CROATICA CHEMICA ACTA CCACAA **70** (2) 599–615 (1997)

ISSN–0011-1643
CCA–2440

Original Scientific Paper

Mechanism of Dehydro-L-ascorbic Acid Reduction at Mercury Dropping Electrode

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Received June 29, 1996; revised December 11, 1996; accepted January 23, 1997

Quantitative substantiation of the difference in the intermediate stages of dehydro-L-ascorbic acid polarographic reduction to L-ascorbic acid and of L-ascorbic acid polarographic oxidation to dehydro-L-ascorbic acid is given. It has been established that the first process is described by the $C_rE_{qr}C_i$ mechanism with the preceding reversible and the following irreversible rate determining chemical stages and with the quasi-reversible transfer of the first electron in two parallel stages with and without participation of proton.

INTRODUCTION

The redox system dehydro-L-ascorbic acid (DHAA) / L-ascorbic acid (AA) is one of the widespread and important redox systems for electrochemistry and electroanalytical chemistry, biochemistry, pharmacology and other fields.[1–5] For processes DHAA + $2e^-$ + $2H^+$ $\longrightarrow$ AA and AA – $2e^-$ – $2H^+$ $\longrightarrow$ DHAA, the mechanism of the second process has been studied in detail at the dropping mercury electrode (DME),[6–16] hanging mercury drop electrode,[17,18] and other electrodes,[19–36] including modified electrodes.[30–36] However, the mechanism of DHAA reduction at DME which is considered in references[8,15,37–40] has not been clearly understood. The aim of this paper is to broaden and to deepen

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broaden and to deepen the notion of the reductive mechanism of DHAA at MDE on the basis of experimental data listed in the references.[8,11,12,15,37] To solve this problem, we have also used new data on the formal redox potentials and the equilibrium constants for DHAA/AA system which were recently obtained by us.[41]

RESULTS AND DISCUSSION

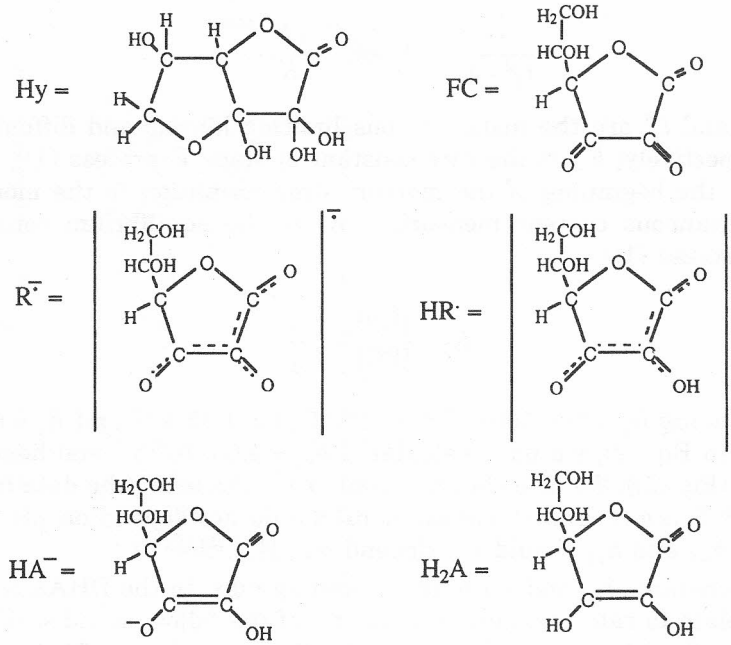
The Same Intermediate Stages for DHAA + 2e⁻ + 2H⁺ ⟶ AA and AA – 2e⁻ – 2H⁺ ⟶ DHAA Processes. Reversible C_rE_r Mechanism

The assumption of the same reaction kinetic pathways for DHAA + 2e⁻ + + 2H⁺ ⟶ AA and AA – 2e⁻ – 2H⁺ ⟶ DHAA is based, first, on the same initial and final products in the two processes[8,9,15] and, second, on the believe that the DHAA electroreduction and the AA electrooxidation are characterized by the CE mechanism ($i_l \ll i_l^d$)[8,11,12,15,37–40] and EC mechanism,[6–13,15] respectively. Thus, on the basis of the exhaustive studies of the E_rC_r mechanism of AA oxidation[6–15,17,27] it can be assumed that the reductive C_rE_r mechanism of DHAA is described by the same process but in the opposite direction, namely:

$$\mathrm{Hy} \underset{\text{slow; } k_{-1}\,(k_{+5})}{\overset{\text{I; slow; } k_{+1}\,(k_{-5})}{\rightleftharpoons}} \mathrm{FC} + \mathrm{H_2O} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \mathrm{R^{\cdot -}} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} \mathrm{HR^{\cdot}} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \mathrm{HA^-} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} \mathrm{H_2A} \qquad (1)$$

where (for structural formulas see Scheme 1): Hy is the hydrated bicyclic form of DHAA[42,43] dominant in the solution of DHAA;[41] FC is a form of DHAA with three free carbonyl groups;[15,17,37,38,44,45] $R^{\cdot -}$ and $HR^{\cdot}$ are the radical anion and radical, respectively;[46–49] HA^- and H_2A are the anion and the undissociated form of AA, respectively.

