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# Kinetics and Equilibrium of the Dehydration-Hydration and Recombination-Dissociation Reactions of Glyoxylic Acid Investigated by Electrochemical Methods

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Equilibrium constants of the glyoxylic acid hydration have been defined more precisely taking into account the values of the DC polarographic limiting kinetic current and the dimerization effect. For the correct calculation of the rate constants for the glyoxylic acid dehydration and recombination reactions, the diffusion contribution of the dehydrated anions into the limiting kinetic current of the first and total DC polarographic waves was considered and the concept of the preceding consecutive rate determining reactions of the dehydration and recombination was used. The rate constants from the DC polarographic data have been obtained that are close to the ones from the pulse polarographic and spectrophotometric data. On the basis of a comparison with the linear-sweep voltammetric data, intermolecular catalysis of the dehydration reaction was noted. The recombination stage corresponds to protonation of the carboxylate group. The fast intramolecular protonation of the carbonyl group after the recombination stage has been considered.

## INTRODUCTION

Kinetics and equilibrium for the glyoxylic acid (GA) dehydration-hydration and recombination-dissociation reactions are important for biochemistry (metabolic processes[1]), electrochemistry (reduction of carbon dioxide,[2,3] theory of the antecedent electrode chemical reactions[4–14]) and other fields. Electrochemical methods for the investigation of these reactions have been used more often[4–19] than nonelectrochemical methods.[20–25]

These reactions in the bulk of aqueous solutions for monomer[4–22] and dimer[19] forms of GA are described by Schemes (1) and (2), respectively.

$$\begin{tikzcd}
& \overset{1}{\mathrm{A}^-} \arrow[r, shift left, "{+\mathrm{H}^+;k_{1,2}}"] \arrow[d, shift right, "{+\mathrm{H_2O} \atop k_{1,4}}"'] & \overset{2}{\mathrm{HA}} \arrow[l, shift left, "{k_{2,1};-\mathrm{H}^+}"] \arrow[d, shift right, "{+\mathrm{H_2O} \atop k_{2,3}}"'] \\
\underset{5}{\mathrm{A}^*\cdot\mathrm{H_2O}^{2-}} \arrow[r, shift left, "{+\mathrm{H}^+;k_{5,4}}"] & \underset{4}{\mathrm{A}\cdot\mathrm{H_2O}^-} \arrow[l, shift left, "{k_{4,5};-\mathrm{H}^+}"] \arrow[u, shift right, "{k_{1,4} \atop -\mathrm{H_2O}}"'] \arrow[r, shift left, "{+\mathrm{H}^+;k_{4,3}}"] & \underset{3}{\mathrm{HA}\cdot\mathrm{H_2O}} \arrow[l, shift left, "{k_{3,4};-\mathrm{H}^+}"] \arrow[u, shift right, "{k_{3,2} \atop -\mathrm{H_2O}}"']
\end{tikzcd} \qquad (1)$$

$$\overset{6}{\mathrm{HA_2\cdot 2H_2O^-}} \underset{+\mathrm{H}^+}{\overset{-\mathrm{H}^+}{\rightleftarrows}} \overset{4}{\mathrm{2A\cdot H_2O^-}} \underset{-2\mathrm{H}^+}{\overset{+2\mathrm{H}^+}{\rightleftarrows}} \overset{3}{\mathrm{2HA\cdot H_2O}} \rightleftarrows \overset{7}{\mathrm{H_2A_2\cdot 2H_2O}} \qquad (2)$$

where: 1 – $HC(O)COO^-$; 2 – $HC(O)COOH$; 3 – $HC(OH)_2COOH$; 4 – $HC(OH)_2COO^-$; 5 – $HC(O^-)(OH)COO^-$; 6 – $HC(OH)_2COOH \cdot HC(OH)_2COO^-$; 7 – $HC(OH)_2COOH \cdot HC(OH)_2COOH$. The corresponding rate constants are indicated in Scheme (1) as well. It should be noted that, unlike some other $\alpha$-keto acids,[26] the keto-enol equilibrium is absent in the case of GA.

For the first time the dehydration rate constants ($k_{4,1}$; Scheme (1)) and the recombination rate constants ($k_{1,2}$) were calculated by us[9,10] on the basis of the DC polarographic data[4] and the linear–sweep voltammetry data.[8] Subsequently, a lower (3–4 times) value of $k_{4,1}$ has been obtained from pulse polarographic[11] and spectrophotometric (scavenger technique)[22,23] methods. Our calculations of $k_{4,1}$ by the same technique[9,10] on the basis of DC polarography data[5,13,14] gave discrepancy analogous to the data.[11,22,23] All these calculations were carried out for the same hydration equilibrium constant.[8]

In the present work, the reasons for the indicated discrepancy are revealed and more correct rate constants of the GA dehydration and recombination as well as the equilibrium constants of the hydration are presented.

## EQUILIBRIUM CONSTANTS

### *Dimerization-Dissociation of Glyoxylic Acid*

Barceza and Mihalyi[19] have determined the equilibrium constants of the GA dimerization by the potentiometric (pH) titration at ionic strength $I = 1$ and 25 °C:

$$K_{4,6} = [\mathrm{HA_2 \cdot 2H_2O^-}] \,/\, [\mathrm{A \cdot H_2O^-}]^2[\mathrm{H^+}] = 1.1 \cdot 10^3 \qquad (3)$$

$$K_{3,7} = [\mathrm{H_2A_2 \cdot 2H_2O}] \,/\, [\mathrm{HA \cdot H_2O}]^2 = 1.2. \qquad (4)$$

For designations of particles see Scheme (1).

Taking into acoount the $K_{4,6}$ value (Eq. (3)) at pH 4.5–11, when anions $A \cdot H_2O^-$ of GA dominate in solution, the GA dimerization is negligible at $C_{GA} \leq 0.2$ M ($C$ is the analytical concentration). At pH ≤ 0.5, when molecules $HA \cdot H_2O$ of GA dominate in solution from the $K_{3,7}$ value (Eq.(4)), it follows that at $C_{GA} \leq 4 \cdot 10^{-2}$ M the GA dimerization is negligible. At the same time, in these conditions (pH ≤ 0.5) at $C_{GA} = 0.9$ M we obtain that the degree of the GA dimerization equals 51%. From these calculations, we can see that, in the conditions of Ref. 8 at pH 9.2 and Refs. 4, 5, 1–14, 22, the GA dimerization is negligible due to the low $C_{GA}$. However, in Ref. 8, the GA dimerization must be taken into account in determination of the equilibrium constant of the HA hydration at $C_{GA} = 0.9$ M (1 M $H_2SO_4$). Corresponding correction to the data[8] will be introduced below.

