STUDY OF THE KINETICS OF ELECTRODE PROCESSES BY MEANS OF ELECTROLYSIS WITH CONSTANT CURRENT. XVII.*

DEPOLARIZER DEACTIVATION BY A SUBSTANCE FORMED BY CHEMICAL CHANGES OF THE ELECTRODE PRODUCT

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A theoretical solution has been derived for the case when the product of galvanostatic reduction is chemically changed by a pseudo-first order homogeneous chemical reaction to give a substance which reacts rapidly with the depolarizer, changing it to an electro-inactive substance. The rate constant of the change of the electrode product can be determined from the slope of the linear dependence of the $i\tau^{1/2}$ value on $i\tau^{3/2}$. The theory was applied to the reduction of the hexamochromium (III) complex in a solution containing a small but constant excess of free cyanide. The rate determining step is the incorporation of the first CN^- group into the co-ordination sphere, the appropriate second-order rate constant being $2250\ 1\ mol^{-1}\ s^{-1}$, at 25°C.

In work dealing with the polarographic reduction of the hexamochromium(III) ion in a cyanide medium[1], it was found that the deactivation of this depolarizer takes place by catalytic action of the adsorbed depolarization product. The deviations from the theoretical course of instantaneous currents during the first stages of the drop growth led to the idea that, in addition to the described mechanism, another depolarizer deactivation process occurs, which does not require the adsorption of the product. Thus galvanostatic study of this system within the range of short transition times, where this deactivation process may play a decisive role, became the topic of the present work.

THEORETICAL

Let us assume that, in constant current electrolysis, the series of reactions proceeds according to the following general scheme

$$O \xrightarrow{e1} R \,,$$

$$R + yY \xrightarrow{k_1} RY_y \,, \quad (A), \quad RY_y + O \xrightarrow{k_2} OY_y + R \,, \quad (B)$$

Let us assume further that reaction (B) is very fast compared to reaction (A) so that reaction (A) is rate-determining, that substance Y is present in a large excess, and that substance OY_y is electro-inactive. In such a case, the problem can be described by equations

$$(\partial C_0/\partial t) = D_0(\partial^2 C_0/\partial x^2) - kC_R ,\tag{1a}$$

$$(\partial C_R/\partial t) = D_R(\partial^2 C_R/\partial x^2) ,\tag{1b}$$

$$\left.\begin{array}{l} t = 0, \quad x \geqq 0 \\ x \to \infty, t \geqq 0 \end{array}\right\} : C_0 \to C_0^* ; \ C_R \to 0 ,\tag{2a}$$

$$x = 0, \quad t > 0 \quad : \ D_0(\partial C_0/\partial x) = -D_R(\partial C_R/\partial x) = i/nF ,\tag{2b}$$

where

$$k = k_1 . C_Y^y .\tag{3}$$

For the characteristics of the Laplace transformation, $\overline{C}_R$, with respect to t, we obtain in the usual way, from equations $(1b)$ and (2)

$$\overline{C}_R = [i/nFp \sqrt{(pD_R)}] \exp[-x \sqrt{(p/D_R)}] ,\tag{4}$$

where p is the transformation variable. Further we can introduce

$$\psi = C_0 - C_0^* .\tag{5}$$

After the Laplace transformation, we obtain from equations $(1a)$ and $(2a)$, using equation (4),

$$p\overline{\psi} = D_0(\partial^2\overline{\psi}/\partial x^2) - [ki/nFp \sqrt{(pD_R)}] \exp[-x \sqrt{(p/D_R)}] .\tag{6}$$

The solution of equation (6) can be written in the form of a sum of the general solution of the homogeneous equation and of the partial solution of the non-homogeneous equation, in the form

$$\overline{\psi} = M \exp[-x \sqrt{(p/D_0)}] + N \exp[x \sqrt{(p/D_0)}] + \tag{7}$$

$$+ [\tfrac{1}{2}/\sqrt{(pD_0)}] . [ki/nFp \sqrt{(pD_R)}] \left\{ \exp[x \sqrt{(p/D_0)}] \int_0^x \exp[-\xi \sqrt{(p/D_0)}] \exp[-\xi \sqrt{(p/D_R)}] d\xi - \right.$$

$$\left. - \exp[-x \sqrt{(p/D_0)}] \int_0^x \exp[\xi \sqrt{(p/D_0)}] \exp[-\xi \sqrt{(p/D_R)}] d\xi \right\} .$$