All stages of process (1) except for I, are fast and are present at the equilibrium. It should be emphasized that the reversibility of electron transfer in polarography was proved only for AA oxidation.[14,15] For DHAA reduction when the initial form of DHAA is FC, the reversibility of electron transfer was also shown.[17,18,44] However, if Hy is the initial form of DHAA, which is usual in the aqueous solution the data about reversible electron transfer are contradictory.[8,15,39] This contradiction will be eliminated below. Since we have so far assumed that process (1) describes also the reductive mechanism of DHAA, the electron transfer is supported to be reversible. In the case of the potentiometric investigation of the DHAA/AA system with Hy, as the in-



Scheme 1.

itial form of DHAA, in the presence of a mediator,[50,51] all the stages of process (1), including stage I are fast and are present at the equilibrium.

Rate constants k_{+1} and k_{-1} (process (1)) correspond to the DHAA electroreduction while rate constants k_{+5} and k_{-5} correspond to the AA electrooxidation. If process (1) is correct in both directions, it must be: $k_{+1} = k_{-5}$ and $k_{-1} = k_{+5}$.

In the analysis of the polarographic waves of the DHAA reduction,[8,11,12,37] we were limited to the condition pH ≤ 5 in order to eliminate the DHAA decomposition at pH > 5.[8] At pH ≤ 5, the second step of the AA dissociation (process (1)) was ignored.[51]

To prove or to deny the correctness of process (1) of the DHAA electroreduction, we carried out analyses of the limiting kinetic current and of the wave equation for the cathodic process of DHAA reduction at DME.

Limiting Kinetic Current

For process (1), this current is determined by the C_rE_r mechanism. The rate of the preceding rate determining stage (r.d.s.) can be calculated from the limiting kinetic current described by Koutecky's equation.[52,53] This equation for instantaneous currents is transformed to the following form:[54–56]

$$\frac{i_1^{\mathrm{k}}}{i_1^{\mathrm{d}} - i_1^{\mathrm{k}}} = 1.368 \frac{(k_{-1}\, t)^{0.545}}{K_1} \tag{2}$$

where i_1^{k} and i_1^{d} are the instantaneous limiting kinetic and diffusion currents, respectively; k_{-1} is the rate constant of stage I (process (1)); t is the time from the beginning of the mercury drop formation to the moment of the instantaneous current measuring; K_1 is the equilibrium constant of stage I (process (1)):

$$K_1 = \frac{[\mathrm{Hy}]}{[\mathrm{FC}]} = \frac{k_{-1}}{k_{+1}} \tag{3}$$

Introducing $(i_1^{\mathrm{d}}/i_1^{\mathrm{k}}) = 500$[11,12,15] at 25 °C, $t = 4.32$ s,[12] and $K_1 = (6 \pm 3) \times \times 10^6$,[41] into Eq. (2), we have calculated $k_{-1} = 4.0 \times 10^6$ s^{-1} and hence $k_{+1} = = 0.67$ s^{-1} (Eq. (3)). We also obtained similar results using the data from references.[8,37] Since i_1^{k} and i_1^{d} values at pH ≤ 5 do not depend on pH,[8,12] rate constants k_{+1} and k_{-1} should not depend on pH, either.

Rate constants k_{+1} and k_{-1} of the preceding r.d.s. in the DHAA electroreduction relate to rate constants k_{+5} and k_{-5} of the following r.d.s. (E_rC_r mechanism) in the AA electrooxidation (process (1) from right to left). At pH ≥ 7.2, constant k_{+5} (Table I) has been obtained using the independent methods by Perone *et al.*[17] and by Jaenicke *et al.*[44] Constant k_{+5} (Table I) was calculated

TABLE I

The rate constants of the following r.d.s. for AA electrooxidation. 25 °C

pH	$(E^{\mathrm{r}}_{1/2})_{\mathrm{AA}}$* / V (SCE)	k_{+5} / s^{-1}	k_{-5} / s^{-1}	Notes
2.0	+0.219	0.63	$1.0 \cdot 10^{-7}$	a
3.0	+0.156	1.5	$2.5 \cdot 10^{-7}$	a
4.0	+0.092	9.5	$1.7 \cdot 10^{-6}$	a
5.0	+0.047	30	$5.0 \cdot 10^{-6}$	a
6.0	0.000	$3.0 \cdot 10^2$	$5.0 \cdot 10^{-5}$	a
7.2	–	$1.4 \cdot 10^3$	$2.3 \cdot 10^{-4}$	b
7.2	–	$1.3 \cdot 10^3$	$2.2 \cdot 10^{-4}$	c
9.0	–	$3.4 \cdot 10^2$	$5.7 \cdot 10^{-5}$	d

* Ref. 12.
[a] Our calculations from the DC polarographic data.[12]
[b] Cyclic voltammetry.[17] k_{-5} was calculated by us.
[c] Potential-step electrolysis.[17] k_{-5} was calculated by us.
[d] Chronopotentiometry with current reversal.[44] k_{-5} was calculated by us.

by us using K_1 values[41] (Eq. (3)). The distinction in the values of the rate constants at pH = 7.2 and pH = 9.0[17,46] was caused by the influence on these constants of the acid-base catalysis[41] (analogously to the acid-base catalysis with participation of other carbonyl compounds).[39,57,58] It should be noted that the rate constants at pH ≤ 5 (Table I) are not influenced by the Hy decomposition.[8] It is caused by the practically complete irreversibility of stage I at the AA electrooxidation which was accounted for in references[6,7] and it also follows from the rate constants k_{-5} (Table I; $k_{+5} >> k_{-5}$) obtained by us.