### *Dehydration-Hydration of Glyoxylic Acid*

Equilibrium constant of the GA anions hydration (Scheme (1)) is:

$$K_{1,4} = [A \cdot H_2O^-] \;/\; [A^-] = k_{1,4} \;/\; k_{4,1} \tag{5}$$

and for molecules

$$K_{2,3} = [HA \cdot H_2O] \;/\; [HA] = k_{2,3} \;/\; k_{3,2}. \tag{6}$$

The reference data on these constants are shown in Table I. It should be noted that the values of $K_{1,4}$ and $K_{2,3}$ obtained in Refs. 20–22 are too low. This conclusion follows from the calculation of the diffusion contribution of the dehydrated $A^-$ anions ($K_{1,4}$) and dehydrated molecules HA ($K_{2,3}$) into the limiting kinetic current of the total wave of GA:[27]

$$\bar{\chi} \cdot [A^-] = \bar{i}_l^{d} \;/\; (1 + K_{1,4}) \tag{7}$$

where $\bar{\chi}$ is Ilkovic's constant; $\bar{i}_l^{d}$ is the average limiting diffusion current. For the instantaneous limiting diffusion current, $\bar{\chi}$ and $\bar{i}_l^{d}$ are replaced by $\chi$ and $i_l^{d}$, respectively, in Eq. (7). In calculation of $\bar{\chi} \cdot [HA]$ in Eq.(7), the $K_{1,4}$ constant should be replaced by $K_{2,3}$. The determination of $\bar{\chi} \cdot [A^-]$ and $\bar{\chi} \cdot [HA]$ or $\chi \cdot [A^-]$ and $\chi \cdot [HA]$ using values $K_{1,4} = 15.1–32.2$ and $K_{2,3} = 1 \cdot 10^2$ from Refs. 20–22 (Table I) showed that the diffusion contributions of $A^-$ and HA are close to, or larger than, the limiting current of the total wave[4,5,13,14] in the definite range of pH 4.5–7.0 for $A^-$ and at pH ≈ 0.5 for HA. This contradicts its kinetic nature and indicates the low (mistaken) values of the used $K_{1,4}$ and $K_{2,3}$. At the same time, the values of $K_{1,4} = 62.5$ (linear-sweep voltammetry)[8] and 72 (pulse polarography),[11] $K_{2,3} = 1.7 \cdot 10^3$ (linear-sweep voltammetry),[8] and $1 \cdot 10^3$ (spectrophotometry)[21] are more correct since the

TABLE I

Equilibrium constants of the glyoxylic acid hydration, 25 °C.

| $K_{1,4}$ | $K_{2,3}$ | Method[a)] | Ref. |
|---|---|---|---|
| – | $(\sim 1 \cdot 10^2)$ | PJ | 20 |
| 62.5[b)] | $1.7 \cdot 10^3$ | LSV | 8 |
| – | $8.3 \cdot 10^2$ | LSV | 8[c)] |
| (16.5) | $\sim 1 \cdot 10^3$ | S | 21 |
| (15.1–32.2) | $(3 \cdot 10^2)$ | S | 22 |
| – | $1.4 \cdot 10^3$ | – | 22[c)] |
| 72.0 ± 1.7 | – | PP | 11 |
| (260)[b)] | – | NMR | 23 |
| (163) | – | NMR | 24 |

a) PJ = Pressure jump; LSV = Linear-sweep voltammetry; S = Spectrophotometry; PP = Pulse polarography; NMR = Nuclear magnetic resonance; b) 22 °C; c) Corrected by us.

diffusion contributions of $A^-$ and HA found on the basis of these constants are considerably lower. This is in agreement with the kinetic nature of the total wave. The reason for the lowered values of $K_{1,4} = 15.1 – 32.2$ calculated in Ref. 22 from the ratio of $k_{4,1}/K_{1,4}$ value[4] is the high (mistaken) $k_{4,1}/K_{1,4}$ value.[4] In calculation of this value,[4] the diffusion contribution of $A^-$ (see below) to the limiting kinetic current of the total wave was not taken into account. The values $K_{1,4} = 260$ and $K_{1,4} = 163$ (Table I) obtained from nuclear magnetic resonance data[23,24] are not accurate since an internal standard should be added to the solution for the determination of this constant. The difference between $K_{1,4}$ values obtained in Refs. 23 and 24 is most likely caused by the different nature of the internal standards used. Moreover, the value of $k_{1,4}$ determined from polarographic or pulse polarographic and spectrophotometric methods would be different if the values of $K_{1,4} = 260$ or 163 were used in the calculation from polarogaraphic data. Constant $K_{1,4}$ should not be used to estimate the value of $k_{1,4}$ from spectrophotometric data.[22,23,25] The $K_{2,3} = 3 \cdot 10^2$ value[22] obtained from the ratio $k_{3,2}/K_{2,3} = 8.34 \cdot 10^{-5}$ s$^{-1}$ (1 M $H_2SO_4$)[4] was calculated inaccurately since the $k_{3,2}{}^{H_2O}$ value[22] instead of the constant of $k_{3,2} = k_{3,2}{}^{H_2O} + k_{3,2}{}^{H}[H^+]$ was used. The catalysts of the acid-base catalysis (*e.g.*, $H^+$, $H_2O$) are indicated by the supperscript. Using the $k_{3,2}{}^{H_2O} = 2.5 \cdot 10^{-2}$ s$^{-1}$, $k_{3,2}{}^{H} = 7.6 \cdot 10^{-2}$ M$^{-1}$ s$^{-1}$ values[22] and $[H^+] = 1.23$ M for 1 M $H_2SO_4$,[28] we calculated the correct value of $K_{2,3} = 1.4 \cdot 10^3$ (Table I). The influence of the HA diffusion contribution can be neglected in this case. We also corrected the $K_{2,3} = 1.7 \cdot 10^3$ value[8] taking into account the dimerization of GA[19] at $C_{GA} = 0.9$ M. As indicated above, the degree of dimerization in these conditions equals 51%. Hence, the correct value of $K_{2,3} = 8.3 \cdot 10^2$.

