ECE MECHANISM IN CURRENT REVERSAL METHOD*

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The case of a first-order chemical reaction interposed between two electrode reactions (ECE mechanism) was solved for the method of current reversal provided that the potential for the second electrode reaction precedes that for the first one. The theoretical dependence of the transition time after current reversal, τ', on the time of current reversal, t_1, passes through a maximum. The possibility of the determination of chemical reaction rate constants and of the ratio of the numbers of electrons in both electrode reactions from experimental results is discussed and the necessary theoretical relations are presented in diagrams and tables.

If the electrode process proper involves more than one electron, it can proceed in more than one step, and chemical reactions can be inserted between certain consecutive steps. The most simple case of this kind is that of two electrode reactions with one chemical reaction in between, which is usually of first order. The latter can either change the intermediate product of the two electrode reactions to an electroinactive compound or change the product of the first electrode reaction to a starting substance of the second. For electrolysis with constant current, the first case was solved in the one paper of this series[1] and the second was solved by Testa and Reinmuth[2]. The latter case is often denoted briefly as ECE mechanism. Two variants of this mechanism can be distinguished according to the potentials of both electrode reactions. If the potential of the first electrode reaction "precedes" that of the second (*i.e.* for oxidation it is more negative, for reduction more positive), an E-t curve with two steps is formed, where the first step corresponds to an electrode process with a follow-up chemical reaction. In the opposite case, only one step is formed on the E-t curve, which is kinetic in character and its distinguishing from the case of a preceding chemical reaction is very difficult[2,3].

The ECE mechanism should be recognizable if the method of a constant current reversal is used which has been introduced for studying follow-up chemical reactions[4]. If the current is reversed during the first step, then with the first variant of the ECE mechanism the results obtained correspond to a solved case of follow-up chemical reaction[4]. The case of the second variant was treated by Herman and Bard[5]. However, from their limited results no conclusion can be drawn for distinction of this mechanism from others and for the possibility of determination of all parameters from the experimental results. The analysis of this case is therefore given in the present

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[*] Part XX in the series Study of the Kinetics of Electrode Processes by Means of Electrolysis with Constant Current; Part XIX: This Journal *38*, 1907 (1973).

paper with the main aim to enable classification of electrode processes by the current reversal method.

Formulation and Solution of the Problem

We assume that the electrode process proceeds prior to the reversion of a constant current according to scheme

$$t < t_1 : \quad \mathrm{O} \xrightarrow{\pm n_1 e} \mathrm{P} \underset{k_a}{\overset{k_b}{\rightleftarrows}} \mathrm{Q} \xrightarrow{\pm n_2 e} \mathrm{R} .$$

The chemical reaction with rate constants k_a and k_b is homogeneous, for the electrode processes either the upper or the lower signs are simultaneously valid, and the equilibrium potential of the system Q/R is so shifted against the equilibrium potential of the system O/P that the concentration of Q at the electrode surface is practically equal to zero during the whole process. After current reversal at time t_1 the following reaction scheme applies:

$$t > t_1 : \quad \mathrm{O} \xleftarrow{\mp n_1 e} \mathrm{P} \underset{k_a}{\overset{k_b}{\rightleftarrows}} \mathrm{Q} \xrightarrow{\pm n_2 e} \mathrm{R} .$$

With respect to the assumed difference in the equilibrium potentials of the systems O/P and Q/R, an step on the E–t curve after the current reversal appears the end of which indicates exhaustion of the substance P at the electrode surface. This step corresponds to the first transition time, τ', after the current reversal measured from the time t_1 as origin. The derivation of differential equations describing the mentioned processes and their solution can be performed analogously as in ref.[4]; the retransformation of certain transforms occurring in the solution is described in ref.[2].