The k_{+5} values at pH < 7 (Table I) for AA electrooxidation (process (1) from right to left) have been calculated by us on the basis of Koutecky's equation,[7] taking into account the instantaneous currents:[54–56]

$$(E^{r}_{1/2})_{AA} = E^{o,f}_{FC/HA^-} - \frac{RT}{2F}\ln K_{a_1} + \frac{RT}{2F}\ln a_{H^+}(K_{a_1} + a_{H^+}) - \frac{RT}{2F}\ln 1.368(k_{+5}t)^{0.545} \quad (4)$$

where $(E^{r}_{1/2})_{AA}$ the half-wave potential at reversible electron transfer for the kinetic wave of the AA oxidation; $E^{o,f}_{FC/HA^-}$ is the formal potential; a_{H^+} is the hydrogen ion activity; K_{a_1} is the first constant of the AA acid dissociation.

In these calculations, we have used: $(E^{r}_{1/2})_{AA}$ listed in Table I,[12] $E^{o,f}_{FC/HA^-}$ = = +0.231 V (SCE),[41] t = 4.32 s,[12] and $K_{a_1} = 1.0 \times 10^{-4}$,[51] (at the ionic strength of 0.2).

Comparison of the values $k_{+1} = 0.67\ s^{-1}$ and $k_{-1} = 4 \times 10^6\ s^{-1}$ with the values of k_{-5} and k_{+5}, respectively, (Table I) shows that the assumed equalities $k_{+1} = k_{-5}$ and $k_{-1} = k_{+5}$ do not exist. The constants calculated for the DHAA electroreduction (k_{+1} and k_{-1}) at pH ≤ 5 are 5–7 orders of magnitude higher than the constants (k_{-5} and k_{+5}) calculated for the AA electrooxidation at the same pH. This conclusion ($k_{+1} >> k_{-5}$ and $k_{-1} >> k_{+5}$) is correct even if possible errors in the determination of K_1 [$(6 \pm 3) \times 10^6$] and i_l^d/i_l^k (±10%) and their influence on the calculation of k_{-1} (and k_{+1}) (Eq. (2) and (3)) have been taken into account. In addition, k_{+1} and k_{-1} do not depend on pH while k_{+5} and k_{-5} depend on pH (Table I). It is worth noting that the higher values of the k_{+1} and k_{-1} constants were not caused by the effect of the surface reaction I (process (1)) due to the Hy adsorption. It is known[59] that the influence of the surface reaction leads to an increase of the rate constant calculated on the basis of Eq. (2). However, in this case, pH affects the kinetics of stage I (as well as the effect on k_{+5} and k_{-5}) which was not observed in the experiment. The volume nature of the limiting kinetic current is confirmed by the calculated thickness of the reaction layer $\mu = 1.2 \times 10^{-6}$ cm ($\mu = (D/k_{-1})^{0.5}$; the diffusion coefficient $D = D_{AA} = 5.3 \times 10^{-6}\ cm^2\ s^{-1}$,[60]) and with the high temperature coefficient *ca.* +7% per degree.[8,15,37] For the surface kinetic current, the temperature coefficient is low and can even be negative.[59,61]

Thus, the difference in the rate constants k_{+1} and k_{-5} as well as k_{-1} and k_{+5} indicates that the intermediate stages of DHAA polarographic reduction

to AA are not the same as the intermediate stages of the AA polarographic oxidation to DHAA. Since there is no reason to doubt the correctness of process (1) (from right to left) for the description of the AA electrooxidation,[6–15,17,27,44] we arrived at the conclusion that the process of DHAA electroreduction has other intermediate stages, including the other preceding r.d.s. This is in agreement with the analysis of the wave equation given below.

Wave Equation

To describe the process (1) for the DHAA electroreduction with the preceding r.d.s. and the reversible electron transfer, Koutecky[7] has used the wave equation:

$$(E^{r}_{1/2})_{DHAA} = E^{o,f}_{Hy/H_2A} + \frac{RT}{2F}\ln a_{H^+}(K_{a_1} + a_{H^+}) + \frac{RT}{2F}\ln\frac{i^{d}_{1}}{i^{d}_{1}} \quad (5)$$

where $(E^{r}_{1/2})_{DHAA}$ is the half-wave potential of the DHAA reduction; $E^{o,f}_{Hy/H_2A}$ is the formal potential. Eq. (5) is the particular case of the general equations of the kinetic waves for the CE mechanism.[62] The physical substantiation of the apparent anomaly that the $E^{r}_{1/2}$ value may be more positive than the formal potential is given in Ref. 63.

Eq. (5) has been used by Koutecky[7] for the calculation of the ratio (i_1^d/i_1^k) at $(E^{r}_{1/2})_{DHAA} = (E^{r}_{1/2})_{AA}$. As it will be shown below, Eq. (5) does not describe correctly the DHAA polarographic behaviour. Therefore, it is impossible to use Eq. (5) for correct determination of the ratio i_1^d/i_1^k at $(E^{r}_{1/2})_{DHAA} = (E^{r}_{1/2})_{AA}$[7] or for valuing the influence of the kinetic parameter on the value $(E^{r}_{1/2})_{DHAA}$.[15]

The comparison of $(E_{1/2})^{exp}{}_{DHAA}$ with $(E^{r}_{1/2})^{calc}{}_{DHAA}$ calculated by us using Eq. (5) and assuming $(i_1^d/i_1^k) = 500$[12] and $E^{o,f}_{Hy/H_2A} = +0.148$ V (SCE)[41,50,51] is