Thus, it follows from Table I that the $K_{1,4} = 62.5$ value[8] and 72.0 value[11] (the average value from Table IV in Ref. 11) and $(K_{1,4})_{AV}$ is 67 ± 5 and the $K_{2,3}$ $8.3 \cdot 10^2$ value[8] (with our correction), $1 \cdot 10^3$ value[21] and $1.4 \cdot 10^3$ value[22] (with our correction) and $(K_{2,3})_{AV}$ is $(1.1 \pm 0.2) \cdot 10^3$ are the most correct.

### *Recombination-Dissociation of Glyoxylic Acid*

The overall-dissociation constant $K_a$ (Table II) is incompletely concentrated and can be calculated from the expression

$$K_a' = a_{H^+}([A \cdot H_2O^-] + [A^-]) \,/\, ([HA \cdot H_2O] + [HA]). \tag{8}$$

We recalculated it using the activity coefficients for the uni-valent ion[29] (Table II) into the completely concentrated constant $K_a$ (Table II):

$$K_a = [H^+]([A \cdot H_2O^-] + [A^-]) \,/\, ([HA \cdot H_2O] + [HA]). \tag{9}$$

The $K_a$ values at $I$ = 0.3; 0.5; 0.6 (Table II) were obtained from the dependence of p$K_a$ on $I$.

Unfortunately, up to now $K_a$ value was used at $I = 0$ ($K_a = 5.0 \cdot 10^{-4}$) though the investigated solutions had $I > 0$. An exception is Ref. 11, in which the recalculation of $K_a$ ($I = 0$) into $K_a$ ($I = 0.3$) was made similarly to

TABLE II

Dissociation constants of the glyoxylic acid, 25 °C.

| $I$ | $f_{z=1}$ | $K'_a$ a) | $K_a$ b) | $K_{2,1}$ | $K_{3,4}$ | Method c) | Ref. |
|---|---|---|---|---|---|---|---|
| 0 | 1 | $5.0 \cdot 10^{-4}$ | $5.0 \cdot 10^{-4}$ | – | – | C | 15 |
| 0 | 1 | – | – | $1.3 \cdot 10^{-2}$ | – | – | 9, 10 |
| 0 | 1 | $3.5 \cdot 10^{-4}$ | $3.5 \cdot 10^{-4}$ | – | – | Pot | 18 |
| 0.1 | 0.81 | $6.6 \cdot 10^{-4}$ d) | $8.1 \cdot 10^{-4}$ | – | – | Pot | 16 |
| 0.3 | 0.81 | – | $8.8 \cdot 10^{-4}$ | $2.1 \cdot 10^{-2}$ | $8.8 \cdot 10^{-4}$ | – | 11 |
| 0.3 | 0.81 | – | $1.1 \cdot 10^{-3}$ | $1.8 \cdot 10^{-2}$ | $1.1 \cdot 10^{-3}$ | – | e) |
| 0.5 | 0.84 | $1.0 \cdot 10^{-3}$ | $1.2 \cdot 10^{-3}$ | $1.9 \cdot 10^{-2}$ | $1.2 \cdot 10^{-3}$ | Pot | 17 |
| 0.6 | 0.87 | – | $1.3 \cdot 10^{-3}$ | $2.0 \cdot 10^{-2}$ | $1.3 \cdot 10^{-3}$ | – | e) |
| 1.0 | 0.99 | – | $1.4 \cdot 10^{-3}$ | – | – | Pot | 19 |

a) $a_{H^+}$; b) $[H^+]$; c) C = Conductometry; Pot = Potentiometry (pH); d) 20 °C; e) calculated by us.

the recalculation of $K_a$ for pyruvic acid solutions.[30] The $K_a$ values for different ionic strength, based on experimental data for glyoxylic acid, are presented in Table II. These $K_a$ values, together with the average values of $K_{1,4}$ and $K_{2,3}$ selected or corrected by us, were used for the calculation of $K_{2,1}$ and $K_{3,4}$ (Scheme (1)).

Equation for $K_{2,1}$ is:

$$K_{2,1} = [H^+] \cdot [A^-] \ / \ [HA] = k_{2,1} \ / \ k_{1,2} \tag{10}$$

and from Eqs. (5), (6), (9) and (10), we obtain

$$K_{2,1} = K_a \ (1 + K_{2,3}) \ / \ (1 + K_{1,4}). \tag{11}$$

For $K_{3,4}$ (Scheme (1)), we have

$$K_{3,4} = [H^+] \cdot [A \cdot H_2O^-] \ / \ [HA \cdot H_2O] = k_{3,4} \ / \ k_{4,3} \tag{12}$$

and from Eqs. (5), (6), (9) and (12), we have

$$K_{3,4} = K_a K_{1,4} \ (1+K_{2,3}) \ / \ K_{2,3} \ (1+K_{1,4}). \tag{13}$$

From Eq. (13) it follows that since $K_{2,3} >> 1$ and $K_{1,4} >> 1$ (Table I), $K_{3,4} \cong K_a$ (Table II). The $K_{2,3}$ and $K_{3,4}$ values calculated by us (Eqs.(11) and (13)) are shown in Table II.

The eqilibrium constants $K_{1,4}$, $K_{2,3}$, $K_{2,1}$ and $K_{3,4}$ which will be used below are presented in Table III.

## RATE CONSTANTS

In further text, the determination of the rate constants of the GA dehydration and recombination by the DC polarographic method will be considered in more detail. These determinations were based on the limiting ki-

TABLE III

Equilibrium Constants of the glyoxylic acid hydration and dissociation used in this work, 25 °C.

| $I$ | $K_{1,4}$ | $K_{2,3}$ | $K_{2,1}$ | $K_{3,4}$ |
|---|---|---|---|---|
| 0.3 | 67 | $1.1 \cdot 10^3$ | $1.8 \cdot 10^{-2}$ | $1.1 \cdot 10^{-3}$ |
| 0.5 | 67 | $1.1 \cdot 10^3$ | $1.9 \cdot 10^{-2}$ | $1.2 \cdot 10^{-3}$ |
| 0.6 | 67 | $1.1 \cdot 10^3$ | $2.1 \cdot 10^{-2}$ | $1.3 \cdot 10^{-3}$ |

netic current measurement at the GA electroreduction at the mercury dropping electrode. Both average[4–6] and instantaneous[13,14] currents have been investigated.

