REDUCTION MECHANISM OF D-RIBONO-γ-LACTONE AT SOLID ELECTRODES

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According to [1], D-ribono-γ-lactone (RL) can be reduced at mercury cathodes under the conditions of amalgam formation, but is electrochemically inactive at solid electrodes [2]. An understanding of the reasons for this difference in the behavior of this compound is of interest not only in theoretical but also in practical respects, since it is a very urgent problem in the reduction of RL, as an intermediate in vitamin B_2 synthesis, to replace the mercury cathodes by a solid cathode. On the basis of the realization that the reduction of organic compounds and the cathodic incorporation of alkali metals may be closely interrelated, the effect of RL on the cathodic incorporation of lithium into lead, mercury, and lead–sodium alloy has been examined in [3]. The results of this study showed that RL hinders the cathodic incorporation of lithium and the anodic decomposition of the intermetallic compound. At concentrations above 5 mM, the inhibiting effect of RL was stronger with undeveloped lead and with the lead–lithium intermetallic compound produced electrochemically than with mercury and with thermal lead–sodium alloy.

With the aim of elucidating the reduction mechanism of RL, we examined the possibilities of reaction between the intermetallic compound and water or RL, determined the rate constants of this reaction, and examined the adsorption behavior of RL in aqueous and nonaqueous solutions in the present work. For this purpose we examined the possibility of D-ribose synthesis at electrodes made of thermal lead–sodium alloy.

Anodic chronopotentiograms showing the amounts of alkali metal extracted from lead electrodes in the presence and absence of RL are reported in Fig. 1. The shortening of the anodic arrest seen in the presence of RL indicates that RL reacts with the intermetallic compound obtained in advance at the electrode (Fig. 1, curves 1 and 2). The potential arrest on the anodic chronopotentiograms is shortened even more strongly when not only the anodic but also the cathodic polarization of the lead electrode was conducted in RL-containing solution (Fig. 1, curve 3). The decrease in the amount of lithium being extracted in the last case seems to be due both to chemical reaction of RL with the incorporation products during polarization and to inhibition of the cathodic process [3].

The reaction rate of the Li–Pb intermetallic compound with the solution components was determined by a technique developed previously [4], in which one compares the lengths of the arrests on anodic chronopotentiograms recorded under different conditions: immediately after prior cathodic polarization, or after a time interval during which the electrode remained at open circuit. We thus determined the reaction rates of the intermetallic compound with H_2O and RL at different H_2O and RL concentrations in an 0.5 N $LiClO_4$ solution in propylene carbonate (Fig. 2). By extrapolation of these data we found the rate constants for the reaction of the intermetallic compound with H_2O and RL; these are 0.08 $A \cdot cm/mole$ and 0.004 $A/cm^{1/2}\ mole^{1/2}$, respectively. In calculating the reaction rate of the intermetallic compound with H_2O we considered possible blocking of part of the electrode surface with reaction products.

One knows that RL can be reduced by amalgam. The process is so effective that amalgam reduction is an industrial method for producing D-ribose from RL [5]. Chemical reaction was also detected between RL and the lead–alkali-metal intermetallic compound (Fig. 1); it was of interest, therefore, to find out whether RL can be reduced with such an alloy in the absence of cathodic polarization.

Lead–sodium intermetallic compound was obtained by fusing the metals at 500°C in argon atmosphere. The alloy obtained was kept for prolonged periods of time in the aqueous boric or pyrophosphoric acid solutions with an RL starting concentration of 0.13 M that usually are used in RL reduction at mercury cathodes [1].

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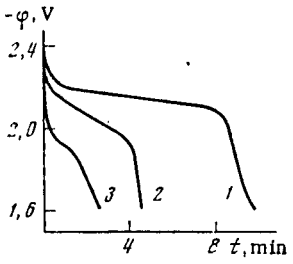

Fig. 1

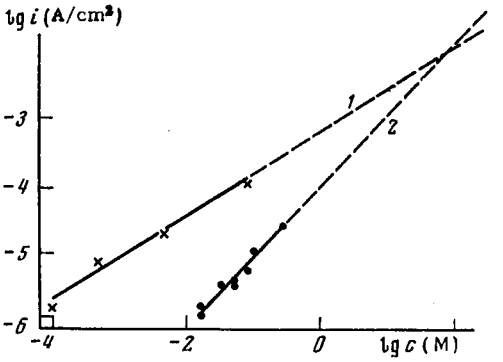

Fig. 2

Fig. 1. Anodic chronopotentiograms in 0.5 N $LiClO_4$ solution in propylene carbonate: 1) base solution; 2) cathodic polarization in the base solution, anodic polarization in the presence of 0.1 M RL; 3) cathodic and anodic polarization in a solution containing 0.1 M RL. Prior cathodic polarization: t = 8 min, $\varphi = -2.4$ V (vs a silver–silver chloride electrode in the same solution). Anodic current density 10^{-4} A/cm^2.