TABLE II

Comparison of $(E_{1/2})^{exp}{}_{DHAA}$ with $(E^{r}_{1/2})^{calc}{}_{DHAA}$ for the DHAA electroreduction

pH	$(E_{1/2})^{exp}{}_{DHAA}$* V (SCE)	$(E^{r}_{1/2})^{calc}{}_{DHAA}$ V (SCE)
1.0	–0.280	+0.169
2.0	–0.335	+0.110
3.0	–0.380	+0.052
4.0	–0.414	+0.001
5.0	–0.461	–0.066

* Ref. 12.

shown in Table II. It is easy to see (Table II) that the $(E^{r}_{1/2})^{calc}{}_{DHAA}$ values differ considerably from the $(E_{1/2})^{exp}{}_{DHAA}$. Thus, this difference confirms the conclusion obtained by us on the basis of the limiting kinetic current that process (1) is not suitable for a correct description of the DHAA polarographic reduction. First, the reduction includes the quasi-reversible electron transfer (see below) which is one of reasons for the inequality of the $(E_{1/2})^{exp}{}_{DHAA}$ and $(E^{r}_{1/2})^{calc}{}_{DHAA}$ (Table II).

The Intermediate Stages of DHAA + 2e⁻ + 2H⁺ ⟶ AA and AA – 2e⁻ – 2H⁺ ⟶ DHAA Processes are Different. Quasi-reversible C_rE_{qr} Mechanism

In order to develop a new reductive mechanism of DHAA at MDE, we have carried out the analysis of the DHAA polarographic waves published in references[9,11,12,37] in the coordinates $\lg[i^k/(i_l^k - i^k)]$ *vs.* E, where i^k is the kinetic current and E is the corresponding potential. The most exact analysis $\lg[i^k/(i_l^k - i^k)]$ *vs.* E was carried out on the basis of the polarographic data[11,12] which were kindly supplied by Prof. J. J. Ruiz. Polarographic curves and the corresponding dependencies in the coordinates $\lg[i^k/(i_l^k - i^k)]$ *vs.* E are shown in Figures 1 and 2, respectively. The currents (Figure 2) are instantaneous (maximum), $t = 4.32$ s.

It can be seen from Figure 2 that the polarographic waves are quasi-reversible at pH ≤ 5.0. The general theory for such waves has been considered by Matsuda[64] (see also Ref. 65).

At a low current density, the electron transfer is almost reversible (Figure 2). The tangent line to the extrapolated part of the curve was drawn

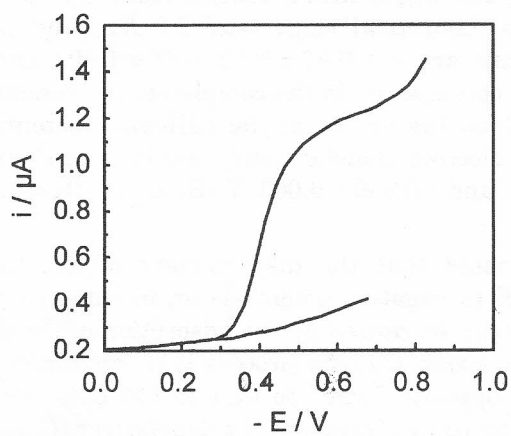


Figure 1. Polarographic curve of the DHAA reduction.[11] $C_{DHAA} = 4.0 \times 10^{-2}$ M. pH = = 3.83. 25 °C.

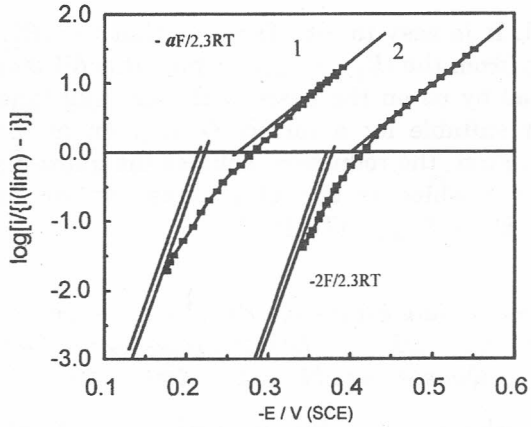


Figure 2. Dependence of $\lg[i^k/(i_l^k - i^k)]$ *vs.* E on the polarographic curves of the DHAA reduction. pH = 1.00 (1), 3.83 (2); $C_{DHAA} = 4.0 \times 10^{-2}$ M.

with the theoretical slope ($-2F/2.3\ RT$) corresponding to the reversible transfer of two electrons. Since the extrapolation of the curve was done with certain errors, we have indicated the most probable interval of this extrapolation (Figure 2). The extrapolation is in agreement with the extrapolation based on the parabola equation. From the tangent lines at $i^k = i_l^k/2$, we obtained the reversible half-wave potentials for the kinetic waves of DHAA: $(E^r_{1/2})_{DHAA} = -0.219 \pm 0.004$ V (SCE) at pH = 1.00 and $(E^r_{1/2})_{DHAA} = -0.376 \pm 0.003$ V (SCE) at pH = 3.83.

