

Fig. 8. Electrochemical hydrogenation of butyne-1,4-diol in 1 N solutions: 1) sulphuric acid; 2) alkali.

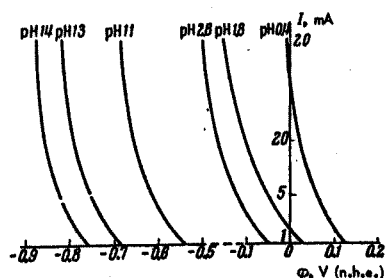


Fig. 9. Variation of the rate of electrochemical hydrogenation of butyne-1,4-diol with the pH.

It is desirable to compare catalytic hydrogenation and electrochemical hydrogenation and to examine each from a number of different points of view, since in both cases we are dealing with an electrochemical system. Workers in both catalysis and electrochemistry will find such an approach useful.

SUMMARY

1. Complete analogy between catalytic hydrogenation and electrochemical hydrogenation of butyne-1,4-diol and its homologues has been demonstrated.
2. At the same potentials the rate of catalytic hydrogenation exceeds that of electrochemical hydrogenation.
3. Hydrogen with low bonding energy is the most active in hydrogenation reactions.
4. The electrochemical reduction of butyne-1,4-diol and its homologues in the range of potentials up to that of the reversible hydrogen electrode takes place by the hydrogen mechanism.

3. A. I. Shlygin, "Trudy Soveshchaniya po Elektrokhemii" (Proceedings of the Electrochemical Conference), Izd. Akad. Nauk SSSR, 1953, p. 322.

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Received 22nd April 1963

U. D. C. 541.124/.128

KINETICS OF THE REDUCTION OF THE PEROXODISULPHATE ANION AT A ROTATING LEAD ELECTRODE

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According to the slow discharge theory, in the absence of specific adsorption on the electrode of the species undergoing reduction and the reaction product, the rate of reaction will be determined solely by the structure of the electrical double layer. When the metal is replaced by one with a more negative zero-charge potential ($\phi_{z.c.p.}$), the ψ_1 -potential (the potential of the diffuse part of the double layer) should become more negative for the same electrode potential ϕ and the electrochemical reduction of anions should be accelerated. This conclusion was confirmed in an investigation of the reduction of anions at a dropping thallium amalgam electrode.¹ However, the acceleration effect is lowered in the case of this electrode both due to the slow variation of the ψ_1 -potential with ϕ in regions far from $\phi_{z.c.p.}$ and to the negative adsorption of thallium on the amalgam surface. In the case of solid electrodes the latter effect is absent and it was therefore of interest to examine for such electrodes the variation of the rate of reduction of anions with the zero-charge point. Studies on lead and cadmium^{2,3}, copper³, and platinum^{3,4} electrodes showed that the potential corresponding to the start of the fall in current along the polarisation curve for the reduction of $S_2O_8^{2-}$ ions varies with the zero-charge point of the metals. Further, in view of the large uncertainty in the current densities due to the fact that the apparent surface varied from experiment to experiment, it was impossible to arrive at a definite conclusion about the variation of the rate of the electrode reaction with the zero-charge point of the electrode. We therefore undertook a more thorough investigation of the cathodic reduction of $S_2O_8^{2-}$ ions at a lead electrode.

Measurements in the range 1400–8000 rev min⁻¹ were made with an apparatus similar to that of Belyanchikov *et al.*,⁵ the sole modification consisting in a rotating mercury seal fixed to the lower part of the electric motor used for the rotation of the electrode, the aim being to render the apparatus more gas-tight. The electrode consisted of a lead rod 5 mm in diameter whose lateral surface was covered with a tight Teflon jacket so that the apparent surface of the electrode was circular in outline and remained constant from experiment to experiment. The electrodes were made from lead whose impurity content was less than 10⁻³% (TUGKKh 1441-60). For each experiment the electrode was washed with twice distilled sulphuric acid, a thin layer of metal was removed from its surface, and it was then polarised at a current of 10⁻⁴ A cm⁻² in a cell with 0.1 N HCl for 3 h in an atmosphere of hydrogen. The state of the

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2. V. M. Tsintsevich, G. P. Khomchenko, and G. D. Vovchenko, Vestnik Moskov. Univ., No. 1 (1963).

electrode surface was checked by measuring the hydrogen overvoltage in 0.1 *N* HCl, our values agreeing satisfactorily with those in the literature.⁶ In order to obtain comparative data on the rate of reduction of $S_2O_8^{2-}$ ions on different types of electrode, we determined i - φ curves for a copper amalgam electrode by the procedure already described.⁷ All the polarisation curves were corrected for the residual current. All the potentials quoted are given in volts relative to the normal calomel electrode.