In order to simplify the kinetic task, we have been limited by the analysis of the two pH ranges: pH ≤ 0.5 when molecules $HA \cdot H_2O$ dominate and pH = 4.5 – 11 when anions $A \cdot H_2O^-$ dominate. The dimerization of GA due to low $C_{GA}$ is negligible (see above).

Depending on pH, either only the total wave of GA (pH ≤ 4.5; pH ≥ 7.5) or the total and first waves (pH 5.0–7.0)[4–7,13,14] were observed. The height of the first wave was decreased with the pH increase from the height of the total wave (pH 4.5) to zero (pH 7.0).

*Limiting Diffusion Current:* This current for GA has not been experimentally obtained to date. Kuta[4] calculated the diffusion coefficient ($D$) for GA on the basis of the $A \cdot H_2O^-$ equivalent conductance and he obtained $D = 1.01 \cdot 10^{-5}\ \mathrm{cm^2\ s^{-1}}$. Then, using Ilkovic's equation,[31] Kuta[4] calculated the limiting average diffusion current of GA. These calculations were used in our work as well.

*Limiting Kinetic Current:* The limiting kinetic current of the total wave at pH ≤ 0.5 corresponds to the scheme:[4]

$$\mathrm{HA{\cdot}H_2O} \xrightleftharpoons[k_{2,3};\ +\mathrm{H_2O}]{-\mathrm{H_2O};\ k_{3,2}} \mathrm{HA} \xrightarrow{+2e^-} \tag{14}$$

and at pH 4.5–11 corresponds to the scheme[4]

$$\mathrm{A{\cdot}H_2O^-} \xrightleftharpoons[k_{1,4};\ +\mathrm{H_2O}]{-\mathrm{H_2O};\ k_{4,1}} \mathrm{A^-} \xrightarrow{+2e^-} \tag{15}$$

The limiting kinetic current of the first wave (pH 5.0–7.0) corresponds to the scheme.[9,10,14]

$$\mathrm{A{\cdot}H_2O^-} \xrightleftharpoons[k_{1,4};\ +\mathrm{H_2O}]{-\mathrm{H_2O};\ k_{4,1}} \mathrm{A^-} \xrightleftharpoons[k_{2,1};\ -\mathrm{H^+}]{+\mathrm{H^+};\ k_{1,2}} \mathrm{HA} \xrightarrow{+2e^-} \tag{16}$$

Kinetic analysis for Schemes (14) and (15), without determination of $k_{3,2}$ and $k_{4,1}$, was carried out by Kuta[4] on the basis of Koutecky's equation[32,33] for average currents. However, this equation cannot be applied to Scheme (16) with the two consecutive rate determining stages. The solution of Koutecky[34] for similar schemes was inaccurate.[35] Therefore, for analysis of Scheme (16), we applied[9,10] the concept of two reaction layers.[36] Later, after the correction of Koutecky's solution,[34] we have obtained[35] the kinetic equation for Scheme (16) ($k_{1,4} >> k_{4,1}$; $k_{2,1} >> k_{1,2}[H^+]$):

$$\frac{\overline{i_1^{d}} - \overline{i_1^{k}}}{\overline{i_1^{k}}}[\mathrm{H^+}] = 1.13\,K_{1,4}\left(\frac{K_{2,1}}{k_{1,2}t_1}\right)^{0.5} + 1.13\left(\frac{K_{1,4}}{k_{4,1}t_1}\right)^{0.5}[\mathrm{H^+}] \tag{17}$$

which practically coincided with the equation for the concept of two reaction layers.[36] In Eq. (17), $\bar{i}_1^{\mathrm{k}}$ is the average limiting kinetic current of the first wave. In the case of GA electroreduction, a simpler equation for Scheme (16) has been obtained[9,10] since $\bar{i}_1^{\mathrm{d}} >> \bar{i}_1^{\mathrm{k}}$ and $\bar{i}_1^{\mathrm{d}} >> \Sigma\bar{i}_1^{\mathrm{k}}$ from Eq. (17):

$$\frac{\sum \overline{i_1^{\mathrm{k}}} - \overline{i_1^{\mathrm{k}}}}{\overline{i_1^{\mathrm{k}}}}[\mathrm{H}^+] = \left(\frac{k_{4,1} \cdot K_{1,4} \cdot K_{2,1}}{k_{1,2}}\right)^{0.5} \tag{18}$$

where $\Sigma\bar{i}_1^{\mathrm{k}}$ is the average limiting kinetic current of the total wave in the pH range (pH 5.0–7.0) at the first wave observation.

Rodriguez - Amaro *et.al*[14] have analyzed the scheme close to Scheme (16) for the first wave and instantaneous current but in a wider pH range. If we are limited by Scheme (16) (pH 5.0–7.0), the solution[14] is close to Eq. (17).

At the same time, all the kinetic equations applied so far in DC polarography for the GA investigation had a common drawback. These equations did not take into account the diffusion contribution to the limiting kinetic current of HA in the case of the total wave (Scheme (14)) and $A^-$ in the case of the total wave (Scheme (15)) and the first wave (Scheme (16)). This contribution was caused by the relatively low hydration equilibrium constant particularly for $A^-$ (Table III) and the relatively low dehydration rate constants. It should be noted that Fond *et. al.*[11] took into account the indicated contribution of $A^-$ in the case of the pulse polarographic study of process (15).

We used the Kuta[4] DC polarographic data obtained from Koutecky's equation[32,33] for Scheme (14) (pH ≤ 0.5), $k_{3,2}/K_{2,3} = 4.32 \cdot 10^{-5}\ \mathrm{s}^{-1}$ (0.5 M $H_2SO_4$), $k_{3,2}/K_{2,3} = 8.34 \cdot 10^{-5}\ \mathrm{s}^{-1}$ (1.0 M $H_2SO_4$). Considering the large $K_{2,3}$ value (Table III), the diffusion contribution of HA to the limiting kinetic current was neglected in the $k_{3,2}$ calculation. Using, together with data[4] for pH ≤ 0.5 (Scheme (14)), the pulse polarographic data obtained by Fonds *et.al.*:[14] $k_{3,2}/K_{2,3} = 2.1 \cdot 10^{-5}$ (0.3 M HCl) the $K_{2,3}$ value (Table III) and from Ref. 28 $[\mathrm{H}^+] = 0.60$ M for 0.5 M $H_2SO_4$ and $[\mathrm{H}^+] = 1.23$ M for 1 M $H_2SO_4$, we obtained the linear dependence of $k_{3,2}$ on $[\mathrm{H}^+]$ for the acid-base catalysis at pH ≤ 0.5

$$k_{3,2} = k_{3,2}^{\mathrm{H_2O}} + k_{3,2}^{\mathrm{H}}\,[\mathrm{H}^+]. \tag{19}$$

The values of the rate constants in the catalysis by $H_2O$ and $H^+$ ions (Eq. (19)) are shown in Table IV.