As the current density increases, the process of the electron transfer becomes less reversible and it is completely irreversible at the highest current density (Figure 2). The upper linear dependencies $\lg[i^k/(i_l^k - i^k)]$ *vs.* E (Figure 2) exhibit the theoretical slope ($-\alpha F/2.3\ RT$) and indicate that the transfer coefficients are $\alpha = 0.57 \pm 0.02$ (pH = 1.00) and $\alpha = 0.56 \pm 0.01$ (pH = 3.83), which corresponds to the completely irreversible electron transfer. We have obtained the values of the half-wave potentials for the completely irreversible electron transfer from these lines at $i^k = i_l^k/2$: $(E^i_{1/2})_{DHAA} = -0.264 \pm 0.004$ V and -0.396 ± 0.003 V (SCE) at pH = 1.00 and 3.83, respectively (Figure 2).

It should be noted that the displacement of the linear dependence $\lg[i^k/(i_l^k - i^k)]$ *vs.* E to negative potentials or, in some cases, the distortion of this dependence can be caused by the adsorption of the depolarizer at the DME, even if the electron transfer process is reversible.[66–68] However, such distortion has the opposite form[67] to that in our case, shown in Figure 2. Except with the high concentration of the depolarizer ($C_{DHAA} = 4.0 \times 10^{-2}$ M) and the low current density in the case of reversible electron transfer, the adsorption of the depolarizer should not influence the $\lg[i^k/(i_l^k - i^k)]$ *vs.* E

dependence. This is explained by the insignificant concentration polarization under these conditions and is specially relevant to the $(E^{r}_{1/2})_{DHAA}$ values found by us at a low current density.

Thus, the new reductive mechanism of DHAA at MDE involves the quasi-reversible electron transfer and the preceding r.d.s. ($i_l^k << i_l^d$) *i.e.* C_rE_{qr} mechanism. However, only one preceding r.d.s. cannot explain the inequality of $(E^{r}_{1/2})^{exp}{}_{DHAA}$ and $(E^{r}_{1/2})^{calc}{}_{DHAA}$ (Eq. (5)) (Table III). Since one of the reasons for the inequality of $(E_{1/2})^{exp}{}_{DHAA}$ and $(E^{r}_{1/2})^{calc}{}_{DHAA}$ in Table II could result from the quasi-reversible electron transfer, we compared also the $E_{1/2}$ values for the reversible electron transfer (Table III). The inequality of $(E^{r}_{1/2})^{exp}{}_{DHAA}$ and $(E^{r}_{1/2})^{calc}{}_{DHAA}$ (Table III), with the $(E^{r}_{1/2})^{exp}{}_{DHAA}$ values being more negative, can be explained by the existence of new r.d.s beside the preceding r.d.s., namely by the following r.d.s. ($C_rE_{qr}C_i$ mechanism; see the next paragraph).

As noted above, the literary data about the reversible electron transfer for the DHAA electroreduction at the MDE are contradictory. Ono *et al.*[9,39]

TABLE III

Comparison of $(E^{r}_{1/2})^{exp}{}_{DHAA}$ (Figure 2) with $(E^{r}_{1/2})^{calc}{}_{DHAA}$

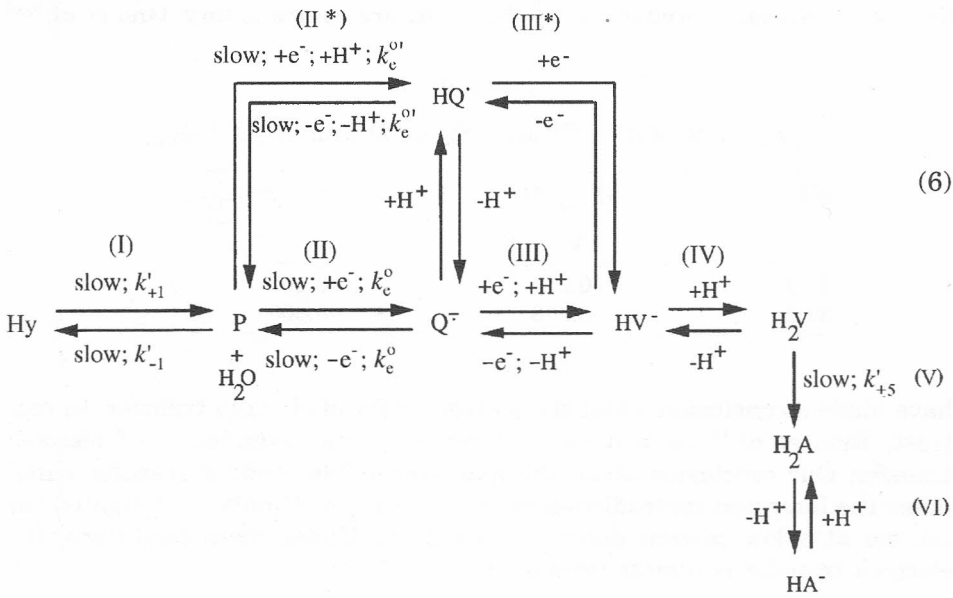
pH	$(E^{r}_{1/2})^{exp}{}_{DHAA}$	$(E^{r}_{1/2})^{calc}{}_{DHAA}$
	V (SCE)	V (SCE)
1.00	–0.219	+0.169
3.83	–0.376	+0.008

have made a conclusion about the irreversibility of electron transfer. In contrast, Ruiz *et al.*[15] have drawn attention to the reversibility of electron transfer. Our conclusion about the quasi-reversible electron transfer eliminates the indicated contradiction because Ruiz *et al.*[15] have investigated the process at a low current density ($i^k < 0.2\ i_l^k$). Under these conditions, the electron transfer is almost reversible.