Investigation of the variation with the rate of rotation of the limiting current for the reduction of $S_2O_8^{2-}$ ions at the lead electrode showed that the diffusion currents agree with those calculated from Levich's formula to within 1-2%, which indicates that the liquid was stirred under laminar conditions and the theory of the disc electrode was applicable to the results obtained.⁸

The polarisation curve for the reduction of 10^{-3} *N* $K_2S_2O_8$ at the lead electrode (Fig. 1, curve 3) shows that the current begins to fall at $\varphi = -1.1$ V, and reaches its minimum value at $\varphi = -1.5$ V. Comparison with the polarisation curve obtained for the copper amalgam electrode in the same solution (Fig. 1, curve 1) shows that the rate of reduction of $S_2O_8^{2-}$ ions is higher at the lead electrode, the acceleration effect depending on φ . The maximum difference in the rates of reduction is observed at potentials close to the zero-charge point of lead; at more negative potentials the difference in current at $\varphi = \text{const}$ diminishes, because of the slow variation of the ψ_1 -potential with φ in regions distant from $\varphi_{z.c.p.}$.

The polarisation measurements at the lead electrode at different rates of rotation can be used to determine the reaction order of the electrochemical reduction of $S_2O_8^{2-}$ ions. For this purpose, the reciprocal of the current density, measured at $\varphi = -1.5$ V in 10^{-3} *N* $K_2S_2O_8$ + 5×10^{-3} *N* KCl solution was plotted against the reciprocal of the square root of the rate of rotation of the electrode. The linear variation of $1/i$ with $1/m^{1/2}$ (m is the rate of rotation) indicated that the reduction of $S_2O_8^{2-}$ ions is a first-order reaction.¹¹ Comparison of data on the effect of electrolyte composition on the rate of reduction at the lead and copper amalgam electrodes showed that, because of the higher rate of reduction at the lead electrode, the retardation of the reaction is removed at lower concentrations of the indifferent

electrolyte. In fact, it is seen from Figs. 1 and 2 that an increase in the concentration of the supporting electrolyte cations results in a faster rate of reduction, complete removal of retardation occurring in 0.1 *N* KCl in the case of the lead electrode, and in 0.5 *N* KCl in the case of the amalgam electrode. It has been shown for dropping mercury⁹ and thallium amalgam¹ electrodes that the effectiveness of the cation increases with its radius. This is also observed in the reduction of $S_2O_8^{2-}$ ions at the lead electrode, as can be clearly seen from Figs. 2 and 4. Fig. 3 shows polarisation curves obtained in the presence of tetraethylammonium (TEA) and tetrabutylammonium (TBA) cations at different concentrations. Like inorganic cations, they remove the retardation of the reaction at the lead electrode at lower concentrations than at the copper amalgam electrode. In contrast to the latter, the polarisation curves for the lead electrode did not show desorption of tetrabutylammonium cations in the potential range investigated.¹⁰ The variation of the rate of reduction of $S_2O_8^{2-}$ ions with the

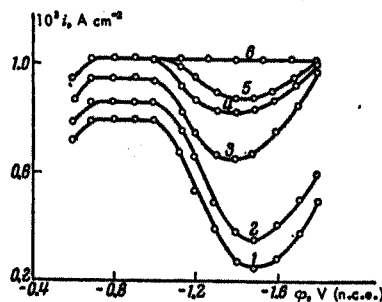


Fig. 2. Polarisation curves for the reduction of 10^{-3} *N* $K_2S_2O_8$ at the rotating lead electrode: 1) without additives; 2) 10^{-3} *N* CsCl; 3) 5×10^{-3} $\times$ *N* KCl; 4) 10^{-2} *N* KCl; 5) 10^{-2} *N* CsCl; 6) 5×10^{-2} *N* CsCl.

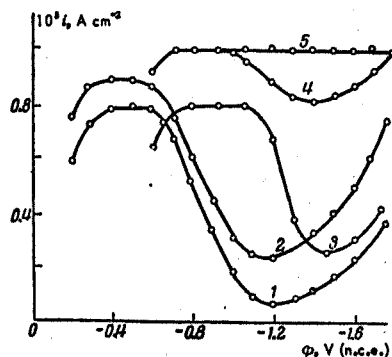


Fig. 1. Polarisation curves for the reduction of 10^{-3} *N* $K_2S_2O_8$ at the rotating copper amalgam electrode: 1) without additives; 2) 10^{-2} *N* KCl; the corresponding curves at a lead electrode: 3) without additives; 4) 10^{-2} *N* KCl; 5) 0.1 *N* KCl.

