

POLAROGRAPHIC INVESTIGATION OF THE TAUTOMERIC TRANSFORMATIONS OF β -FORMYLACRYLIC ACID AND OF THE HYDROLYSIS OF ITS ETHYL PSEUDOESTER. I

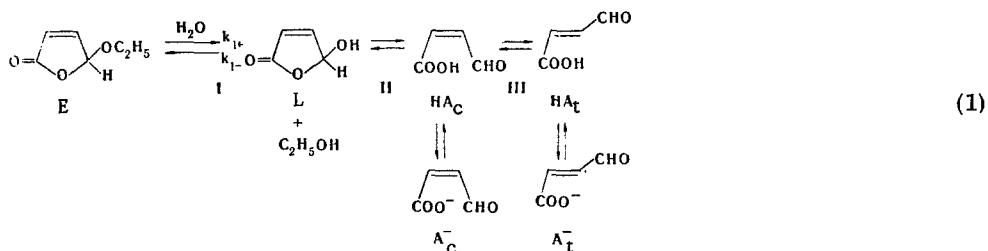
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A polarographic method was used to study the cis (HA_c), trans (HA_t), and lactol (L) forms of formylacrylic acid (FAA) and its ethyl pseudoester (E) and their interconversions. It is shown that the slow step in the process $E \rightleftharpoons L \rightleftharpoons HA_c \rightleftharpoons A_c^-$ is hydrolysis of E. The pH of the solution has a substantial effect on the state of the equilibrium in all of the steps because of the shift in the equilibrium $HA_c \rightleftharpoons A_c^-$. The equilibrium constants of all of the steps and the rate constant of the hydrolysis of E as a function of the pH of the solution were found. The most stable of the three forms of FAA is HA_t . The cis form exists only in solutions. The polarographic reduction of HA_c and HA_t at the ethylene bond proceeds at more positive potentials than the reduction of maleic and fumaric acids. In contrast to HA_c , HA_t does not form a polarographic dissociation curve; this is explained by the closeness of the potentials for the reduction of HA_t and A_t^- .

A number of studies of the synthesis of formylacrylic acid (FAA) and its pseudoester (E) from furan compounds have been made in recent years [1, 2].

Formylacrylic acid in the lactol form and its open cis and trans isomers can be formed by hydrolysis of the ethyl pseudoester of β -formylacrylic acid (Scheme 1), but only the lactol and the trans form of FAA could be isolated from solution [1, 3].



In analogy with the polarographic behavior of maleic, fumaric, and cis- and trans-acetylacrylic acids [4, 5], one might expect that both HA_t and HA_c should be polarographically active, and a polarographic method was therefore used to study processes (I).

The polarographic characteristics of the individually isolated trans form of FAA as a function of the pH of the solution are presented in Figs. 1 and 2. In this case, as below, only the first wave, corresponding to the reduction of the ethylene bond, is considered. The more positive $E_{1/2}$ value of the trans form of FAA as compared with fumaric acid is explained by the more pronounced negative inductive effect of the carbonyl group. In contrast to fumaric acid, the so-called polarographic dissociation curve was not detected in the case of the trans form of FAA (Fig. 1); this is apparently due to the closeness of the potentials for the reduction of HA_t and its anion A_t^- . The trans form of the acid proved to be quite stable over the entire pH range, and a decrease in the limiting current and a change in it with the pH of the solution could be ob-

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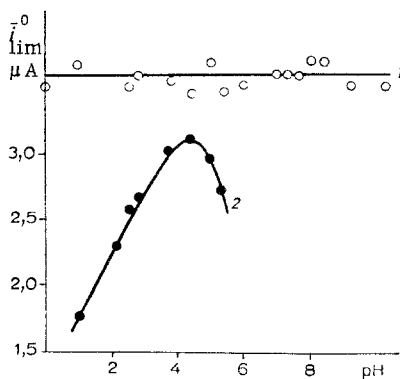


Fig. 1

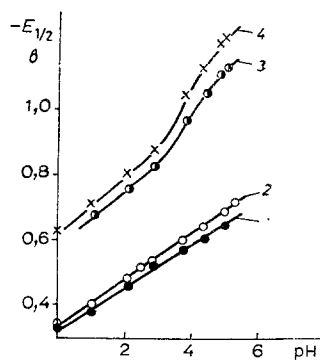


Fig. 2

Fig. 1. Dependence of the limiting current on the pH of the trans form of β -formylacrylic acid ($C_{HA_t} = 4.0 \cdot 10^{-4}$ M): 1) freshly prepared solution; 2) the same solution after 15 days.

Fig. 2. Dependence of the half-wave potentials on the pH: 1) cis form of FAA; 2) trans form of FAA; 3) maleic acid; 4) fumaric acid.