The Intermediate Stages of DHAA + $2e^-$ + $2H^+$ ⟶ AA and AA – $2e^-$ – $2H^+$ ⟶ DHAA Processes are Different. Quasi-reversible $C_rE_{qr}C_i$ Mechanism

We have used the scheme for the DHAA electroreduction proposed by Ruiz *et al.*[15] for the development of a quasi-reversible $C_rE_{qr}C_i$ mechanism. In this scheme, the intermediate stages and substances (they are indicated in scheme 6) were different from those in process (1) but the same mechanism was accepted,[15] namely the reversible C_rE_r mechanism. Besides the

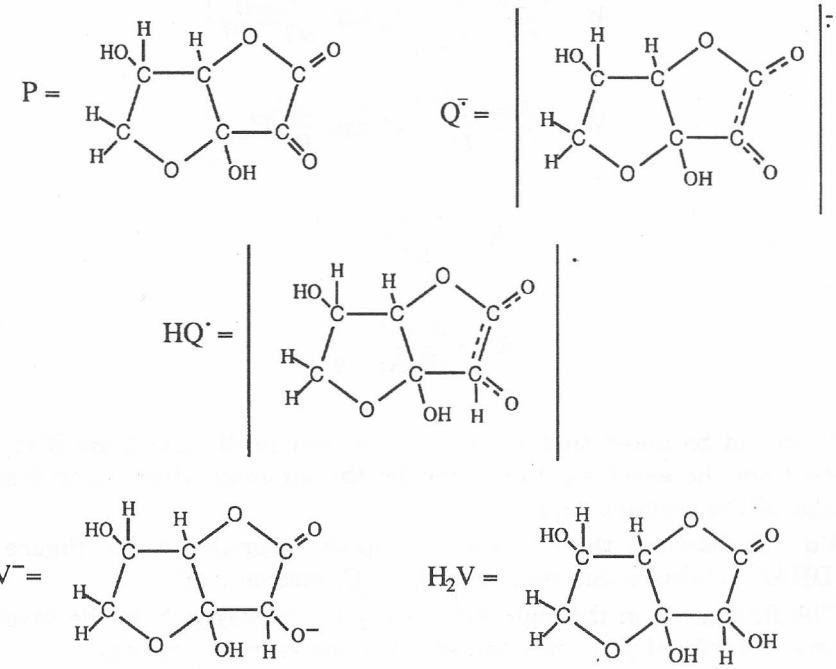
substitution of the reversible C_rE_r mechanism by the quasi-reversible $C_rE_{qr}C_i$ mechanism with the following rate determing stage, we postulate also that the transfer of the first electron is slow. This transfer is realized in two parallel stages without and with participation of the proton. Thus, the quasi-reversible $C_rE_{qr}C_i$ mechanism corresponds to the process (6) where k'_{+1}, k'_{-1}, k'_{+5} are the corresponding rate constants of the chemical r.d.s.; k_e^o is the standard rate constant of the first electron transfer in stage (II) and $k_e^{o'}$ is the standard rate constant of the first electron and proton transfer in stage (II*). The influence of the double-layer effect on the electrode reaction rate is considered as constant. It is worth noting that among the following chemical stages in processes (1) and (6) only one stage (the isomerization stage V in process (6)) can be accepted as the following r.d.s. because the protonization stages in the volume of the solution are usually very fast.



The structural formulas of substances in process (6), except for those already indicated above, are the following (Scheme 2).

The existence of the preceding r.d.s. I is proved by the relation $i_l^k << i_l^d$. The existence of the following r.d.s. V causes the shift of $(E^r_{1/2})_{DHAA}$ to negative potentials (at a low current density when the electron transfer is reversible).

If stages III and III* (the stages of the second electron transfer) are slow (instead of the stages II and II*), the slope of the straight line $\lg[i^k/(i_l^k - i^k)]$



Scheme 2.

vs. E at a high current density should be equal to $[-(1+\alpha)F/2.3\,RT]$. The experimental slope under these conditions is $(-\alpha F/2.3\,RT)$ (Figure 2), which indicates that the first electron transfer is slow.

Participation of the proton in one of the routes of the slow transfer of the first electron (II or II*) is proved by the pH influence on $(E_{1/2})_{\mathrm{DHAA}}$. If only route II* exists (without route II), this influence will be in a great extent larger than the influence observed experimentally.

For the description of the quasi-reversible process (6), we have used Matsude's equation,[64,65] taking into account both the preceding r.d.s. and the following r.d.s. as well two parallel electron transfer routes. For the instantaneous current,[54–56] this equation has a form:

$$\frac{i_1^{\mathrm{k}} - i^{\mathrm{k}}}{i^{\mathrm{k}}} = \frac{i_1^{\mathrm{k}}}{A i_1^{\mathrm{d}}\, a_{\mathrm{H}^+}^2} \exp\left[\frac{2F}{RT}(E - E^{\mathrm{o,f}}_{\mathrm{Hy/H_2A}})\right] + \frac{i_1^{\mathrm{k}}}{(M + N a_{\mathrm{H}^+}) i_1^{\mathrm{d}}} \exp\left[\frac{\alpha F}{RT} E\right] \quad (7)$$