The technique of the $k_{4,1}$ determination from the total wave at pH 4.5–6.5 (Scheme (15)) should be changed because the diffusion contribution of the $A^-$ anions to the limiting kinetic current of the total wave should be considered. The neglect of this effect is the reason why the $k_{4,1}$ value[4,8–10] (Table IV) is

TABLE IV

Rate constants of the glyoxylic acid dehydration and recombination, 25 °C.

| $k_{3,2}^{H_2O}$ / $s^{-1}$ | $k_{3,2}^{H}$ / $M^{-1}s^{-1}$ | $k_{4,1}^{H}$ / $M^{-1}s^{-1}$ | $k_{4,1}^{H_2O}$ / $s^{-1}$ | $k_{4,1}^{OH}$ / $M^{-1}s^{-1}$ | $k_{4,1}^{Buf_i}$ / $M^{-1}s^{-1}$ | $k_{1,2}$ / $M^{-1}s^{-1}$ | Method a) | Ref. |
|---|---|---|---|---|---|---|---|---|
| – | – | – | $2.3 \cdot 10^{-2}$ | – | – | $2.3 \cdot 10^{10}$ | P | 4, 8–10 |
| – | – | – | $5.9 \cdot 10^{-3}$ | – | – | $2.0 \cdot 10^{10}$ | P | 4 b) |
| – | – | – | $4.4 \cdot 10^{-3}$ c) | – | – | – | P | 5 b) |
| – | – | 29 | – | – | – | $4.8 \cdot 10^{7}$ | P | 14 |
| – | – | – | $6.3 \cdot 10^{-3}$ | – | – | $2.0 \cdot 10^{9}$ | P | 14 b) |
| $4.0 \cdot 10^{-3}$ | $7.0 \cdot 10^{-2}$ | – | – | – | – | – | P; PP | 4, 11 b) |
| – | – | – | – | $1.3 \cdot 10^{4}$ | 3.7 d) | – | P | 4 b) |
| – | – | – | $7.8 \cdot 10^{-3}$ | – | – | $1.4 \cdot 10^{10}$ | PP | 11 |
| – | – | – | – | – | – | $1.1 \cdot 10^{10}$ | PP | 11 b) |
| $2.5 \cdot 10^{-2}$ | $7.6 \cdot 10^{-2}$ | – | $5.5 \cdot 10^{-3}$ | $9 \cdot 10^{3}$ | – | – | S | 22 |
| – | – | $25 \cdot 10^{2}$ | $\leq 6 \cdot 10^{-4}$ | $2.6 \cdot 10^{5}$ | – | – | TJ | 21 |
| – | – | – | $7 \cdot 10^{-3}$ | $(0.5–1.1) \cdot 10^{4}$ | – | – | S | 23 |
| – | – | – | $1.1 \cdot 10^{-2}$ | $2.5 \cdot 10^{4}$ | 0.38 e) | – | S | 25 |
| – | – | – | – | – | 0.11 f) | – | S | 25 |

a) P = Direct current polarography; PP = Pulse polarography; S = Spectrophotometry (scavenger technique); TJ = Temperature-jump; b) Calculated by us; c) 20 °C; d) Buf$_i$ is $H_2BO_3^-$; e) Buf$_i$ is $HPO_4^{2-}$; f) Buf$_i$ is $H_2PO_4^-$.

larger than the ones obtained from the pulse polarographic[11] and spectrophotometric[22,23,25] data (Table IV).

The diffusion contribution of the dehydrated anions $A^-$ to the limiting kinetic current of the total wave can be calculated by Eq. (7). Hence, the purely kinetic part of the total limiting kinetic current or the corrected limiting kinetic current is:[27]

$$(\Sigma \bar{i}_l^{k})_{corr} = \Sigma \bar{i}_l^{k} - \bar{i}_l^{d} / (1 + K_{1,4}). \tag{20}$$

Similarly, for the corrected limiting diffusion current, we obtain Eq. (21):

$$(\bar{i}_l^{\mathrm{d}})_{\mathrm{corr}} = \Sigma\bar{i}_l^{\mathrm{d}} - \Sigma\bar{i}_l^{\mathrm{d}} / (1 + \mathrm{K}_{1,4}). \tag{21}$$

For instantaneous currents, Eqs. (20) and (21) are the same.

From the ratio of the corrected kinetic and diffusion current, applying Koutecky-Weber's Table,[32,33] we calculated the correct $k_{4,1}$ value close to the pulse polarographic[11] and spectrophotometric[22,23,25] data (Table IV). In these calculations, the DC polarographic data (total wave) for the average limiting current[4,5] and instantaneous current[14] were used. In the latter case, the limiting kinetic current of the total wave was leveled to the limiting kinetic current of the first wave at pH 4.2–4.5. Besides, the limiting diffusion current,[14] using Ilkovic's equation and $D = 1.01 \cdot 10^{-5}$ cm$^2$ s$^{-1}$, was corrected and the value of 118 μA was obtained.

In the pH 4.5–6.5 range, the equation of the general acid–base catalysis has the form:

$$k_{4,1} = k_{4,1}^{\mathrm{H_2O}} + k_{4,1}^{\mathrm{H}}[\mathrm{H^+}] + k_{4,1}^{\mathrm{OH}}[\mathrm{OH^-}] + \Sigma k_i^{\mathrm{Buf}_i}[\mathrm{Buf}_i] \tag{22}$$

where $\mathrm{Buf}_i$ is the catalytic component of a buffer. The term with $\mathrm{OH^-}$ concentration at pH ≤ 6.5 is negligible taking into account the rate constant in $\mathrm{OH^-}$ catalysis (Table IV). As it was shown in Ref. 4 and 5 for the pH 4.5–6.5 range[4] and pH 4.5–5.5 range,[5] the limiting kinetic current of the total wave does not depend on pH and the buffer nature. It corresponds to the spectrophotometric data[22,23] (pH 5.0–6.5). Hence, from Eq. (22) for pH 4.5–6.5 range, we obtain

$$k_{4,1} = k_{4,1}^{\mathrm{H_2O}} \tag{23}$$

and the $k_{4,1}$ values in Table IV are shown as $k_{4,1}^{\mathrm{H_2O}}$.

