USE OF CURRENT-LESS POTENTIAL–TIME CURVES FOR THE DETERMINATION OF RATE CONSTANTS OF OTHER THAN REDOX REACTIONS*

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The use of current-less potential–time curves for kinetic measurements and determination of rate constants is demonstrated on five different reaction types, *viz.*, nitration, copulation, diazotation, addition of bromine to a double bond and hydrolysis.

Our preceding work[1] dealt with a simple graphical-numerical method for the determination of the rate constant of a redox reaction from the dependence of the current-less nonequilibrium potential of an indicator electrode on the time. The aim of the present work is to show that the mentioned method is not restricted to redox reactions, but it can be used also for other reactions, *e.g.*, addition to a double bond, diazotation, copulation, or hydrolysis, so far as their course can be followed by potential measurements.

THEORETICAL

We shall consider the reaction $v_a A + v_b B \rightarrow v_c C + v_d D$. If A, C, B, and D correspond, respectively, to the forms Red_1, Ox_1, Ox_2, and Red_2, and $v_a = v_c$, $v_b = v_d$, then we have to deal with a redox reaction between two redox systems, $A - v_b e^- \rightarrow C$ and $B + v_a e^- \rightarrow D$, for which the theory of the potential–time curves[2,3] and their use in the determination of the rate constants[4-7] were given and discussed earlier. The above formulation involves a limiting case, where only one of the redox systems, *e.g.*, $D - v_a e^- \rightarrow B$, is electroactive (*e.g.*, Br_2/Br^- in bromination of organic compounds), whereas the other is not potential-determining owing to a vanishingly small value of the rate constant of the electrode reaction.

Now, we shall consider the case where only the form B is electroactive (*e.g.*, Br_2 during addition to a double bond, RN_2^+ during copulation, NO_2^+ in diazotation, H^+

in hydrolysis), whereas the corresponding reduced form is not produced in the reaction.

For instance, during addition of bromine to a double bond $R=R$ (form A), the reaction course being followed by a platinum indicator electrode dipped in the reaction mixture, the oxidised form Br_2 (B in the above scheme) has no reduced counterpart (Br^-), which would limit the increase of the electrode potential due to the oxidised form. Therefore, the potential increases until the role of the reduced form is accepted by some other substance, *e.g.*, the solvent. The other reaction component, $R=R$, is either electroinactive or can be oxidised on the electrode to a radical $R=R^+$ (form $A^{z'+}$) and act as the reduced form in the electrode reaction $A - z'e^- \rightarrow A^{z'+}$, or it can act as the Ox form capable of reduction on the electrode to $RH\text{—}RH$ $(A^{z''-})$ according to $A + z''e' \rightarrow A^{z''-}$.

The condition for the calculation of the nonequilibrium electrode potential follows from the balance of the partial cathodic and anodic currents, whose sum (on open circuit and with neglection of the charging current) is equal to zero:

$$\sum_i I_i = \sum_i (I_{ik} - I_{ia}) = \sum_i z_i F A k_i^0 \{[Ox_i]_0 P_{\alpha_i} - [Red_i]_0 P_{1-\alpha_i}\} = 0, \qquad (1a)$$

$$P_{\alpha_i} = \exp\left[-\alpha_i(E - E_{0i})\frac{z_i F}{RT}\right], \quad P_{1-\alpha_i} = \exp\left[(1 - \alpha_i)(E - E_{0i})\frac{z_i F}{RT}\right]. \qquad (1b)$$

Here, conventional symbols are used[17]. The concentrations at the electrode surface (with subscript zero) are related to those in the bulk of the solution by the equations

$$[Ox_i] - [Ox_i]_0 = I_i \lambda_i = [Red_i]_0 - [Red_i], \qquad (1c)$$

where λ_i is a coefficient depending on hydrodynamic conditions. The concentrations at the electrode expressed from these equations can be introduced into the expression for the difference of the partial cathodic and anodic currents, I_i, to obtain after rearrangement*

$$I_i = \frac{z_i F A k_i^0 \{[Ox_i] P_{\alpha_i} - [Red_i] P_{1-\alpha_i}\}}{1 + z_i F A k_i^0 \lambda_i (P_{\alpha_i} + P_{1-\alpha_i})}. \qquad (1d)$$