where

$$A = 1.386\, K'_5\, (k'_{+5}\, t)^{0.545} \quad (8)$$

$$M = \frac{1.386}{K'_1}\left(\frac{t}{D}\right)^{0.5} k_e^{o} \exp\left[\frac{\alpha F}{RT} E^{o,f}_{P/Q^-}\right] \tag{9}$$

$$N = \frac{1.386}{K'_1}\left(\frac{t}{D}\right)^{0.5} k_e^{o\prime} \exp\left[\frac{\alpha F}{RT} E^{o,f}_{P/Q^-}\right] \tag{10}$$

$$K'_1 = \frac{[\mathrm{Hy}]}{[\mathrm{P}]} = \frac{k'_{-1}}{k'_{+1}} \tag{11}$$

$$K'_5 = \frac{[\mathrm{H_2V}]}{[\mathrm{H_2A}]} = \frac{k'_{-5}}{k'_{+5}} \tag{12}$$

It should be noted that Eq. (7) will be practically the same if it is obtained from the exact solution[64] and by the approximation using a simple concept of the reaction layer.[65]

Eq. (7) describes the whole kinetic quasi-reversible wave (Figure 1) of the DHAA polarographic reduction ($C_rE_{qr}C_i$ mechanism).

The first term on the right side of Eq. (7) corresponds to the reversible electron transfer ($C_rE_rC_i$ mechanism at a low current density):

$$E = E^{o,f}_{\mathrm{Hy/H_2A}} + \frac{RT}{F}\ln a_{\mathrm{H^+}} + \frac{RT}{2F}\ln\frac{i_1{}^{d}}{i_1{}^{k}} + \frac{RT}{2F}\ln A - \frac{RT}{2F}\ln\frac{i^{k}}{i_1{}^{k} - i^{k}} \tag{13}$$

and hence:

$$(E^{r}_{1/2})_{\mathrm{DHAA}} = E^{o,f}_{\mathrm{Hy/H_2A}} + \frac{RT}{F}\ln a_{\mathrm{H^+}} + \frac{RT}{2F}\ln\frac{i_1{}^{d}}{i_1{}^{k}} + \frac{RT}{2F}\ln A \tag{14}$$

In Refs. 69–72 the wave equations for the $C_rE_rC_i$ mechanism which are similar to Eqs. (13) and (14) have been considered for polarography[69–71] and linear-sweep voltammetry.[72]

The second term on the right side of Eq. (7) corresponds to the completely irreversible stage of the first electron transfer in parallel routes II and II* ($C_rE_iC_i$ mechanism at a high current density):

$$E = \frac{RT}{\alpha F}\ln\frac{i_1{}^{d}}{i_1{}^{k}} + \frac{RT}{\alpha F}\ln(M + Na_{\mathrm{H^+}}) - \frac{RT}{2F}\ln\frac{i^{k}}{i_1{}^{k} - i^{k}} \tag{15}$$

and hence:

$$E^{i}_{1/2} = \frac{RT}{\alpha F}\ln\frac{i_1{}^{d}}{i_1{}^{k}} + \frac{RT}{\alpha F}\ln(M + Na_{\mathrm{H^+}}) \tag{16}$$

The experimental data (Figure 2) correspond to Eqs. (13) and (15). The $E^{r}_{1/2}$, $E^{i}_{1/2}$, and α values obtained by us are given above. Independence of the α values of pH shows that the electron transfer coefficients in stages II and II* are very similar. This has been used in the evaluation of Eq. (7).

On the basis of Eq. (14) and using $(E^{r}_{1/2})_{DHAA}$, $E^{o,f}_{Hy/H_2A}$, pH, (i_l^d/i_l^k) values (see above), we have calculated the value of $A = (1.2 \pm 0.4) \times 10^{-13}$. Using Eq. (16) and the $E^{i}_{1/2}$ values, we have obtained the values of $M = (2.98 \pm 0.02) \times 10^{-7}$ and $N = (5.46 \pm 0.51) \times 10^{-5}$ M^{-1}.

We have calculated the $(E_{1/2})_{DHAA}$ values at different pH on the basis of Eq. (7) and the A, M, N, α and $E^{o,f}_{Hy/HA}$ values by the method of successive approximations. The coincidence of the $(E_{1/2})^{exp}{}_{DHAA}$ and $(E_{1/2})^{calc}{}_{DHAA}$ values is good enough (Figure 3). The independence of the A value (Eq. (7)) of pH is caused by the absence of any appreciable influence of the acid-base catalysis on stage V in process (6) (similarly to stage I since i_l^k do not depend on pH).

The important advantage of Eq. (14), evaluated from the general Eq. (7), is also the possibility to explain the considerable displacement of the $(E^{r}_{1/2})_{DHAA}$ to the negative potentials (parameter $A << 1$) in comparison with $(E^{r}_{1/2})_{DHAA}$ calculated from Eq. (5) for the C_rE_r mechanism. The very low A value (Eq. (8)) might be caused by a very low equilibrium constant K'_5 (Eq. (12)).