Similar correction in the diffusion contribution of $\mathrm{A^-}$ anions was also carried out by us for the calculation of $k_{4,1}^{\mathrm{OH}}$ and $k_{4,1}^{\mathrm{H_2BO_3}}$ values (Table IV) obtained by Kuta[4] (pH 8.27–9.97; borate buffer) without the indicated correction and as the ratio of $k_{4,1}/K_{1,4}$.

For determination of the rate constant recombination, it is necessary to consider the limiting kinetic current of the first wave depending on pH for both average[4] and instantaneous[14] currents. Eqs. (17) or (18) are not suitable for this purpose because they were obtained[9,10] without considering the diffusion contribution of dehydrated anions.

Correction of the limiting kinetic and diffusion currents of the first wave on the basis of Eqs. (20) and (21) is not possible because anions $\mathrm{A^-}$ are not reduced at the potentials of the first wave. Therefore, to obtain the kinetic equation corresponding to Scheme (16), we have used the concept of two reaction layers[9,10,36] but, in contrast to Refs. 9, 10, 36, the diffusion contribution of $A^-$ anions was taken into account. In this solution, the condition $\mu_1 >> \mu_2$[9,10,36] should be kept ($\mu_1$ is the thickness of the reaction layer for the dehydration stage; $\mu_2$ is the thickness of the reaction layer for the recombination stage). Initial equations for obtaining the final kinetic equation are:[36]

$$\bar{i}_{\mathrm{l}}^{\mathrm{k}} = \bar{i}_{\mathrm{l}}^{\mathrm{d}} - \bar{\chi}\,[\mathrm{A\cdot H_2O^-}]_{\mathrm{s}} \quad ([\mathrm{A\cdot H_2O^-}]_{\mathrm{s}} >> [\mathrm{A^-}]_{\mathrm{s}}) \tag{24}$$

$$\bar{i}_{\mathrm{l}}^{\mathrm{k}} = \bar{a}\mu_1 k_{4,1}\,[\mathrm{A\cdot H_2O^-}]_{\mathrm{s}} - \bar{a}\mu_1 k_{1,4}\,[\mathrm{A^-}]_{\mathrm{s}} + \bar{\chi}\,([\mathrm{A^-}] - [\mathrm{A^-}]_{\mathrm{s}}) \tag{25}$$

$$\bar{i}_{\mathrm{l}}^{\mathrm{k}} = a\mu_2 k_{1,2}[\mathrm{A^-}]_{\mathrm{s}}\,[\mathrm{H^+}] \tag{26}$$

$$\mu_1 = (D/k_{1,4})^{0.5} \tag{27}$$

$$\mu_2 = (D/k_{2,1})^{0.5} \tag{28}$$

$$\bar{a}\,/\,\bar{\chi} = 0.886\,(t_1/D)^{0.5} \tag{29}$$

$$(\Sigma\bar{i}_{\mathrm{l}}^{\mathrm{k}} - \bar{\chi}\,[\mathrm{A^-}])\,/\,(\bar{i}_{\mathrm{l}}^{\mathrm{d}} - \Sigma\bar{i}_{\mathrm{l}}^{\mathrm{k}}) = \bar{a}\mu_1 k_{4,1}\,/\,\bar{\chi}. \tag{30}$$

From Eqs. (5), (7), (10), (24)–(30), taking into account $\bar{i}_{\mathrm{l}}^{\mathrm{d}} >> \Sigma\bar{i}_{\mathrm{l}}^{\mathrm{k}}$ and $\bar{i}_{\mathrm{l}}^{\mathrm{d}} >> \bar{i}_{\mathrm{l}}^{\mathrm{k}}$, we obtain Eq. (31):

$$(\Sigma\bar{i}_{\mathrm{l}}^{\mathrm{k}} - \bar{i}_{\mathrm{l}}^{\mathrm{k}})[\mathrm{H^+}]\,/\,\bar{i}_{\mathrm{l}}^{\mathrm{k}} = (k_{4,1}\cdot K_{1,4}\cdot K_{2,1}\,/\,k_{1,2})^{0.5} + 1.13\,(K_{2,1}\,/\,k_{1,2}\cdot \mathrm{t}_1)^{0.5}. \tag{31}$$

Eq. (31) is confirmed by the experimental data[4] for the first wave: the linear dependence lg $[(\Sigma\bar{i}_{\mathrm{l}}^{\mathrm{k}} - \bar{i}_{\mathrm{l}}^{\mathrm{k}})\,/\,\bar{i}_{\mathrm{l}}^{\mathrm{k}}]$ on pH with the slope equals to one. For $[\mathrm{H^+}]_{1/2}$ (first wave) when $\bar{i}_{\mathrm{l}}^{\mathrm{k}} = \Sigma\,\bar{i}_{\mathrm{l}}^{\mathrm{k}}/2$ from Eq. (31) we can write Eq. (32):

$$k_{1,2} = (K_{2,1}\,/\,[\mathrm{H^+}]_{1/2}^{\,2})\cdot[(k_{4,1}\cdot K_{1,4})^{0.5} + 1.13\,t_1^{-0.5}]^2. \tag{32}$$

From Eq. (32), on the basis of the above found value of $k_{4,1} = k_{4,1}^{\mathrm{H2O}}$ (Table IV) from the total wave, the $[\mathrm{H^+}]_{1/2}$ value for the first wave (activity coefficients for the $[\mathrm{H^+}]$ calculation from pH are shown in Table II) and the $K_{1,2}$ and $K_{1,4}$ values (Table III), we have calculated the rate constant of recombination $k_{1,2}$ (Table IV).