After computing the given integrals and enumerating the integration constants M and N using conditions (2), we finally arrive at the relation

$$(\overline{\psi})_{x=0} = -(i/nFp \sqrt{(pD_0)}) - \{2ki/nFp^2 \sqrt{(pD_R)}[1 + \sqrt{(D_0/D_R)}]\}\tag{8}$$

which, after inverse transformation and application of relation (5), yields

$$(C_0)_{x=0} = C_0^* - (2i \sqrt{t})/nF \sqrt{(\pi D_0)} - 8kit^{3/2}/3nF \sqrt{(\pi D_R)[1 + \sqrt{(D_0/D_R)}]} .\tag{9}$$

From relation (9) we obtain, for transition time τ, the following relation

$$i\tau^{1/2} = (1/2) \, nFC_0^* \sqrt{(\pi D_0)} - \{4k/3[1 + \sqrt{(D_R/D_0)}]\}i\tau^{3/2} . \qquad (10)$$

For the case being solved, the $i\tau^{1/2}$ vs $i\tau^{3/2}$ dependence is a straight line of negative slope, from which the rate constant k, can be determined, if the D_R/D_0 ratio is known. In our concrete case it is assumed that, in the general scheme, substance O is $Cr(NH_3)_6^{3+}$, substance R is $Cr(NH_3)_6^{2+}$, and substance Y is CN^-.

EXPERIMENTAL

Constant current electrolysis was carried out with the previously described apparatus[2]. Hexamochromium(II) nitrate was obtained from Professor Heine's laboratory in Jena (GDR). The substance purity was checked spectrophotometrically[3]. Other chemicals were of p.a. purity; mercury and water were redistilled.

To suppress the spontaneous conversion of chromium amocomplexes to cyanocomplexes, fresh solutions were always used and experiments with them were carried out within one hour after mixing the components. In addition to the base electrolyte ($0.5\text{M-Na}_2\text{SO}_4$), the tetracyanonickel(II) complex was present in 0.05M concentration in the solution. Regarding the high stability constant[4] ($K_4 = 10^{22}$) it practically does not contribute to the amount of free cyanide in the solution. On the contrary, after addition of NaCN it forms a higher complex, $Ni(CN)_5^{4-}$, with a stability constant[5] of $2 . 10^3$. By this means a relatively low but constant excess of free CN^- ions in the solution and at the electrode is secured. The relatively low stability constant value suggests a mobile equilibrium and a sufficiently fast dissociation of the complex. This was also confirmed by preliminary experiments with various amounts of tetracyanonickel(II) ions. The determined rate constant, k_1, was independent of its concentration. If this complex is used, nickel, which is discharged at substantially more negative potentials, does not interfere in determination of the transition times of the hexamochromium(III) ion reduction.

RESULTS AND DISCUSSION

The concentration of the chromium complex in solutions was varied from $5.5 . 10^{-4}\text{M}$ to $1.3 . 10^{-3}\text{M}$, and the concentration of NaCN added from 0.01 to 0.04M. Transition times were well defined and reproducible within the range, $5 . 10^{-3}\text{s}-1\,\text{s}$. Corrections for the capacity current component were carried out according to the method proposed earlier[6]; it was found that, at transition times smaller than 10^{-2}s, the results are subject to too large errors and for this reason they were not included in further treatment.

Within the transition time range, $0.01\,\text{s} - 0.2\,\text{s}$, it was possible to find, in the treatment of the results of all solutions, a region within which the $i\tau^{1/2}$ values linearly decreased with increasing values of the $i\tau^{3/2}$ product. Moreover, in agreement with relation (10), extrapolated values $\lim_{\tau \to 0} i\tau^{1/2} = (i\tau^{1/2})_{\text{dif}}$ were proportional to depolarizer concentrations (Table I) and, within experimental error, equal to average $i\tau^{1/2}$ values, found in the same solutions in the absence on cyanides. The average diffusion coefficient of the hexamochromium complex, obtained from these values, is