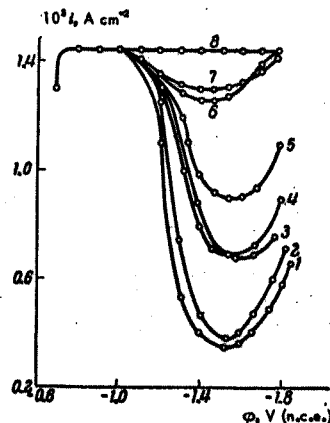


Fig. 3. Polarisation curves for the reduction of 10^{-3} *N* $K_2S_2O_8$ at the rotating lead electrode: 1) without additives; 2) 10^{-6} *N* TEA; 3) 10^{-6} *N* TEA; 4) 5×10^{-6} *N* TBA; 5) 5×10^{-6} *N* TEA; 6) 10^{-4} *N* TEA; 7) 2.5×10^{-6} *N* TBA; 8) 10^{-4} *N* TBA.

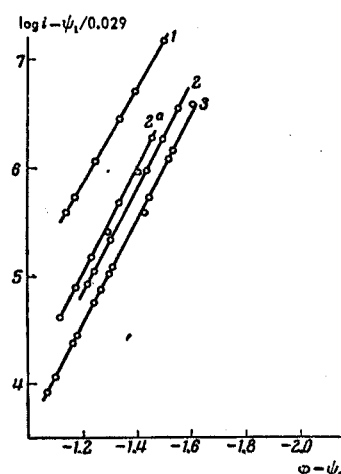


Fig. 4. Corrected Tafel plots for the reduction of 10^{-3} N $K_2S_2O_8$ in the presence of different additives: 1) 5×10^{-3} N CsCl; 2) 5×10^{-3} N KCl; 3) 5×10^{-3} N LiCl (for the lead electrode); 2^a) 5×10^{-3} N KCl (for the copper amalgam electrode).

nature and composition of the solution, which we observed, may be explained on the basis of the slow discharge theory. As shown by Frumkin and Petrii¹³, calculation of the charge of the reacting species from the variation of the rate of reaction with the electrode potential and the concentration of the supporting electrolyte cations can serve as a criterion of the applicability of the slow discharge theory. Our calculation showed that in the case of reduction at the lead electrode the charge of the reacting species $n \approx -2$, which agrees with data for the mercury electrode.¹³ According to the slow discharge theory, in the absence of specific adsorption on the electrode of both the reacting species and the reaction products, the variation of the reaction rate with the potential plotted as $(\log i - \psi_1/0.029)$ against $(\phi - \psi_1)$ (i is the experimental current corrected for the concentration polarisation) should be the same for electrodes of different metals, as already demonstrated for the mercury and thallium amalgam electrodes.¹ The data in Fig. 4 provide a good illustration of this finding for the lead and the amalgam electrodes (the difference in the straight lines 2 and 2^a is 2–5%)†. The transfer coefficient α calculated from these data proved to be approximately 0.3 for both electrodes, in good agreement with the data for the dropping mercury electrode.¹²

We are glad to take this opportunity to acknowledge our great indebtedness to Academician A. N. Frumkin for discussion of the present results.

† In the literature there are no reliable data on the variation of the differential capacitance with the potential for the zinc electrode, and therefore in calculating the ψ_1 -potentials it was assumed that, for the same values of ϕ_a (the potential reckoned from the zero-charge point), the charges of the mercury and lead electrodes are the same. The zero-charge potential of the lead electrode was taken to be -0.96 V.

SUMMARY

1. A study has been made of the reduction of $S_2O_8^{2-}$ ions at a rotating lead electrode in the presence of different supporting electrolyte cations. According to the slow discharge theory, the rate of reduction at a lead electrode should be higher than at an amalgamated copper electrode.
2. The experimental data for the lead electrode have been compared quantitatively with the predictions of the slow discharge theory.

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Received 3rd May 1963

U. D. C. 541.11

THE SECOND VIRIAL COEFFICIENT OF VAPOURS AND THEIR MIXTURES. IV. ACETONEBENZENE SYSTEM

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Since there are no data on the second virial coefficients for the acetone-benzene system, it was of interest to fill this gap by continuation of previous work¹⁻⁴. These data are necessary for further analysis of the system from the

† E. Ya. Gorodinskaya participated in the experimental work.