The limiting kinetic current for quasi-reversible process (6) ($C_rE_{qr}C_i$ mechanism), in spite of the existence of the following r.d.s., is expressed by the same equation as for the reversible C_rE_r mechanism (Eq. (2)) but with other rate and equilibrium constants. This equation explains the directly propor-

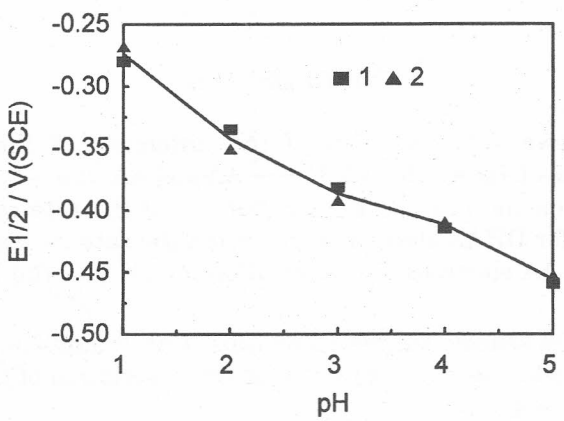


Figure 3. Comparison of $(E_{1/2})^{exp}{}_{DHAA}$ (1) and $(E_{1/2})^{calc}{}_{DHAA}$ (2) (Eq. (7)) as a function of pH. $C_{DHAA} = 4.0 \times 10^{-2}$ M.

tional inter dependence of i_l^k and C_{DHAA}[11] since $i_l^d \gg i_l^k$ and $i_l^d = \kappa C_{DHAA}$, where κ is the Ilkovic constant.

Ruiz[11] has shown that the increase of C_{DHAA} ($1 \times 10^{-2} - 8 \times 10^{-2}$ M) leads to displacement of $(E_{1/2})_{DHAA}$ to more negative potentials. The author[11] connected this phenomenon with the effect of DHAA adsorption. We have considered this effect on the basis of process (6). The influence of DHAA adsorption on the kinetics of the preceding r.d.s. is unlikely (see above). The same applies to the kinetics of the following r.d.s., since the adsorption of the DHAA should increase the rate constant k'_{+5} and hence shift the $(E_{1/2})_{DHAA}$ to positive potentials. At the same time, the increase of the DHAA adsorption at a high DHAA concentration may decrease the rate constants of the electron transfer and hence shift the $(E_{1/2})_{DHAA}$ to negative potentials (Eq. (7)).

Thus, the developed quasi-reversible $C_rE_{qr}C_i$ mechanism for the description of the DHAA electroreduction at DME allowed us to explain quantitatively the whole kinetic wave of DHAA beginning from the reversible electron transfer at a low current density and finishing by the completely irreversible transfer of the first electron. The proposed mechanism enabled us to explain also the considerable displacement of the $(E^r_{1/2})_{DHAA}$ to negative potentials in the case of the reversible electron transfer and the displacement of $(E_{1/2})_{DHAA}$ in the same direction with the C_{DHAA} increase.

In conclusion, we consider the question: why does the quasi-reversible $C_rE_{qr}C_i$ mechanism with the irreversible transfer of the first electron and with the preceding and the following r.d.s. (process (6)) take place, instead of the reversible C_rE_r mechanism with the reversible electron transfer and with the preciding r.d.s. (process (1))? This can be explained by the considerable increase of the rate constant k'_{+1} in process (6) in comparison with the very low rate constant k_{+1} ($k_{+1} = k_{-5}$; Table I) in process (1).

CONCLUSIONS

1. Quantitative substantiation of the difference of the intermediate stages in processes DHAA + $2e^-$ + $2H^+$ $\longrightarrow$ AA and AA – $2e^-$ – $2H^+$ $\longrightarrow$ DHAA has been given on the basis of the comparison of the rate constants of the preceding r.d.s. for DHAA electroreduction and the rate constants for the following r.d.s. for AA electrooxidation at different pH and the analysis of the wave equation.

2. We used the scheme suggested by Ruiz *et al.*,[15] supplemented with the stage of two parallel electron transfers for the description of the DHAA electroreduction process.

3. On the basis of this scheme, the quasi-reversible $C_rE_{qr}C_i$ mechanism of DHAA electroreduction with the preceding reversible r.d.s. and the follow-

ing irreversible r.d.s. and with the quasi-reversible transfer of the first electron in two parallel stages, with and without participation of the proton, has been proposed.

4. The $(E^{r}_{1/2})_{DHAA}$ for the reversible electron transfer (low current density) and $(E^{i}_{1/2})_{DHAA}$ for the completely irreversible transfer of the first electron (high current density) and the corresponding transfer coefficients have been found.

5. On the basis of the proposed mechanism, the explanations for: the $(E^{r}_{1/2})_{DHAA}$ displacement to negative potentials, the influence of pH and DHAA adsorption on the kinetics and the existence of the directly proportional interdependence between the limiting kinetic current and the DHAA concentration have been given.

Acknowledgement. – The authors would like to express their gratitude to Prof. J. J. Ruiz for valuable discussion and for supplying some initial experimental data.

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SAŽETAK

Mehanizam redukcije dehidro-L-askorbinske kiseline na kapajućoj živinoj elektrodi

Yakov I. Tur'yan i Ron Kohen

Dokazano je da su međuprodukti polarografske redukcije dehidro-L-askorbinske kiseline u L-askorbinsku kiselinu i oksidacije L-askorbinske kiseline u dehidro-L-askorbinsku kiselinu različiti. Utvrđeno je da se redukcija može opisati mehanizmom $C_rE_{qr}C_i$. Kemijska reakcija koja prethodi redoks-reakciji reverzibilna je, a slijedi je ireverzibilna. Prijenos prvog elektrona je kvazireverzibilan i odvija se u dva usporedna procesa od kojih samo prvi uključuje protonaciju.