Further we define

$$\bar{P}_{\alpha_i} = P_{\alpha_i}/[1 + z_i F A k_i^0 \lambda_i (P_{\alpha_i} + P_{1-\alpha_i})],$$

$$\bar{P}_{1-\alpha_i} = P_{1-\alpha_i}/[1 + z_i F A k_i^0 \lambda_i (P_{\alpha_i} + P_{1-\alpha_i})]. \qquad (1e)$$

Thus, Eq. (1a) takes the form

$$\sum_i I_i = \sum_i z_i F A k_i^0 ([Ox_i] \bar{P}_{\alpha_i} - [Red_i] \bar{P}_{1-\alpha_i}) = 0. \qquad (1f)$$

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* It is also seen that the product $I_i \lambda_i$ approaches zero if $A k_i^0 \lambda_i$ approaches zero, *i.e.* for a small electrode surface area A, low rate constant of the i-th electrode reaction, k_i^0, and intense stirring for which $\lambda_i \rightarrow 0$. Under these conditions, the concentrations at the electrode are practically equal to those in the bulk, as follows from Eq. (1c).

It is apparent that only substances whose concentrations in the bulk of the solution are different from zero are involved in the equation for the electrode potential.

By applying Eq. (1f) to the case of the components A. B. solvent S and their electrode processes described in the preceding text, we obtain

$$z_b k_b^0 \bar{P}_{\alpha_b}[B] - z_s k_s^0 \bar{P}_{1-\alpha_s}[S] + z_a k_a^0 \bar{P}_{\alpha_{a'}}[A] - z_{a''} k_{a''}^0 \bar{P}_{1-\alpha_{a''}}[A] = 0 . \qquad (2a)$$

Now, we express the concentrations of the reactants A and B by the initial concentrations a, b, and the concentration drop x, and we denote $z_s k_s^0 \bar{P}_{1-\alpha_s}[S] = G(E)$. Eq. (2a) thus takes the form

$$z_b k_b^0 \bar{P}_{\alpha_a}(b - v_b x) + \left[z \cdot k_a^0 \cdot \bar{P}_{\alpha_{a'}} - z_{a''} k_{a''}^0 \bar{P}_{1-\alpha_{a''}} \right](a - v_a x) = G(E) . \qquad (2b)$$

By expressing x explicitly and introducing it into the integrated kinetic equation for an irreversible second-order reaction with a stoichiometry $v_a : v_b$ we obtain the equation

$$v_b \, akt \, (1 - n) = \ln \left(n \, \frac{1 - nR(E) + Q(E)}{n(1 - R(E)) + Q(E)} \right), \qquad (3a)$$

where $n = b v_a / a v_b$ and

$$R(E) = \frac{z_b k_b^0 \bar{P}_{\alpha_b}}{z_b k_b^0 \bar{P}_{\alpha_b} + (v_a/v_b)(z_a \cdot k_a^0 \cdot \bar{P}_{\alpha_{a'}} - z_{a''} k_{a''}^0 \bar{P}_{1-\alpha_{a''}})} \qquad (3b)$$

$$Q(E) = \frac{(v_a/v_b)(-z_a \cdot k_a^0 \cdot \bar{P}_{\alpha_{a'}} + z_{a''} k_{a''}^0 \bar{P}_{1-\alpha_{a''}} + G(E)/a)}{z_b k_b^0 \bar{P}_{\alpha_b} + (v_a/v_b)(z_a \cdot k_a^0 \cdot \bar{P}_{\alpha_{a'}} - z_{a''} k_{a''}^0 \bar{P}_{1-\alpha_{a''}})} . \qquad (3c)$$

Now, we want to bring Eq. (3a) to the same form as that of the dependence of $t(1 - n)$ on $\ln n$ derived for second-order redox reactions[2] and an ideal electrode. To this purpose, we introduce

$$Q(E)/R(E) = A(E), \quad (Q(E) + 1)/R(E) - 1 = D(E). \qquad (4a,b)$$

Thus, Eq. (3a) can be rewritten as

$$v_b \, akt \, (1 - n) = \ln \left(n \, \frac{1 - n + D(E)}{A(E)(1 - n) + nD(E)} \right). \qquad (5a)$$

This equation was already analysed[2] for arbitrary values of the parameters $D(E)$ and $A(E) > 0$.