RESULTS AND DISCUSSION

The relation for the first transition time, τ', after the current reversal is obtained in the implicit form

$$\begin{aligned} &\operatorname{erf}\,[k(t_1 + \tau')]^{1/2} + \varrho(1 - \varrho^2)^{-1/2} \{Z[k(t_1 + \tau')/(1 - \varrho^2)]^{1/2} + \\ &+ \mathrm{e}^{-k(t_1+\tau')} Z[\varrho^2 k(t_1 + \tau')/(1 - \varrho^2)]^{1/2}\} = (u + 1) \{\operatorname{erf}\,(k\tau')^{1/2} + \\ &+ \varrho(1 - \varrho^2)^{-1/2} \{Z[k\tau'/(1 - \varrho^2)]^{1/2} + \mathrm{e}^{-k\tau'} Z[\varrho^2 k\tau'/(1 - \varrho^2)]^{1/2}\}\} , \end{aligned} \tag{1}$$

where

$$\varrho = (n_2 - Kn_1)/(n_1 + n_2) , \quad k = k_a + k_b ,$$

$$K = k_a/k_b , \quad Z[x] = \mathrm{e}^{-x^2}(2/\sqrt{\pi}) \int_0^x \mathrm{e}^{v^2}\, \mathrm{d}v \tag{2}$$

and u denotes the ratio of current intensities before and after the current reversal.

Eq. (*1*) gives the dependence of $k\tau'$ on kt_1, u and ϱ. Its analysis shows that the value of $k\tau'$ attains a limit with increasing kt_1 which is given by

$$kt_1 \to \infty : \operatorname{erf}(k\tau')^{1/2} + \varrho(1-\varrho^2)^{-1/2}\left\{Z[k\tau'/(1-\varrho^2)]^{1/2} + \right.$$
$$\left. + \, e^{-k\tau'}Z[\varrho^2 k\tau'/(1-\varrho^2)]^{1/2}\right\} = 1/(u+1)\,. \tag{3}$$

To analyze the rate and mode of convergence of $k\tau'$ to its limit, we use an asymptotic expansion of the Dawson integral in Eq. (*1*) valid for large values of the argument[6]. Thus, for $kt_1 > 5$ we obtain instead of the right-hand side of Eq. (*1*) the expression $\{1 + \varrho/[k\pi(t_1+\tau')]^{1/2}\}/(1+u)$. Denoting the limiting value of τ' from Eq. (*3*) as τ'_∞, using expansions in series and neglecting the terms of higher order we obtain

$$kt_1 \gg 1: \quad k\tau' = k\tau'_\infty\left\{1 - \frac{\partial \ln(k\tau'_\infty)}{\partial \ln u}(1 + 1/u)\,\varrho(\pi kt_1)^{-1/2}\right\}. \tag{4}$$

The dependence of τ' on t_1 obtained by numerical solution of Eq. (*1*) is shown fo- certain values of ϱ and u in Fig. 1. For $\varrho = 0$, Eq. (*1*) gives the relation for an irreverrsible follow-up reaction of first order[4]. In view of the fact that for the mentioned ECE mechanism is normally $K \ll 1$ we choose for the analysis of results such values of ϱ as characteristic which correspond to small whole values of n_1 and n_2 and to

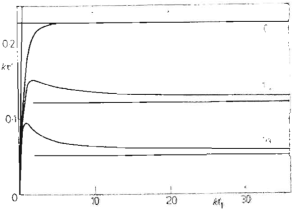

FIG. 1

Dependence of τ' on t_1 for Different ϱ Values at $u = 0{\cdot}1$

Numbers give the value of ϱ, straight lines are asymptotes for $kt_1 \to 0$ and $kt_1 \to \infty$.

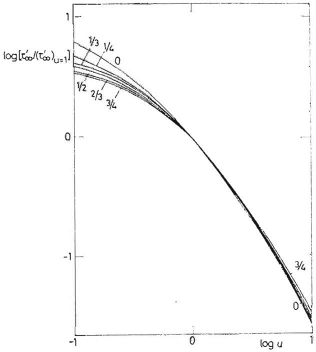

FIG. 2

Dependence of $\tau'_\infty/(\tau'_\infty)_{u=1}$ on u for Different Values of ϱ in Bilogarithmic Coordinates

Numbers give the values of ϱ.

$K = 0$. However, this does not mean a restriction of the analysis to irreversible reactions; the mentioned values of ϱ can be obtained also with different n_1, n_2 and $K > 0$. Moreover, all dependences on ϱ are monotonous so that all discussed dependences for any other ϱ values can be estimated from those for the selected ϱ values by interpolation.