$(5{\cdot}52 \pm 0{\cdot}09) \cdot 10^{-6} \ \text{cm}^2 \ \text{s}^{-1}$. The linear descent region (the transition time range) increased with increasing depolarizer concentration, and also somewhat with increasing free cyanide concentration. The lower limit was roughly at the values $1/2(i\tau^{1/2})_{\text{dif}}$. The transition time range, $0{\cdot}01 \ \text{s}-0{\cdot}05 \ \text{s}$ is shown for all the test solutions in Fig. 1. The straight lines have the same slope for all solutions with the same free cyanide concentration, the negative slope value increases linearly with the free cyanide concentration. This means, in agreement with equations (3) and (10), that incorporation of the first CN^- group into the co-ordination sphere $(y = 1)$ is the decisive step. For this reason, a not too large excess of cyanide in some solutions does not interfere. Since experimental points obey equation (10), it may be assumed that the above reaction scheme is valid for the system studied. Apparently, the inequality, $k_2 \gg k_1$ is also fulfilled. If reaction (B) became rate determining, the dependence on the cyanide concentration would be hard to explain and the experimental values would have to obey the linear dependence of $i\tau^{1/2}$ on $i^{2/3}$, according to[7]. As follows from Table I, the average value of the second-order rate constant for reaction (A) is $2250 \pm 10 \ \text{l} \ \text{mol}^{-1} \ \text{s}^{-1}$ at 25°C, at an ionic strength of approx. 3·3 and under the assumption that $D_R = D_0$.

The linear descent region on the $i\tau^{1/2}$ vs $i\tau^{3/2}$ dependence is followed by a curved part with a decreasing negative slope. Apparently this is a case of mixed kinetics, since an attempt to attribute the results to some known mechanism was unsuccessful. If the results of the work[1] are taken into consideration, an acceptable explanation is that the deactivating effect of the adsorbed depolarization product plays a greater role in later stages of the electrolysis. Since this is not an immediate electrode product (it is formed only by a following chemical conversion), its formation requires a certain time and it does not interfere at transition times lower than 0·2 s. Several times recently we have dealt with the deactivation of a depolarizer by an electrode reaction product.
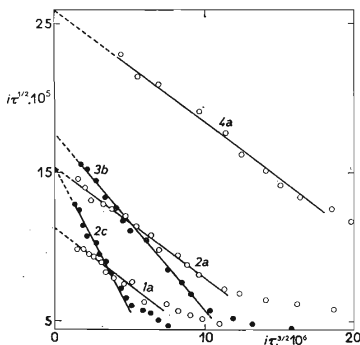

Fig. 1

The Dependence of $i\tau^{1/2}$ Values on $i\tau^{3/2}$ in the Galvanostatic Reduction of the $Cr(NH_3)_6^{3+}$ Complex in a Solution of $0{\cdot}5\text{M-Na}_2SO_4$ and $0{\cdot}05\text{M-K}_2Ni(CN)_4$ at 25°C

Cr(III) conc.: *1* 0·55 mM; *2* 0·75 mM; *3* 0·90 mM; *4* 1·30 mM; conc. of NaCN added: *a* 10 mM; *b* 20 mM; *c* 40 mM.

TABLE I

The Rate of Deactivation of $Cr(NH_3)^{2+}$ in the Galvanostatic Reduction of $Cr(NH_3)_6^{3+}$ in a CN^- Medium at 25°C

C_0^* mM	C_Y^*(free) mM	$(i\tau^{1/2})_{dif}/C_0^*$ A cm s$^{1/2}$ mol^{-1}	$d(i\tau^{1/2})/d(i\tau^{3/2})$ s^{-1}	k s^{-1}	$k_1 \cdot 10^{-3}$ l m^{-1} s^{-1}
0·55	5·1	204	7·8	11·7	2·29
0·75	5·1	203	7·6	11·4	2·24
0·75	13·5	205	19·6	29·4	2·18
0·90	7·9	196	12·0	18·0	2·28
1·30	5·1	199	7·7	11·5	2·26

While in the paper[7], immediate depolarizer deactivation by an electrode product occurred, in the present work a relatively slow (rate-determining) chemical change of the depolarizer precedes the deactivating step proper in the mechanism. The chemically related system studied in the paper[2] (a chemical change of Cr(II) complexes in the vicinity of the electrode also occurs) is different in that the product determining the rate of the chemical reaction is oxidizable at the potentials of the depolarizer reduction. Qualitatively, the effect of intermediate reactions on transition times in the paper[2] and that in the present paper are analogous (shortening of τ with decreasing current density compared to τ_{dif}. — for a purely diffusion controlled process). The different mechanism, however, leads to different functional dependences so that the two cases can be distinguished.

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