Nonideality of the electrode is distinguished by the dependence of the parameter $A(E) = \beta(E) n^{1-\theta}$ on n and can be taken into account[3] by introducing the parameter θ. Accordingly,

$$v_b \, akt \, (1 - n) = \ln \left(n^\theta \, \frac{1 - n + D}{\beta(1 - n) + Dn^\theta} \right). \qquad (5b)$$

This equation involves also the case where the potential is given by an equation for ion-selective

electrodes

$$E = E_0 + \frac{RT}{nF} \ln{([B])} + K),$$ (5c)

or (for $K = 0$) by the Nernst equation. In such a case, we must set $\beta = D$ in Eq. (5b).

Hence, the method for analysis of E–t curves in the form of the dependence of $t(1 - n)$ on $\ln n$ can be used not only in determining the rate constant of redox reactions[1-7] but also for other types of second-order reactions, whereby the application possibilities of current-less E–t curves in reaction kinetics are considerably broadened. Several illustrative examples are given in the text below.

EXPERIMENTAL

Chemicals. (The chemicals were from Lachema, Brno, unless otherwise stated.) Bromine of reagent grade (Berlin, Adlershof) was dissolved in pure methanol (0.1 mol/dm³) and its concentration was checked iodometrically[8] before and after every experiment. Ammonium nitrate of reagent grade was dissolved also in methanol (1 mol/dm³) and used as indifferent electrolyte. Allyl alcohol was purified by distillation (b.p. $96°C$) and its purity was checked by gas chromatography (99%); its 0.01 mol/dm³ solution in methanol was used. Sodium nitrite of reagent grade (Spolana, Neratovice) was used as diazotation agent (0.01 mol/dm³ in water); its concentration was checked by potentiometric titration with sulphanilic acid[9]. Hydrochloric acid of reagent grade was dissolved in water to 0.1 mol/dm³. Pure aniline hydrochloride (Spolana, Neratovice) was dissolved in ethanol, filtered through an active carbon layer, and precipitated with ether; this procedure was repeated twice. The concentration of its 0.01M solution in 0.1M-HCl was checked potentiometrically with sodium nitrite[9]. Disodium salt of chromotropic acid of reagent grade (Loba Chemie, Wien) was used in the form of a 0.05M solution in 0.1M HCl (it is more stable in acid medium). Sulphanilic acid of pure grade was dissolved in boiling water, filtered in the hot state through active carbon and cooled to precipitate; this procedure was repeated twice and the purity of the product was checked by elementary analysis. A 0.05M solution in 0.1M-HCl was prepared. The diazotation was carried out after cooling this solution to $2°C$ by adding solid sodium nitrate in a 50% excess after half an hour, the remainder of sodium nitrite was decomposed by the addition of crystalline urea (a iodine-starch paper served as an indicator) and the solution was made up to the desired volume with 0.1M-HCl and stored at $-5°C$ (at this temperature, the solution remains without change for 24 h). The reaction medium was an acetate buffer of pH 4 and ionic strength equal to 1 (94.58 cm³ of glacial acetic acid with 29.52 g of melted sodium acetate and 120.77 g KCl was made up with water to 2 000 cm³). Ethyl formiate of reagent grade was dissolved to give a 0.2M solution in acetone (pure). Hydrolysis was carried out with 0.2M-NaOH (reagent grade), the reaction medium was 1M-KCl (reagent grade), both in water. Phenol of reagent grade (Spolana Neratovice) was used as 1M solution in acetic acid. The reaction medium was a 40 : 3 mixture of acetic acid and 95% H_2SO_4. Nitration was carried out with 0.777M-HNO_3 in acetic acid; its concentration was checked potentiometrically with the use of Mohr's salt[10].