For the equation of the instantaneous limiting kinetic current for the first wave, the initial equations are analogous to Eqs. (5), (7), (10), (24)–(26), (30). However, instead of equations (27)–(29), equations obtained by Smith *et al.*[37] for instantaneous limiting kinetic current should be used in the following form:

$$a\mu_1 k_{4,1} \,/\, \chi = 1.386\ (k_{4,1.} \cdot t \,/\, K_{1,4})^{0.545} \tag{33}$$

$$a\mu_2 k_{1,2}[\mathrm{H}^+] \,/\, \chi = 1.386\ (k_{1,2} \cdot t \,/\, K_{2,1})^{0.545}\ [\mathrm{H}^+]^{1.091}. \tag{34}$$

On the basis of Eqs. (5), (7), (10), (24)–(26), (30), (33), (34), we found

$$(\Sigma i_1^{\mathrm{k}} - i_1^{\mathrm{k}})\ [\mathrm{H}^+]^{1.091} \,/\, i_1^{\mathrm{k}} =$$

$$= K_{1,4}\ (k_{4,1} \cdot K_{2,1} \,/\, k_{1,2} \cdot K_{1,4})^{0.545} + 0.722\ (K_{2,1} \,/\, k_{1,2} \cdot t)^{0.545} \tag{35}$$

and analogously to Eq. (32) we obtain Eq. (36):

$$k_{1,2} = (K_{2,1} \,/\, [\mathrm{H}^+]_{1/2}{}^2)\ [K_{1,4}\ (k_{4,1} \,/\, K_{1,4})^{0.545} + 0.722\mathrm{t}^{-0.545}]^{1.835}. \tag{36}$$

In accordance with Eq. (35), the linear dependence of $\lg[(\Sigma i_1^{\mathrm{k}} - i_1^{\mathrm{k}}) / i_1^{\mathrm{k}}]$ on pH for the first wave with the slope slightly larger than one (1.04) is confirmed by data.[14] From Eq. (36) by using $k_{4,1} = k_{4,1}{}^{\mathrm{H_2O}}$ (Table IV) from the total wave, the $[\mathrm{H}^+]_{1/2}$ value from the first wave[14] and $K_{1,2}$ and $K_{1,4}$ (Table III), we have calculated the value of $k_{1,2}$ for instantaneous currents (Table IV).

In Table IV, the rate constants of dehydration and recombination are shown. Using the corresponding equilibrium constants (Table III), the rate constants of hydration and dissociation can be easily calculated.

## DISSCUSION

The $k_{3,2}{}^{\mathrm{H}}$ values calculated by us using DC polarographic[4] and pulse polarographic[11] data in the wide range of $[\mathrm{H}^+]$ (0.30–1.23 M) are close to the spectrophotometric data[22] (Table IV) that show their reliability. However, $k_{3,2}{}^{\mathrm{H_2O}}$ calculated by us from these data[4,11] is lower than that obtained in Ref. 22 (Table IV). At the same time, the value of $k_{3,2} = 0.11\ \mathrm{s}^{-1}$ calculated by us using DC polarographic data[13] at pH = 0 leads to the $k_{3,2}{}^{\mathrm{H_2O}}$ value closer to the data.[22] Thus, we can at present speak only about the reliability of the constant $k_{3,2}{}^{\mathrm{H}} = (7–8) \cdot 10^{-2}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ (Table IV).

The values of $k_{4,1}{}^{\mathrm{H_2O}}$ calculated by us using DC polarographic data[4,14] are close to the corresponding $k_{4,1}{}^{\mathrm{H_2O}}$ values obtained from the pulse polarographic[11] and spectrophotometric[22,23] data (Table IV). The $k_{4,1}{}^{\mathrm{H_2O}}$ value calculated from the data[5] at 20 °C is a little lower than considered above because the latter ones were obtained at 25 °C. High $k_{4,1}{}^{\mathrm{H_2O}}$ value in Refs. 9, 10 (Table IV) is caused by the absence of correction of the diffusion contribution of anions $\mathrm{A}^-$ to the limiting kinetic current. Thus, the reliable values of $k_{4,1}{}^{\mathrm{H_2O}}$ are $(6–8) \cdot 10^{-3}\ \mathrm{s}^{-1}$ (Table IV). For these rate constants, the thickness of the reaction layer $\mu_1$ (Eq. (27)) is close to the thickness of the diffusion layer. However, due to high concentration $C_{GA}$ ($\bar{i}_1^{d} >> \Sigma\bar{i}_1^{k}$ and $i_l^{d} >> \Sigma i_1^{k}$), the violation of the stationary condition of the diffusion and chemical reaction is negligible. Calculated by Eqs. (27) and (28), $\mu_1$ and $\mu_2$ values support the correlation of $\mu_1 >> \mu_2$ that was used in drawing Eqs. (31) and (35).

The $k_{4,1}^{OH}$ value calculated by us using the DC polarographic data[4] corresponds to the spectrophotometric data[22] (Table IV) and allows the hope that the value $k_{4,1}^{OH} = (0.9–1.3) \cdot 10^4$ $M^{-1}$ $s^{-1}$ is reliable.

It was interesting to compare the $k_{4,1}$ value obtained by Eggins *et al.*[12] using the linear-sweep voltammetry with the $k_{4,1}$ value calculated on the basis of $k_{4,1}^{H_2O}$, $k_{4,1}^{OH}$ and $k_{4,1}^{H_2BO_3}$ (Table IV) from the DC polarographic data.[4] The $k_{4,1} = 1.14$ $s^{-1}$ value was found[12,38] for 0.2 M $H_3BO_4$ + 0.1 M $(CH_3)_4NOH$ (up to pH 9.0). The value of $k_{4,1} = 0.83$ $s^{-1}$ was obtained by us from linear-sweep voltammetric data[12] taking into account the diffusion contribution of $A^-$ (Eqs. (20) and (21)) and $K_{1,4} = 67$ (Table III). The evaluation of $k_{4,1}$ from the Eq. (37) of the acid-base catalysis at pH = 9.0 ($[H_2BO_3^-] \cong 0.05$ M):

$$k_{4,1} = k_{4,1}^{H_2O} + k_{4,1}^{OH}[OH^-] + k_{4,1}^{H_2BO_3}[H_2BO_3^-] \qquad (37)$$

gave $k_{4,1} = 0.32$ $s^{-1}$. It can be believed that the higher $k_{4,1}$ value corresponding to data[12] is caused by higher concentration $C_{GA} = 0.2$ M (salt) while $C_{GA} = 4 \cdot 10^{-3}$ M was used in Ref. 4. Hence, in the conditions of Ref. 12, the intermolecular acid-base catalysis is observed together with the $H_2O$, $OH^-$, $H_2BO_3^-$ catalysis.

Table IV supports the conclusion of Sorensen *et al.*[22] on the unreliability of the $k_{4,1}^{H_2O}$ and $k_{4,1}^{OH}$ values obtained in Ref. 21 by the temperature jump method.

