment the electrode was first cathodically polarized in the base-electrolyte solution in the same conditions. Then the cathode current was switched off, a certain quantity of organic compound added, and the time dependence of the electrode potential measured. As we see from Fig. 4, in the base-electrolyte solution the electrode potential remains constant for a long time and corresponds to the equilibrium potential of the intermetallide formed by implantation. But in the presence of organic compounds we observe a rapid fall in potential to values close to the steady potential of the electrode metal in the given solution. This shows that the organic compounds interact with the products of cathodic implantation of alkali metals in lead and tin.

If we assume that all the implanted alkali metal takes part in reduction of the organic compounds, than the proportion which participates in reduction can be approximately estimated from the data in Fig. 3. It depends on the electrode potential and the nature of the organic substance. For example, at a potential of −1.7 V for p-hydroxypropiophenone it is about 20% and for indolalhydantoin, about 70%. These figures show merely the minimum fraction of alkali metal participating in the process of reduction. The actual figures may be higher, because the rate of the electrochemical stage is high, and in the presence of organic substances, owing to the continuous consumption of alkali metals, the role of diffusion limitations in the solid phase is reduced.

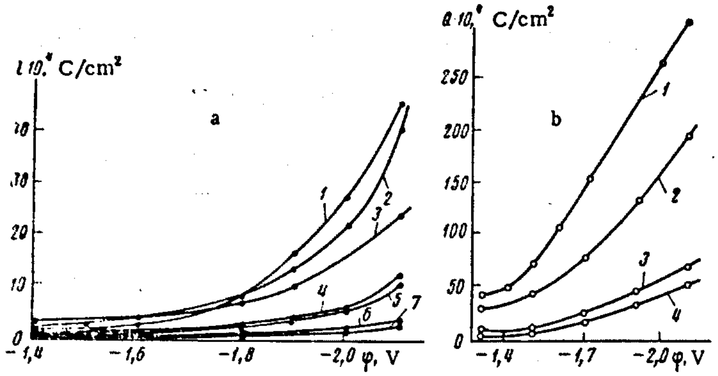

Fig. 5. Quantities of sodium found on tin (a) and lead (b) electrodes vs cathodic polarization potential, for various concentrations of organic compounds. Time of cathodic polarization 3 min, anode current densities $1.45 \cdot 10^{-5}$ A/cm² (a) and $3.6 \cdot 10^{-5}$ A/cm² (b). 1) 0.5 N $NaClO_4$ in dimethylformamide (base electrolyte) (a, b); concentrations of benzalhydantoin in mole/liter: 2) $6 \cdot 10^{-4}$; 3) $6 \cdot 10^{-3}$; 4) $6 \cdot 10^{-2}$.

Note that the products of reduction of p-hydroxypropiophenone and benzalhydantoin (the pinacones of p-hydroxypropiophenone and benzylhydantoin, respectively) are not inert with respect to the products of cathodic implantation (Fig. 2, curve 2, and Fig. 4, curves 2 and 3). We can suppose that in the case of the pinacone of p-hydroxypropiophenone there is a reaction between the phenol hydroxyl and the implantation product with the formation of a disodium salt. The carbonyl groups in the benzylhydantoin molecule can apparently be reduced.

To assess the behavior of the product of cathodic implantation in the presence of an organic compound which does not react with it, we studied the time dependence of the potential of tin without current after cathodic polarization and addition of isooctane. The resulting curve coincides with curve 1 in Fig. 4.

On the basis of these results we must expect that the influence of organic compounds on cathodic implantation depends on their concentration.

In the case of lead, the quantity of alkali metal found decreases with increasing concentration of benzalhydantoin (Fig. 5). For tin, when the concentration of p-hydroxypropiophenone or benzalhydantoin is $6 \cdot 10^{-4}$ mole/liter we observe the opposite effect: The quantity of alkali metal found increases. Since the proportion of the current expended on reducing the organic substance must be small at low concentrations, its role apparently consists in influencing the process of cathodic implantation. We can suppose that benzalhydantoin and p-hydroxypropiophenone are specifically adsorbed on the cathode surface and reduce its surface energy. It is known that reduction in the surface energy leads to an increase in the concentration of atomic vacancies on the surface of the cathode metal, and this, in turn, should lead to an increase in the rate of implantation of alkali metal [1]. The difference between the behavior of tin and that of lead at low concentrations (Fig. 5) may be due to the different adsorption capacities of these metals, to the different chemical activities of their implantation products, and also to the fact that the quantity of alkali metal for lead is greater than that for tin.

Thus, we have found that organic compounds influence the cathodic implantation of alkali metals. The results suggest that one route for the reduction of the compounds under test is interaction with the products of cathodic implantation of the alkali metals. This agrees with the well-known method of reducing p-hydroxypropiophenone to the corresponding pinacone by alloys of tin with alkali metals obtained thermally [6]. However, we must not fail to consider direct electrochemical reduction. In this case, the mutual influence of the processes of electroreduction and cathodic implantation consists, firstly, of a redistribution of the proportion of the current expended on each of them in relation to the conditions. In addition cathodic implantation leads to a change in the state of the electrode surface, in particular, to a shift of the zero-charge potential toward more negative values [1], as in the case of alkali metal amalgams [7]. Owing to the change in the range of adsorption potentials, more favorable conditions must be created for the reduction of the organic compounds concerned.

In this sense we can discern an analogy with the reduction of organic compounds on a mercury cathode in the conditions for amalgam formation [8]. During reduction on a solid electrode, the role of the accompanying process of cathodic implantation may be more important than in the case of mercury, owing to diffusion limitations on the conveyance of the implanted alkali metal into the depths of the metal cathode.

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