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On Inhibition of Polarographic Reduction of the Dioxalatocuprate(II) Ion by the One-Electron Reduction Product of Phenylmercury Hydroxide

Teisuke MURAYAMA and Akio TAKAYANAGI

Department of Industrial Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu

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Organomercury salts are reduced at a dropping mercury electrode in double one-electron steps. Benesch and Benesch observed that the first wave of phenylmercury hydroxide has severe irregularities on the diffusion current plateau.[1] They considered that this is due to the coating of the electrode caused by an insoluble product. They also showed that the polarographic reduction of Cd^{2+} and Pb^{2+} ions is inhibited in the range of potentials between the end of the first and the beginning of the second waves of phenylmercury hydroxide. We studied inhibition of the polarographic reduction of the dioxalatocuprate(II) ion in oxalate buffer solutions.

Experimental

The phenylmercury hydroxide was made from phenylmercury acetate (Shudzui, Tokyo) and sodium hydroxide,[2] and recrystallized from water: mp with decomposition 226—230°C (lit.[3] 226—233°C). The stock solution of phenylmercury hydroxide was prepared by dissolving a weighed amount.

The concentration of the copper sulfate was determined by means of complexometric titration.[4]

The oxalate buffer solution of pH 4.08 was prepared from guaranteed reagents.

The test solution was prepared by mixing stock solutions of phenylmercury hydroxide, oxalate buffer, copper sulfate, and sodium nitrate, and diluting it to the desired volume. Sodium nitrate was added to control the ionic strength of the test solution to 0.35. Five one-thousandths of 1% gelatin was also added as a maximun suppressor.

All solutions were prepared with redistilled water.

Test solutions were degassed with nitrogen and thermostated at 25.0±0.1°C.

The dropping mercury electrode had the following characteristics (in 0.3M KNO_3 at zero applied potential *vs.* SCE). Rate of flow of mercury, 1.978 mg/sec; drop time, 4.13 sec. The cell and the salt bridge were described elsewhere.[5] Polarograms were recorded with a Yanagimoto PA-102 polarograph. Current-time curves were recorded by a Mini Writer-H (Watanabe Instruments Co.) in terms of a potential drop across a resistor inserted in series with the cell circuit.

Results and Discussion

Polarograms of the dioxalatocuprate(II) ion (I) are shown in Fig. 1. They are corrected for the current due to the reduction of phenylmercury hydroxide (II) and for the residual current. In the presence of II the single step reduction of I splits into two waves.

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[1] R. Benesch and R. E. Benesch, *J. Amer. Chem. Soc.*, **73**, 3391 (1951); R. E. Benesch and R. Benesch, *J. Phys. Chem.*, **56**, 648 (1952).

[2] L. G. Makarova and A. N. Nesmeyanov, "Methods of Elemento-Organic Chemistry," Vol. IV, North-Holland Publishing Co., Amsterdam (1967), p. 420.

[3] L. R. Barlow and J. M. Davidson, *J. Chem. Soc., A*, **1968**, 1613.

[4] G. Schwarzenbach, "Complexometric Titrations," Methuen & Co., London (1957), p. 82.

[5] T. Murayama, T. Sawaki, and S. Sakuraba, This Bulletin, **43**, 2820 (1970).

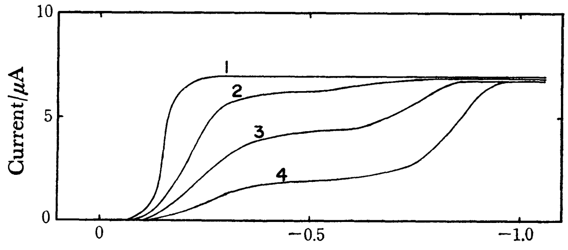

Fig. 1. Polarograms of I in the presence of II. Concentration of I, 0.934 mM. Concentration of II: 1, 0 mM; 2, 0.123 mM; 3, 0.198 mM; 4, 0.297 mM.