The $k_{1,2}$ constant calculated by us using DC polarographic data[4] corresponds to the value obtained from pulse polarographic data[11] (Table IV). For comparison with other data, the results[11] were recalculated by us on the $[H^+]$ concentration and all the proton donors of the buffer were considered (Table VI in Ref.11). This led to an increase of the rate constant of the recombination in comparison with $H_3O^+$-donor[11] only by ≈20%.

It should be noted that the close value of $k_{1,2}$ obtained from Refs. 9 and 10 to the correct by calculated $k_{1,2}$ value in this work (Table IV) is a random coincidence because in Refs. 9 and 10 the not correct high $k_{4,1}$ ($k_{4,1}^{H_2O}$) value (Table IV) and Eq. (18) without consideration of the diffusion contribution of the $A^-$ anions have been used.

The $k_{1,2}$ value obtained in Ref. 14 is by about three orders lower than the $k_{1,2}$ value[11] and the $k_{1,2}$ value calculated by us from the data[4] (Table IV). This is probably caused by the following reasons: i) use of low values $K_{1,4} = 15.1$ and $K_{2,3} = 3 \cdot 10^2$ (see above) in Ref. 14; ii) neglect in this Ref of the diffusion contribution of the anions $A^-$; iii) neglect of the $k_{4,1}{}^{H_2O}$ value; taking into account that $k_{4,1}{}^{H}$ = 29 $M^{-1}s^{-1}$ from Ref. 14 at pH ≥ 5 the $k_{4,1}{}^{H_2O} >> k_{4,1}{}^{H}[H^+]$. On the basis of our recalculation of the DC polarographic data[14] using Eq. (36), the $k_{4,1}{}^{H_2O}$ value from the total wave (pH 4.2–4.5)[14] and the more correct $K_{1,4}$ value (Table III), the $k_{1,2}$ value from data[14] was found close to that from data[4,11] (Table IV).

Comparison of the obtained $k_{1,2}$ values with the rate constants of recombination of other acids using Bronsted equations[39] shows that: 1) $k_{1,2} = (1–2) \cdot 10^{10}$ $M^{-1}$ $s^{-1}$ is reliable and 2) the adsorption effect of GA on the rate recombination is negligible unlike in the case of phenylglyoxylic acid.[39–41] The recombination corresponds to protonation of the carboxylate group. This stage, along with the preceding dehydration stage, causes the observation of the limiting kinetic current of the first wave at GA electroreduction (pH 5.0–7.0). Fleury *et al.*[42] noted for other $\alpha$-keto acids that the recombination stage connected with the kinetic current is caused by the protonation of the carbonyl group. However, this is contrary to the above indicated Bronsted correlation with the dissociation constants for the carboxyl groups.[39] At the same time, for explanation of the data[42] on the correlation of the half-wave potential and Taft's polar substituent constants in the conditions of the initial protonation of the carboxylate group, it is necessary to assume the following chemical and electrochemical stages of the electrode process (Eqs. (38–41)):

$$HC(OH)_2COO^- \xrightarrow{k_{4,1}{}^{H_2O}} HC(O)COO^- + H_2O \tag{38}$$

$$HC(O)COO^- + H^+ \xrightarrow{k_{1,2}} HC(O)COOH \tag{39}$$

$$HC(O)COOH \rightleftarrows HC(O^+H)COO^- \tag{40}$$

$$HC(O^+H)COO^- + 2e^- + H^+ \rightleftarrows H_2C(OH)COO^- \tag{41}$$

In Schemes (38)–(41), the protonation of the carbonyl group is absent in the stage of recombination (39), as mentioned by Fleury *et al.*[42] Protonation of the carbonyl group is the result of the following fast equilibrium stage (40) of the intramolecular protonation. The limiting kinetic current is caused by only slow stages (38) and (39) because in the conditions of the limiting current, the stage (41) is also fast. However, at the current lower than the limiting current (when the half-wave potential is measured in the case of the GA irreversible wave), stage (41) becomes slow similarly to stages (38) and (39). Hence, the half-wave potential should be dependent on the nature of the polar substituents, including carboxylate-anion, that were observed by Fleury *et al.*[42]

## CONCLUSIONS

1. Values of the limiting kinetic current and the dimerization effect were taken into account for calculation and selection of the correct values of equilibrium constants of the glyoxylic acid hydration reactions.

2. Methods of determination of the rate constants were developed for conditions of the preceding electrode chemical reaction (including consecutive ones) and of the diffusion contribution of a reaction product into the limiting kinetic current.

3. Correction of the rate constants of the glyoxylic acid dehydration and recombination reaction, investigated by the DC polarographic method, was performed. The corrected values are close to the ones obtained by the pulse polarographic[11] and spectrophotometric[22,23] methods for different acid-base catalysts.

4. On the basis of the linear-sweep voltammetric data[12] at high concentration of glyoxylic acid, the intermolecular acid-base catalysis of the dehydration reaction was noted together with the $H_2O$, $OH^-$, $H_2BO_3^-$ catalysis.

5. The recombination reaction corresponds to protonation of the carboxylate group. The fast intramolecular protonation of the carbonyl group after the recombination stage has been considered.

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## SAŽETAK

### Kinetika i ravnoteže reakcija hidriranja-dehidriranja i rekombinacije-disocijacije glioksilne kiseline istražene elektrokemijskim metodama

*Yakov I. Tur'yan*

Konstante ravnoteže hidratacije glioksilne kiseline preciznije su definirane uzevši u obzir vrijednosti graničnih kinetičkih struja dc polarograma te učinak dimerizacije.

Za točno računanje konstanti brzina reakcija dehidriranja i rekombinacija glioksilne kiseline uzet je u obzir doprinos difuzije dehidratiziranih aniona graničnim kinetičkim strujama prvoga i ukupnog dc polarografskog vala. Pri tome je korišten koncept uzastopnih koraka koji prethode reakcijama dehidratacije i rekombinacije i određuju im brzinu. Iz dc polarografskih podataka određene su konstante brzina reakcija koje su slične vrijednostima izračunanima na osnovi pulsno-polarografskih i spektrofotometrijskih podataka. Usporedbom s voltammetrijskim podatcima s linearnim posmikom uočena je intermolekulska kataliza reakcije dehidratacije. Stupanj rekombinacije odgovara protonaciji karboksilatne skupine. Uzeta je u obzir brza intermolekulska protonacija karbonilne skupine poslije rekombinacijskog stupnja.