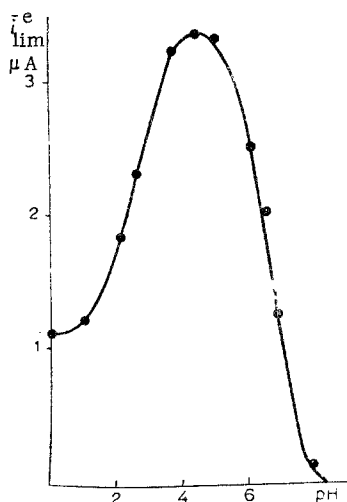


Fig. 3. Dependence of the equilibrium limiting current of the cis form of FAA on the pH (the starting solution was the ethyl pseudoester of FAA; $c_E^0 = 4.0 \cdot 10^{-4}$ M).

served only after 10-15 days (Fig. 1). This may be explained by the slow conversion of the trans form to the cis form and cyclization of the latter.

We were able to investigate the polarographic characteristics of the cis form of FAA in solution, without isolation of HA_c , by hydrolysis of the ester or tautomeric conversion of the lactol. This sort of investigation was facilitated by the fact that the ester and lactol, like other similar substances [6], are polarographically inactive. The polarographic characteristics of $HA_c (+A_c^-)$ after reaching equilibrium in the steps involving hydrolysis of the ester and tautomeric conversion of the lactol to HA_c (the conversion of HA_c to HA_t can be disregarded in moderately acidic solutions and at room temperature) are presented in Figs. 2 and 3.

The $E_{1/2}$ value of the cis form of FAA is more positive than the $E_{1/2}$ value of maleic acid (Fig. 2); as in the case of the $E_{1/2}$ value of trans FAA as compared with the $E_{1/2}$ value of fumaric acid, this can be explained by the stronger negative inductive effect of the carbonyl group. Like the $E_{1/2}$ values of maleic and fumaric acids, the $E_{1/2}$ values of trans- and cis-FAA in the acidic pH range are close (Fig. 2). The \bar{i}_{lim}^e values for HA_c are presented in Fig. 3. Inasmuch as the rate of conversion of the ester to HA_c depended on the pH of the solution (see below), the \bar{i}_{lim}^e value was reached at different times that were longer, the higher the pH of the solution (Table 1).

The dependence of \bar{i}_{lim}^e on pH passes through a maximum (Fig. 3). From the effect on the limiting current of the height of the reservoir containing the mercury it was established that the current at $pH \leq 4$ (rising branch of the curve) is by nature a diffusion current, while at $pH > 5$ the current is by nature a kinetic current. The increase in \bar{i}_{lim}^e as the pH increases can be explained by a shift in the equilibrium to favor the formation of the polarographically active product ($HA_c + A_c^-$) due to dissociation of HA_c , inasmuch as the sum ($HA_c + A_c^-$) is polarographed in this pH region ($pH < 4$), and the current by nature is a diffusion current. The descending branch of the \bar{i}_{lim}^e pH curve, in analogy with maleic and fumaric acids [4], is due to kinetic inhibition in the step involving protonation of A_c^- . This anion is reduced directly at more negative potentials, and in the case of HA_c , in contrast to HA_t , we observe the usual polarographic dissociation curves.

A comparison of the \bar{i}_{lim}^e value of the cis form of FAA with the limiting current of HA_t or maleic acid showed that complete conversion of the ester to the cis form of FAA (89%) is not achieved even at the maximum limiting current (pH 4-5). This conversion comes to only 33% at pH 0-1. After the tautomeric trans-

TABLE 1. Equilibrium and Kinetic Parameters of the Conversion of the Ethyl Pseudoester of α -Formylacrylic Acid to Its Open cis Form ($C_E^0 = 4.00 \cdot 10^{-4}$ M, $C_L^0 = 3.76 \cdot 10^{-4}$ M; 25°C)

pH	Time required to reach equilibrium for the ester	$(\bar{i}_{\lim}^{eq})_L, \mu A$	$(\bar{i}_{\lim}^{eq})_E, \mu A$	k_{1+}, min^{-1}
0.00	~0.4	—	1.13	87
1.00	~0.5	1.2	1.18	36
2.09	~3	1.66	1.85	9.4
2.56	~4	2.16	2.30	8.8
3.29	~4.5	2.83	2.97	8.8
3.78	~5	2.95	3.22	8.8

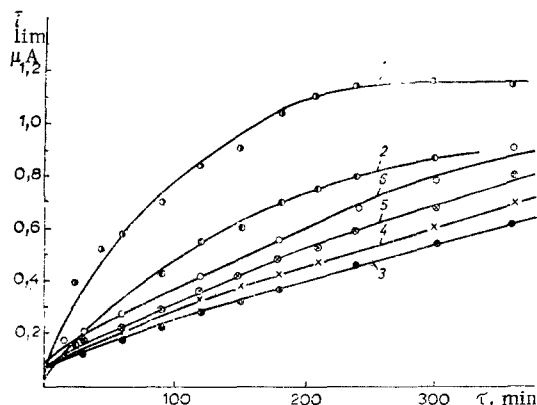


Fig. 4. Change in the limiting current of the cis form of FAA with time during the hydrolysis of the ethyl pseudoester of FAA in solutions with the following pH values: 1) 0.00; 2) 1.00; 3) 2.09; 4) 2.56; 5) 3.29; 6) 3.78.

formation reaches equilibrium, the individually synthesized lactol showed the same polarographic characteristics as in the case of solutions of the ester. The difference here consisted only in the fact that the equilibrium in the case of the lactol was reached considerably more rapidly than in the case of the starting ester.