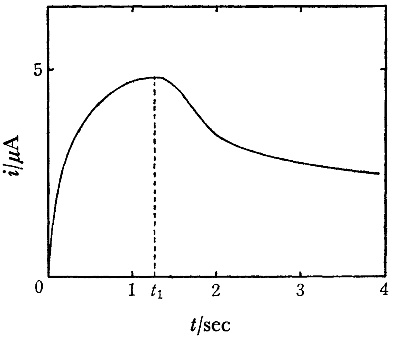

Fig. 2. Current-time curve for the reduction of I in the presence of II at a potential of −0.50 V *vs.* SCE. Concentration of I, 0.934 mM; concentration of II, 0.198 mM.

The potential of the second wave coincides with that of the second step of II, which shifts to negative potentials with increasing concentration of II. Current-time curves were recorded at a potential of −0.50 V *vs.* SCE, which lies in the limiting current region of the first wave of I. A current-time curve is shown in Fig. 2, where the current is corrected for that due to the reduction of II and the residual current. The current reaches a maximum at t_1 and then decreases. This is caused by the reduction product of II, adsorbed as soon as it was formed. If Q is the quantity of electricity consumed for the reduction of II until t_1, the quantity $Q/t_1^{2/3}$ is proportional to the fraction of the electrode surface covered by the reduction product of II. Figure 3 shows the relation between $Q/t_1^{2/3}$ and $\log t_1$. Since t_1 increases tenfold, it is surprising that there is a linear relationship between these two quantities.

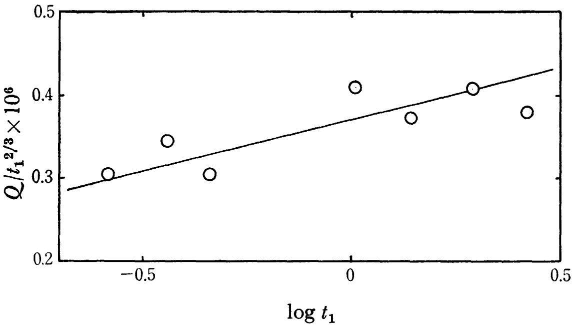

Fig. 3. Relation of $Q/t_1^{2/3}$ *vs.* $\log t_1$.

This relationship may be explained as follows. The current which flows at the electrode surface is a function of the concentration gradient of I and the surface area of the electrode. At around t_1 the fraction Θ of the electrode surface covered by the reduction product of II increases so rapidly that the concentration gradient decreases very slowly. Thus the change of the surface area gives rise to a larger effect on the current than the change of the concentration gradient does. Under these circumstances one may assume that the concentration gradient is constant at around t_1. Hence, the increase of Θ is equal to the increase of the electrode surface divided by the total surface area of the electrode dq/q at t_1, where $di/dt=0$. Thus

$$d\Theta = \frac{dq}{q} \tag{1}$$

at t_1. Integrating Eq. (1), one has

$$\Theta = \ln q + b \tag{2}$$

where b is a constant. The surface fraction Θ is related to Q by the following equations.

$$\Theta = \frac{\Gamma}{\Gamma_\mathrm{m}} \tag{3}$$

$$\Gamma = \frac{Q/F}{q} \tag{4}$$

where Γ is the surface concentration of the reduction product of II at t_1, Γ_m the maximum surface concentration in a monolayer of the product, and F Faraday. By introducing Eqs. (3) and (4) and the relation $q=0.00852(mt_1)^{2/3}$ into Eq. (2), and rearranging, one obtains

$$Q/t_1^{2/3} = 0.0131F\Gamma_\mathrm{m}m^{2/3}\log t_1 + b' \tag{5}$$

where m is the rate of flow of mercury in mg/sec, and b' a constant. Equation (5) shows that $Q/t_1^{2/3}$ is a linear function of $\log t_1$, in agreement with results given in Fig. 3.

From the slope of the straight line in Fig. 3 and Eq. (5), $1/\Gamma_\mathrm{m}$ was calculated to be 291 Å^2/molecule. It seems to be too large compared with a value of 60 Å^2/molecule which was estimated from a molecular model. This is not the case, however. Inhibition occurs not only at the surface covered by adsorbed molecules, but also at narrow strips which encircle islets of adsorbed molecules with a width equal to the radius of the ion of I. In addition, hydration increases the apparent ionic size of I. If these facts are taken into consideration, $1/\Gamma_\mathrm{m}$ might be several times as large as the area of cross section of the molecule. Thus Γ_m should be redefined as the minimum surface concentration to inhibit the electrode reaction completely.