Apparatus

The addition of bromine to allyl alcohol was studied in a flow-through reactor with stopped flow[6]. Changes of the parameter $n = [Br_2(t = 0)]/[allylalc. (t = 0)]$ were achieved at constant inlet

rate by changing the bromine concentration in the solution fed into the apparatus by a syringe. A platinum indicator electrode and a saturated calomel reference electrode with a salt bridge were used. The values of the parameter n along with the starting concentrations are given under Fig. 1. Automatic recording of the transparency in the flow and stop-flow methods on the apparatus described earlier[11] but with the optical axis perpendicular to the reactor axis served as an independent method.

The other reactions were carried out in a batch type reactor with an apparatus for recording the $E-t$ curves described earlier[12] except that the high-resistance voltage divider was replaced by an emitor follower. The parameter n was changed by adding one substance into the base solution of the other one at constant volume of the reaction mixture. The values of n and starting concentrations are given under Figs 2—5.
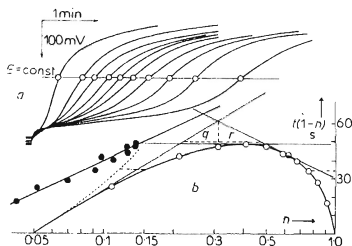

Fig. 1

Addition of bromine to allyl alcohol. a Set of $E-t$ curves with parameter n (from left to right): 0.109; 0.213; 0.314; 0.410; 0.504; 0.594; 0.681; 0.765; 0.845; 0.923. Pt electrode — s.c.e, flow-through electrode with stopped flow, base electrolyte $1\text{-M}NH_4NO_3$ in methanol at 298 K, initial concentration of allyl alcohol 0.001 mol/dm^3. b Dependence of $t(1 - n)$ on $\log n$ (open symbols) obtained from $t - n$ data at $E = \text{const.}$; parameters: $n(t = 0) = 0.05$, $n_e = 0.45$, $n_2 = 0.48$, calculated $\theta = 1.28$, xn_e (half-solid symbol) 0.623, graphically $\theta = r/q = 1.27$. Linearization (solid symbols) is based on these data; – $\cdot$ – $\cdot$ – construction of points of the dashed curve for the determination of the tangent in the point $n(t = 0)$
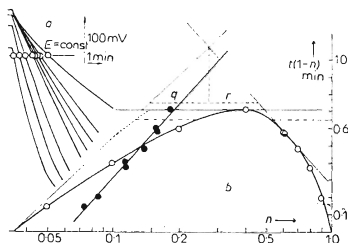

Fig. 2

Diazotation of aniline. a Set of $E-t$ curves with parameter n (from left to right): 0.0503; 0.1006; 0.2012; 0.402; 0.503; 0.604; 0.704; 0.805; 0.905. Pt electrode — s.c.e., batch type reactor, base solution 28 cm^3 of 0.1M-HCl at 293 K, initial concentration of aniline $7.14 \cdot 10^{-3}$ mol/dm^3. b Dependence of $t(1 - n)$ on $\log n$ (open symbols) obtained from $t - n$ data at $E = \text{const.}$; parameters: $n(t = 0) = 0.0345$, $n_e = 0.38$, $n_2 = 0.36$, calculated $\theta = 0.855$, xn_e (half-solid symbol) 0.609, graphically $\theta = r/q = 0.83$. Linearization (solid symbols) is based on these data; – $\cdot$ – $\cdot$ – construction of points of the dashed curve for the determination of the tangent in the point $n(t = 0)$

With the diazotation reaction, the aniline solution was added to the nitrite solution of variable concentration and the Pt electrode was after every run rinsed with a solution of urea. A gold electrode proved to be inactive for following this reaction. An independent method was recording of current–time curves based on a biamperometric indication of nitrous acid[13] at a polarization voltage of 400 mV on an EZ-3 type recorder.

With the copulation reaction, the solution of the diazonium salt of sulphanilic acid was dosed into the chromotropic acid solution and the reaction was followed by a ground gold rotating electrode. A platinum electrode proved inactive to this purpose. Spectrophotometry served as an independent method[14–18].

With the hydrolytic reaction, the sodium hydroxide solution was dosed into the ethyl formiate solution and the reaction was followed with a Pt electrode.