It is seen from Fig. 1 that whereas for an irreversible follow-up reaction ($\varrho = 0$) the transition time τ' converges rapidly and monotonously to a limiting value for $t_1 \rightarrow \infty$, for a normal ECE mechanism the dependence of τ' on t_1 passes through a maximum and then converges to a limiting value for $t_1 \rightarrow \infty$ very slowly. This convergence is so slow that τ' may seem to be practically independent of t_1 well before its limit is reached. This type of the dependence of τ' on t_1 was not found hitherto with any of the cases treated theoretically so that it can serve as a good criterion for distinguishing the ECE mechanism from others. The fact that τ' approaches a constant value with increasing t_1 shows that a possible reversibility of the chemical reaction in the case of the ECE mechanism remains practically without any effect similarly as in the case of electrolysis with constant current without reversal[3].

The dependence of $k\tau'_\infty$ on u obtained by numerical solution of Eq. (*3*) is shown in Fig. 2. For practical reasons (comparison of the curve forms, comparison with

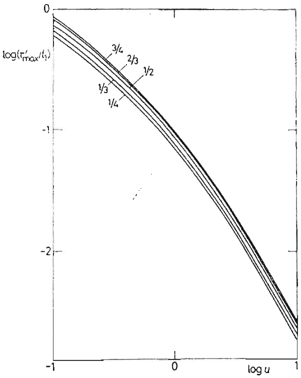

FIG. 3

Dependence of $\tau'_{\max}/t_1$ on u for Different Values of ϱ in Bilogarithmic Coordinates

Numbers give the values of ϱ.

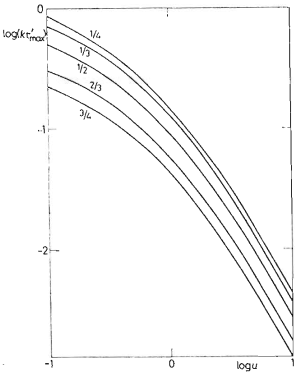

FIG. 4

Dependence of $k\tau'_{\max}$ on u for Different Values of ϱ in Bilogarithmic Coordinates

Numbers give the values of ϱ.

TABLE I

Dependence of Several Parameters on ϱ at $u = 1$

ϱ	$k\tau'_\infty$	$k\tau_{\max}$	$\tau'_{\max}/t'_1$	$\tau'_{\max}/\tau'_\infty$
0	0·2275	—	—	—
$\frac{1}{4}$	0·1230	0·1519	0·0701	1·235
$\frac{1}{3}$	0·09592	0·1310	0·0761	1·365
$\frac{1}{2}$	0·05262	0·09303	0·0862	1·768
$\frac{2}{3}$	0·02283	0·05910	0·0931	2·588
$\frac{3}{4}$	0·01269	0·04335	0·0961	3·415

experiments, reduction of the size of diagram) the dependence of $\tau'_\infty/(\tau'_\infty)_{u=1}$ on u in bilogarithmic coordinates was chosen. It is obvious that $\partial \ln (k\tau'_\infty)/\partial \ln u < 0$ so that in the region of validity of Eq. (*4*) $\partial\tau'/\partial t_1 < 0$ for $\varrho > 0$. Since for $kt_1 \to 0$ the dependence of τ' on t_1 approaches asymtotically the dependence for pure diffusion $(\tau' = t_1/(u^2 + 2u))$, it will have for the ECE mechanism and $\varrho > 0$ allways the described course with a maximum. It follows from Fig. 1 that this maximum will be the sharper the larger the ϱ value. We denote the value of τ' in the maximum as $\tau'_{\max}$. To find this maximum easily, it is convenient to know the value of $\tau'_{\max}/t_1$, where t_1 corresponds to $\tau'_{\max}$. Therefore, in Fig. 3 is shown the calculated dependence of $\tau'_{\max}/t_1$ on u in bilogarithmic coordinates for various values of ϱ; this dependence as

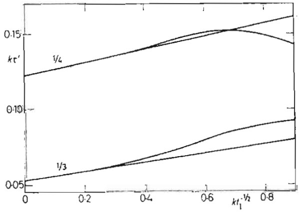

FIG. 5

Dependence of τ' on $1/\sqrt{t_1}$ for Different Values of ϱ at $u = 0{\cdot}1$

Numbers give the values of ϱ, straight lines are asymptotes according to Eq. (*4*).

well as the values of $k\tau'_{\max}$ given below were obtained by numerical determination of the maximum of the dependence of $k\tau'$ on kt_1 based on Eq. (*1*).