Fig. 2. The reaction rates of the intermetallic compound with RL (1) and with H_2O (2) as functions of concentration.

The solutions were then analyzed for their content of the reduction product, D-ribose. The formation of small quantities of D-ribose (3×10^{-4} mole after 31 h) was observed in both solutions. The data obtained indicate that basically it is possible to reduce RL to D-ribose with the intermetallic compound. The low reaction rate may be due to low activity of the alkali metal in the intermetallic compound at the surface, caused by slow supply of the alkali metal from the bulk of the alloy to the surface. The fact that the cathodic current does not increase when, at constant potential, RL is added to the solution [3] implies that RL is not reduced electrochemically, but that reduction via a secondary mechanism (by reaction with the intermetallic compound) is the only pathway for RL reduction.

From these results, and also from the results of [3], where it had been shown that RL inhibits incorporation of the alkali metal, one can gather that the activity of the electrode is determined by the conditions under which the alkali-metal intermetallic compound is regenerated at the electrode. The similarity in the electrochemical behavior of electrodes consisting of mercury and of lead–sodium alloy gave rise to the expectation that at the alloy electrode, RL reduction will be possible when the intermetallic compound is continuously regenerated electrochemically. This hypothesis was verified experimentally.

The electroreduction of RL at a cathode of lead–sodium alloy was conducted under the optimum conditions established previously for mercury cathodes [1]. The formation of D-ribose was noticed at the alloy electrode, both in aqueous boric acid and aqueous pyrophosphoric acid solution. The amount produced was substantially higher than that obtained at the alloy in the absence of cathodic polarization: 2×10^{-3} mole of D-ribose was obtained after 1.5 h of electrolysis, i.e., the average reduction rate with polarization is two orders of magnitude higher than that at the unpolarized alloy. This is direct proof for the importance of regeneration of the intermetallic compound during RL reduction. A significant fluctuation in the product yield is observed when an alloy electrode is used repeatedly (Fig. 3). The reasons for the unstable behavior of the electrodes in aqueous solutions are not clear as yet, but the results obtained indicate that basically it is possible to reduce RL to D-ribose in aqueous solution at a solid electrode.

The adsorption behavior of RL was examined under different conditions in order to understand the RL reduction mechanism. The adsorption of RL at the lead electrode was studied by measurements of the impedance over a wide range of potentials while polarizing the electrode in aqueous and nonaqueous solutions. The obtained plots of capacitive impedance component against potential are shown in Fig. 4. There is a substantial difference between the adsorption behavior at electrodes in aqueous and propylene carbonate solutions. In aqueous solution, RL has practically no effect on the size of the capacitive impedance component; in the nonaqueous solution, RL decreases this component. Data are available which indicate that RL is not adsorbed on the mercury electrode in aqueous solution [6]. The above difference in the adsorption behavior of RL on the lead electrode in aqueous and nonaqueous solutions can be attributed to a difference in the nature of the electrode surface. In nonaqueous solution, the electrode surface during cathodic polarization is covered with a

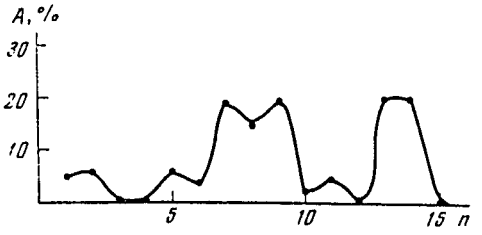

Fig. 3

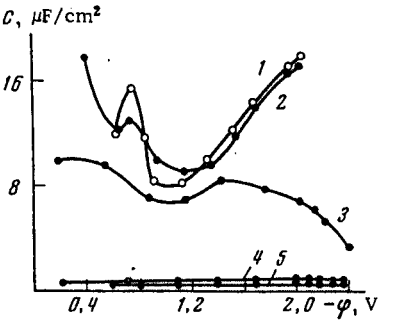

Fig. 4

Fig. 3. The D-ribose yield obtained during RL reduction at a cathode made of $NaPb_3$ produced by fusion of the metals; the electrode was used repeatedly (n is the number of the run).

Fig. 4. Potential dependence of the capacitive impedance component of lead electrodes measured in series substitution at a frequency of 1000 Hz: 1) 1 N aqueous $LiClO_4$ solution; 2) the same solution, with 10^{-3} M RL; 3) 0.5 N $LiClO_4$ solution in propylene carbonate; 4) and 5) the same solution, with 10^{-4} and 10^{-2} M RL.

layer of intermetallic compound or solid solution, even in the presence of RL. In aqueous solution, the intermetallic compound at first accumulates only at structural defects; coating of the entire surface which will give rise to different electrochemical and adsorption properties of the surface only occurs nonuniformly and gradually, since the alkali metal being incorporated is actively interacting with the water [7].