In the nitration of phenol, the solution of nitric acid was added into the phenol solution and the potential of a platinum electrode was recorded. The reaction was followed at the same time also polarographically: samples of the reaction mixture were taken at intervals and added to 50
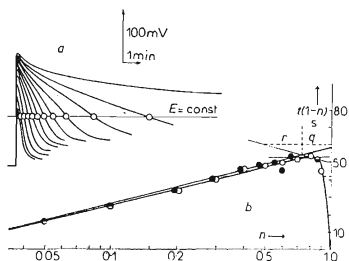

Fig. 3

Copulation of chromotropic acid with diazotated sulphanilic acid. a Set of E–t curves with parameter n (from left to right): 0·025; 0·05; 0·1; 0·2; 0·3; 0·4; 0·5; 0·6; 0·7; 0·8; 0·9; 1·0. Ground Au electrode — s.c.e., batch type reactor, base solution 29 cm³ of 1M acetate buffer of pH 4, ionic strength 1, 288 K, initial concentration of chromotropic acid $3·45 . 10^{-3}$ mol/dm³. b Dependence of $t(1 - n)$ on log n (open symbols) at $E =$ const.; parameters: $n(t = 0) = 0·016$, $n_e = 0·81$, $n_2 = 0·81$, calculated $\theta = 1$, xn_c (half-solid symbol) = 0·867, graphically $\theta = r/q = 1$. The linearization (solid symbols) is based on these data; –·–·– construction of points of the curve for determining the tangent in the point $n(t = 0)$
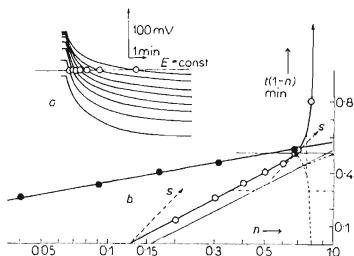
Fig. 4

Alkaline hydrolysis of ethyl formiate. a Set of E–t curves with parameter n (from left to right): 0·1; 0·2; 0·3; 0·4; 0·5; 0·6; 0·7; 0·8. Pt electrode — s.c.e., batch reactor, base solution 26 cm³ of 1M-KCl, initial ester concentration $7·69 . 10^{-3}$ mol/dm³. b Dependence of $t(1 - n)$ on log n (open symbols) at $E =$ const.; parameters: $n(t = 0) = 0·126$, $n_\infty = 0·81$, $\bar{n} = 0·68$, calculated $\theta = 2·664$. Linearization (solid symbols) is based on these data. Straight line S gives the doubled slope of the tangent in the point $n(t = 0)$. The point of contact is denoted by half-solid symbol; –·–·– turned curve and construction of an auxiliary curve

cm^3 of 5M-KOH, whereby the reaction was stopped, the solution was made up to 100 cm^3 with water, diluted 1 : 50 with 0·1M-KCl, and after acidifying with sulphuric acid (1 cm^3 6M-H$_2$SO$_4$) the polarographic curve was recorded, corresponding to reduction of a mixture of o- and p-nitrophenol.

RESULTS AND DISCUSSION

The recorded potential–time curves were treated by the graphical-numerical method described in the preceding communication[1]. The results for each reaction are shown graphically in Figs 1−5, where the potential–time curves are in part a) and their transformation in the coordinates $t(1 - n) - \log n$ in part b) together with the graphical determination of the parameter θ, whose numerical values calculated by the method of ref.[1] from the extremum value of n_e and from the value of xn_e

TABLE I

Values of rate constants (dm^3 mol^{-1} s^{-1})

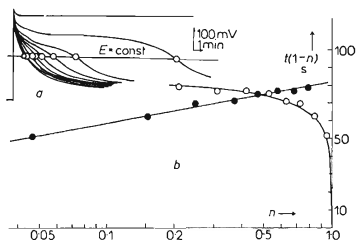| Reaction No	Temper. °C	From slope of left tangent	From slope of right tangent	From slope of straight line	By independ. method	Reference
1	25	38·5	38·1	39·4	40·0 ± 0·8	—
2	20	3·39	3·17	3·18	3·8 ± 0·5	3·16[13]
3	15	22·2	21·8	22·2	26·2 ± 0·31[a]	25·7 ± 5[14]
4	25	20 87	nonexistent	22·38	—	26·8[15]
5	20	nonexistent	nonexistent	1·57	1·69 ± 0·07	—

[a] At hundred-fold dilution[16].

