

STUDY OF THE KINETICS OF ELECTRODE PROCESSES  
 BY MEANS OF ELECTROLYSIS WITH CONSTANT CURRENT. XIX.\*  
 COMPARISON OF PRECEDING AND SUCCEEDING  
 FIRST-ORDER REACTIONS

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Single-impulse and double-impulse galvanostatic methods with current reversal were used in studying the reaction  $[\text{Co en}_2]^{2+} + \text{en} \rightleftharpoons [\text{Co en}_3]^{2+}$ , which was assumed either to precede the oxidation of  $[\text{Co en}_3]^{2+}$  or to follow the reduction of  $[\text{Co en}_3]^{3+}$ .

The galvanostatic single-impulse and double-impulse methods with current reversal enable to study a particular chemical reaction in both cases, either as preceding or as succeeding the electrode process proper. A suitable change of the reaction sequence makes it possible to eliminate in certain cases the distortion of results due to adsorption of one form of the redox system on the electrode. Up to now studies of this kind have not appeared.

A suitable system that can be studied on a mercury electrode is  $[\text{Co en}_3]^{3+}/[\text{Co en}_3]^{2+}$ , for which a kinetic character of the polarographic oxidation wave of Co(II) at a low concentration of ethylenediamine was proved<sup>1</sup>. The electrode process proper is rather rapid<sup>2</sup> (roughly 0.01 to 0.1 cm/s). Near to the redox potential of the mentioned system, the complexes with a smaller number of ligands are electroinactive<sup>1,3</sup>. The  $[\text{Co en}_3]^{3+}$  complex in the presence of  $\text{Cl}^-$  ions in solution is adsorbed on the mercury electrode<sup>4</sup> (about  $10^{-11}$  mol/cm<sup>2</sup>).

### EXPERIMENTAL

The galvanostatic pulse generator and the electrolytic vessel were described previously<sup>5</sup>. The surface area of the indicator electrode was 2.73 cm<sup>2</sup>, the volume of the electrolyzed solution 150 ml. The solution was deaerated with nitrogen purified with activated copper at 150°C and a Cr(II) solution. The  $[\text{Co en}_x]^{2+}$  complexes were prepared directly in the electrolytic vessel by adding crystalline  $\text{CoCl}_2$  to a deaerated ethylenediamine solution. The complex  $[\text{Co en}_3]^{3+}$  was prepared according to Fernelius<sup>6</sup>, mercury and water were redistilled. The temperature of the electrolyzed solution was kept at  $20 \pm 0.2^\circ\text{C}$  by a thermostat.

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## RESULTS AND DISCUSSION

At high concentrations of free ethylenediamine (about 100 times the depolarizer concentration) in 1M-NaClO<sub>4</sub> the product  $i\tau^{1/2}$  is constant in a broad range of  $\tau$  values from 0.02 to 10 s both in the reduction of  $[\text{Co en}_3]^{3+}$  and in the oxidation of Co(II). If the current is reversed, the ratio of the time  $t_1$  before reversal and the transition time  $\tau'$  after reversal corresponds to the equations for diffusion-controlled processes<sup>7,8</sup>. Hence, the electrode process in this case is not complicated by chemical reactions or adsorption in accord with other authors<sup>1,4</sup>. The diffusion coefficients of  $[\text{Co en}_3]^{3+}$  and  $[\text{Co en}_3]^{2+}$  were found to be  $5.50 \cdot 10^{-6}$  and  $5.73 \cdot 10^{-6}$  cm<sup>2</sup>/s, respectively, at 20°C and at unit ionic strength. With transition times shorter than 1 s a correction for the charging current<sup>7</sup> was applied.

At a low, constant concentration of free ethylenediamine (about  $10^{-5}$ M) the reversible first-order reaction.

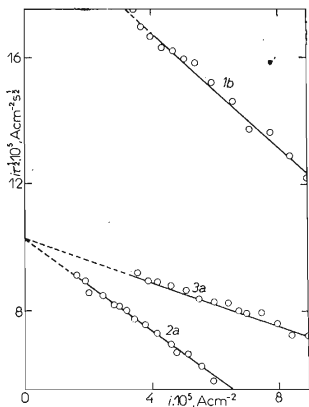


FIG. 1

Dependence of  $i\sqrt{\tau}$  on Current Density  $i$  for Galvanostatic Oxidation of Co(II)

Conc. of Co(II): a 0.50 mM; b 1.00 mM; conc. of free ethylenediamine ( $[\text{en}] \cdot 10^5$ M): 1 1.00; 2 1.38; 3 2.61. The points represent always a set of measurements, lines correspond to parameters obtained by the least squares method from 2–4 sets.