The experimental data obtained show that the cathodic incorporation of alkali metal and the reduction of RL are closely interrelated.

The following conclusions as to the mechanism of RL reduction can be drawn after analysis of these results. The reduction of RL is due to its chemical reaction with the alkali-metal intermetallic compound. Uuually, complete coating of the electrode surface with intermetallic compound is not necessary for a reaction occurring via a secondary mechanism, since the alkali-metal atoms can chemically react with the solution components directly after incorporation, without accumulating at the electrode. But in the case of RL, only those electrodes are suitable for the reduction which have intermetallic compound or solid solution on their surface. Reduction of the lactone in propylene carbonate does not occur when these conditions are not realized, since RL inhibits the regeneration of intermetallic compound; in aqueous solution, the lactone is not reduced owing to the competition of water. The reaction rate constants of the intermetallic compound with RL and with water are little different. Hence during electrolysis in aqueous solution, where the molar concentration of water is substantially higher than that of RL, decomposition of the intermetallic compound being produced should chiefly occur by reaction with water, and only in part by reaction with RL. In nonaqueous solution, the electrode is covered with a layer of intermetallic compound or solid solution. Hence the zero point of such an electrode is displaced toward more negative potentials as compared to lead [7], and RL adsorption becomes possible. This creates the conditions needed for the interaction of RL with the intermetallic compound, and makes it possible that RL is reduced at such an electrode.

Thus, the cathodic incorporation of alkali metal and the reduction of RL are closely interrelated processes. The reduction of RL is brought about by its chemical reaction with the alkali-metal intermetallic compound. The reduction of RL is only possible when alkali metal is incorporated simultaneously into the cathode. The rate of the incorporation step should be higher than the chemical reaction rate of RL with the incorporation product, but RL adsorption should not be so high as to inhibit regeneration of the intermetallic compound.

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ADSORPTION AND DEHALOGENATION OF THE CHLORINE DERIVATIVES OF METHANE AT THE PLATINIZED PLATINUM ELECTRODE

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The method of fast potentiodynamic sweeps had been used previously to show that the adsorption of chlorine derivatives of methane on the smooth platinum electrode is attended by dehalogenation, i.e., rupture of the C–Cl bond. Adsorption by rupture of the C–Cl bond is much easier than adsorption by rupture of the C–H bond, and it occurs more readily the more C–Cl bonds there are in the molecule. Dehalogenation during adsorption is the reason for the potential shift of degassed platinized electrodes which occurs when they are brought in contact with CCl_4 [2, 3].

In the present work, the dehalogenation of chlorine derivatives of methane during adsorption at the platinized platinum electrode was investigated by a combination of the method of nonsteady-state currents and that of fast potentiodynamic sweeps [4]. The coverage of the electrode surface by chemisorbed organic particles in solutions of the chlorine derivatives of methane was determined from the decrease in hydrogen adsorption with the technique of fast sweeps.

One can see from Fig. 1 that the surface coverage of the platinized platinum electrode in solutions of the chlorine derivatives of methane increases linearly with the logarithm of adsorption time, and the adsorption kinetics on the platinized platinum electrode is described by the Roginskii–Zel'dovich equation. The k_{ads} and $\alpha f'$ values for different chlorine derivatives of methane are reported in Table 1.

One can see from Table 1 that the adsorption rate constant increases as one goes from methane to methylene chloride, chloroform, and carbon tetrachloride. The steady-state coverage of the surface with organic particles, i.e., the adsorbability, increases in the same series.

It must be noted that the adsorption rate constants of the chlorine derivatives of methane, like those of a number of other materials [6-9], are about 40 times lower on the platinized platinum electrode than on the smooth platinum electrode [1], even though the steady-state coverages are the same in both cases.

If carbon tetrachloride is added to a solution in contact with a platinized platinum electrode where the potential is potentiostatically maintained at a constant value of $\varphi_r = 0.5$ V, then a large cathodic nonsteady-state current is observed at first (Fig. 2), which gradually falls practically to zero. Neither oxidation nor reduction of carbon tetrachloride is found to occur with noticeable rates at $\varphi_r = 0.5$ V under steady-state conditions; hence the nonsteady-state cathodic current is due to adsorption and dehalogenation of the carbon tetrachloride:

TABLE 1. Values of the Adsorption Parameters for Different Chlorine Derivatives of Methane

Parameters	CH_4	CH_2Cl_2	$CHCl_3$	CCl_4
$k_{ads} \cdot \theta \cdot c^{-1}$ (φ_r=0,5 V)	$5 \cdot 10^{-2}$ [5]	$4 \cdot 10^{-2}$	$8{,}1 \cdot 10^{-1}$	2,3
$\alpha f'$	–	5,1	4,5	3,8
θ_R' (φ_r=0,4 V; $c = 5 \cdot 10^{-3}$ M)	–	0,30	0,50	0,75

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