FIG. 5

Nitration of phenol. a Set of E–t curves with parameter n (from left to right): 0·21; 0·317; 0·423; 0·53; 0·635; 0·741; 0·847; 0·953. Pt electrode — s.c.e., batch reactor, base solution 33 cm^3 of a mixture of 40 parts acetic acid + 3 parts sulphuric acid, 293 K. Initial phenol concentration 6·06 . 10^{-2} mol/dm^3. b Dependence of $t(1 - n)$ on $\log n$ (open symbols) at $E = $ const. forms a descending arc. Its linearization in coordinates $t(1 - n)$ against $\log (1 - n)$ is shown by solid symbols

corresponding to the point in which the tangent $\partial[akt\,(1 - n)]/\partial \ln n = -1$ are also given. It is seen that all three types of the $t(1 - n)$ — log n curves were obtained: with an extremum for reactions $(1)-(3)$ (reaction number corresponds to the number of the figure), with a vertical asymptote for reaction (4) and with a descending arc for reaction (5). Linearization of Eq. $(5b)$ based on the found parameter values is denoted by solid symbols.

The values of the rate constants found by the method of E–t curves, by the independent method (see Experimental), and from the literature are given in Table I. Data from the E–t curves refer to the respective set of curves and are therefore given without average errors. In treating a larger number of data, it turned out that the maximum relative error did not exceed $\pm 7\%$, similarly to theoretical model systems[1].

As follows from Table I, a higher accuracy can be attained in cases where the dependence of $t(1 - n)$ on log n shows an extremum (reactions 1, 2 and 3) or only a descending arc (reaction 5). In the case where these curves have a vertical asymptote, the method is very sensitive toward the determination of a point in which the tangent has exactly a doubled slope as compared with the left limiting point[1]. The values of the rate constants found from the sets of E–t curves are in good agreement with the data of the independent methods or of the literature, suggesting that the method of current-less E–t curves is suitable for studying reactions of a nonredox type. Its advantage — especially in the batch reactor atrangement — consists in simplicity of the apparatus; the disadvantage of the somewhat complicated numerical calculations is unimportant in view of the use of a programable pocket calculator.

REFERENCES

1. Tockstein A., Skopal F.: This Journal, in press.
2. Tockstein A., Skopal F.: This Journal *39*, 1518 (1974).
3. Tockstein A., Skopal F.: This Journal *39*, 3016 (1974).
4. Tockstein A., Matušek M.: This Journal *34*, 27 (1969).
5. Tockstein A., Matušek M.: This Journal *34*, 316 (1969).
6. Tockstein A., Skopal F.: This Journal *39*, 3024 (1974).
7. Tockstein A., Skopal F.: This Journal *39*, 3430 (1974).
8. Čůta F.: *Analytická chemie odměrná*. Published by Nakladatelství ČSAV, Prague 1956.
9. Matrka M.: Chemie *8*, 13 (1952).
10. Szebelledy L.: Fresenius' Z. Anal. Chem. *73*, 145 (1928).
11. Tockstein A., Skopal F.: This Journal *41*, 1956 (1976).
12. Tockstein A., Matušek M.: This Journal *32*, 3089 1967).
13. Štěrba V., Ságner Z., Matrka M.: Chem. Listy *59*, 1361 (1965).
14. Ludvík B.: *Thesis*. Institute of Chemical Technology, Pardubice 1972.
15. Leimu X.: Suomen Kem. *19D*, 95 (1946); Chem. Abstr. *41*, 5370 (1947).
16. Velich V.: Private communication.
17. Electrochemical Nomenclature, J. Pure Appl. Chem. *37*, 499 (1974).
18. Elektrochemické názvosloví, Chem. Listy *71*, 1198 (1977).

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