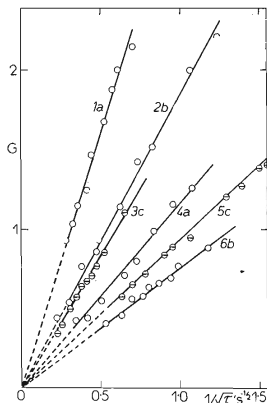
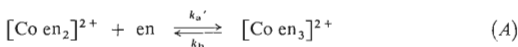


FIG. 2

Dependence of G Function, Eq. (2), on  $1/\sqrt{\tau'}$  for Reduction of  $[\text{Co en}_3]^{3+}$  with Current Reversal

Conc. of the complex: a 0.41 mM; b 0.82 mM c 1.64 mM. Conc. of free ethylenediamine ( $[\text{en}] \cdot 10^6$ M): 1 3.7; 2 4.9; 3 6.0; 4 8.2; 5 12.0; 6 12.2.



preceding the oxidation of Co(II) was studied. Its equilibrium constant  $K_3$  is equal to  $k_a'/k_b = k_a/k_b[\text{en}] = K/[\text{en}]$ . The product  $K\sqrt{k}$ , where  $k = k_a + k_b$ , can be determined from the slope of the dependence of  $i\sqrt{\tau}$  on  $i$  according to the equation<sup>9</sup>

$$i\sqrt{\tau} = \frac{1}{2}nF c_R^0 \sqrt{(\pi D)} - i\sqrt{(\pi)/2K}\sqrt{k} \quad (1)$$

valid for  $\sqrt{(k\tau)} > 2.4$ .

The low concentration of ethylenediamine was maintained by a relatively low pH (about 7), its analytical concentration being 0.1M in the form of perchlorate. The equilibrium concentration of free ethylenediamine was calculated from its  $pK$  values determined titrimetrically in 1M-NaClO<sub>4</sub> at 20°C:  $pK_1 = 7.48 \pm 0.02$  and  $pK_2 = 10.27 \pm 0.03$ , which are close to those found<sup>10</sup> at a ionic strength of 3M. The buffering capacity was ensured by the en H<sup>+</sup> ions prevailing in the solution at pH close to 7. The presence of 0.05M phosphate buffer did not influence the results provided that the ionic strength was kept at 1M.

The linear dependences of  $i\sqrt{\tau}$  on  $i$  for oxidation of Co(II) (Fig. 1) correspond to Eq. (1) and reaction (A). Extrapolated value for  $i \rightarrow 0$  is in accord with the mentioned diffusion coefficient of the Co(II) complex within the range of experimental accuracy. The negative values of the slope are inversely proportional to the calculated concentrations of free ethylenediamine so that the term  $K_3\sqrt{k}$  is constant and its mean value is  $(9.4 \pm 0.2) \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1/2}$ .

In similar solutions, the reaction (A) was studied as succeeding after the reduction of  $[\text{Co en}_3]^{3+}$  with the use of current reversal after the time interval  $t_1$ . The ratio of currents before and after reversal is denoted as  $i/j = u$ . The  $K\sqrt{k}$  was found from the dependence of the function  $G$  on transition time  $\tau'$  after reversal according to the equation<sup>11</sup>

$$G = u^{-1}(1 + t_1/\tau')^{1/2} - 1 = \sqrt{(\pi)/2K}\sqrt{(k\tau')} \quad (2)$$

valid again for  $\sqrt{(k\tau')} > 2.4$ . The direct proportionality between  $G$  and  $1/\sqrt{\tau'}$  was proved (Fig. 2) as well as the indirect proportionality between the slopes of these straight lines (obtained by the least squares method) and the concentration of ethylenediamine. The mean value of  $K_3\sqrt{k} = (9.0 \pm 0.3) \cdot 10^4 \text{ l mol}^{-1} \text{ s}^{-1/2}$  was calculated from ten such dependences. Hence, the results of both methods are practically the same. The single-impulse method operating with two variables ( $i$  and  $\tau$ ) is supposed to be somewhat more precise than the method of current reversal operating with four experimental variables at constant composition of the solution. This assumption could be checked of course only on a larger ensemble of measured systems.

The value of  $K_3 = (1.42 \pm 0.28) \cdot 10^3 \text{ l/mol}$  (in 1M-NaClO<sub>4</sub> at 20°C) was determined in the same way as in ref.<sup>10</sup> This shows that with the low equilibrium concentration of free ethylene-

diamine of  $3 \cdot 10^{-6} - 2.6 \cdot 10^{-5} M$ , the value of  $K$  is much smaller than 1 so that  $k_a \ll k_b$  and  $k \approx k_b$ . From the mean value of  $K_3 \sqrt{k_b}$  it follows that  $k_b = 4.2 \cdot 10^3 s^{-1}$ . The inequalities conditioning the validity of eqs (1) and (2) are fulfilled with all experiments (with respect to the value of  $k_c$ ). Similar values follow from polarographic measurements. The smaller value of the rate constant as compared with ref.<sup>1</sup> is due apparently to a lower ionic strength.

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