The sum of the chemical rate constants, k, can be determined from the measured transition times provided that the values of ϱ is known. To this purpose, the values of $k\tau'_\infty$ and $k\tau'_{\max}$ for typical values of ϱ at $u = 1$ are given in Table I, whence the values of $k\tau'_\infty$ for other values of u can be obtained with the aid of Fig. 2 as nomogram. The values of $k\tau'_{\max}$ for other values of u can be read from the dependence of $k\tau'_{\max}$ on u in bilogarithmic coordinates in Fig. 4.

With respect to the very slow convergence of the dependence of τ' on t_1, the value of τ'_∞ is in most cases experimentally inaccessible. It is seen from Eq. (*4*) that τ'_∞ can be obtained by extrapolation of the dependence of τ' on $1/\sqrt{t_1}$ to zero. Examples of such extrapolation based on the calculated dependences of τ' on t_1 are shown in Fig. 5.

The parameter ϱ can be in some cases determined or at least estimated regardless of the measurement of chemical reaction kinetics[3]. If this is not possible, such estimate can be based on one of the mentioned dependences. When the results of measurements lead to the value of τ'_∞, the dependence of τ'_∞ on u can be utilized. Its course depends on the value of ϱ (Fig. 2) so that ϱ can be estimated from the ratio of the transition times for different u values. The limited accuracy of this estimate enables at best to determine the most probable value of n_2/n_1 for $K = 0$ (*i.e.* for an irreversible chemical reaction). The reliability of this estimate is conditioned by the fact that the dependence of τ' on u in the case of an irreversible follow-up reaction can be influenced in the same way by adsorption[7] so that it can be analogously assumed that a possible adsorption of the substances P and Q could simulate a course corresponding to a different value of ϱ.

If the measurements are related only to the region of the maximum on the $\tau' - t_1$ curve then the value of ϱ can be estimated only from the dependence of $\tau'_{\max}/t_1$ on u; the form of the plot of $\tau'_{\max}$ against u is almost independent of ϱ as can be seen from Fig. 4. With respect to difficulties in finding the position of the maximum and to the rather weak dependence of $\tau'_{\max}/t_1$ on ϱ it is expected that the estimation of ϱ by this method will be still less accurate than from the dependence of τ'_∞ on u.

The best estimate of the ϱ value is based on simultaneous determination of the values of $\tau'_{\max}$ and τ'_∞. Besides the both mentioned dependences it is possible to use in such a case also the dependence of $\tau'_{\max}/\tau'_\infty$ on ϱ. This is given also in Table I for $u = 1$ as obtained from the preceding data; for other u values it can be easily derived from the values of $k\tau'_{\max}$ and $k\tau'_\infty$, which can be obtained as described above. It is seen that the accuracy of the determination of ϱ from the mentioned dependence improves with increasing ϱ. If all three possibilities discussed are combined, a further improvement of the accuracy can be expected.

REFERENCES

1. Dračka O.: This Journal *28*, 3194 (1963).
2. Testa A. C., Reinmuth W. H.: Anal. Chem. *33*, 1320 (1961).
3. Testa A. C., Reinmuth W. H.: J. Am. Chem. Soc. *83*, 784 (1961).
4. Dračka O.: This Journal *25*, 338 (1960).
5. Herman H. B., Bard A. J.: J. Phys. Chem. *70*, 396 (1966).
6. Miller W. L., Gordon A. R.: J. Phys. Chem. *35*, 2785 (1931).
7. Fischer O., Dračka O., Kaláb P.: *Extended Abstracts*, p. 132. CITCE 21st Meeting, Prague 1970.

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