The difference in the polarographic characteristics of the product of the process $E \rightarrow L \rightarrow$ and the individually investigated HA_t (compare Figs. 1 and 3) additionally indicate that the hydrolysis of the ester terminates with the formation of HA_c ($+A_c^-$) under the selected conditions (pH 0-8).

In the region of the limiting diffusion current (pH < 5) we have

$$i_{\lim}^0 = \kappa C^0; \quad (2)$$

at equilibrium:

$$\bar{i}_{\lim}^{eq} = \kappa ([HA_c]_{eq} + [A_c^-]_{eq}) \quad (3)$$

and at a given time:

$$\bar{i}_{\lim} = \kappa ([HA_c] + [A_c^-]), \quad (4)$$

where the "0" pertains to the starting concentration (C_E^0 for the ester and C_L^0 for the lactol) and the limiting current corresponding to it (\bar{i}_{\lim}^0 was found from the wave of HA_t); the superscript "e" expresses the magnitude of the concentration and the current under equilibrium conditions; κ is the Il'kovich constant, and the symbols of the substances are indicated in Scheme (1).

Using (2) and (3) and the expressions at equilibrium in the case of the starting lactol solutions:

$$K''_{eq} = \frac{[HA_c]_{eq}}{[L]_{eq}}, \quad (5)$$

$$K_a = \frac{[H^+][A_c^-]_{eq}}{[HA_c]_{eq}}, \quad (6)$$

$$C_L^0 = [L]_{eq} + [HA_c]_{eq} + [A_c^-]_{eq}, \quad (7)$$

we find:

$$K''_{eq} = \frac{\bar{i}_{\lim}^{eq} [H^+]}{(\bar{i}_{\lim}^0 - \bar{i}_{\lim}^{eq}) \cdot ([H^+] + K_a)}, \quad (8)$$

$$K_a = \frac{[H^+] \{ \bar{i}_{\lim}^{eq} K''_{eq} (\bar{i}_{eq}^0 - \bar{i}_{eq}) \}}{K''_{eq} (\bar{i}_{\lim}^0 - \bar{i}_{\lim}^{eq})}. \quad (9)$$

From the same equations [(2) and (3)] and also using (5) and (6) and the expressions at equilibrium in the case of the starting ester solutions

$$K'_{eq} = \frac{[L]_{eq} [\tilde{A}]_{eq}}{[E]_{eq}}, \quad (10)$$

$$C_E^0 = [E]_{eq} + [L]_{eq} + [HA]_{ceq} + [A_c^-]_{eq}, \quad (11)$$

$$[Al]_{eq} = [L]_{eq} + [HA_c]_{eq} + [A_{II}^-]_{eq}, \quad (12)$$

we find

$$K'_{eq} = \frac{(\bar{i}_{lim}^{eq})^2 \cdot f \cdot (1+f)}{\bar{\alpha}(\bar{i}_{lim}^0 - (1+f) \cdot \bar{i}_{lim}^{eq})}, \quad (13)$$

where

$$f = \frac{[\text{H}^+]}{K_{\text{eq}}''([\text{H}^+] + K_a)}. \quad (14)$$

In the acidic pH range (0-1) Eq. (8) is simplified ($[\text{H}^+] \gg K_a$), because $i_{\text{lim}}^{\text{eq}}$ is practically independent of the pH (Fig. 3):

$$K''_{eq} = \frac{\bar{i}_{lim}^{eq}}{\bar{i}_{lim}^0 - \bar{i}_{lim}^{eq}}. \quad (15)$$

The K_{eq} value (0.55 ± 0.05) was determined by means of (15) in the case of the starting lactol solution (pH 1, $i_{\text{lim}}^0 = 3.38 \mu\text{A}$, $i_{\text{lim}}^{\text{eq}} = 1.20 \mu\text{A}$). Using this value and the $i_{\text{lim}}^{\text{eq}}$ values (pH 2.09–3.29) for the starting lactol solution, on the basis of (9) we found $K_a = (5.4 \pm 1.0) \cdot 10^{-3}$ (Table 1).

The K'_{eq} value was calculated from (13) and (14) for quite acidic solutions (pH 0-1) of the ester, inasmuch as in this case the accuracy in finding K'_{eq} increased owing to the high equilibrium concentration of the ester: $K_{eq} = (1.8 \pm 0.1) \cdot 10^{-3}$.

It follows from a comparison of $(K_a)_{HA_c}$ with $(K_a)_{MA}$ (MA is maleic acid) that $(K_a)_{HA_c} < (K_a)_{MA}$; this can be explained by reinforcement of the first-stage dissociation of maleic acid due to hydrogen bonding and the opposing effect of the hydrogen bond in the case of the cis form of FAA. In the cis form of FAA this effect apparently prevails over the negative inductive effect of the carbonyl group, which reinforces dissociation.

Since the equilibrium was reached rapidly in the case of the starting lactol, it can be assumed that the slow step in the conversion of the ester to $(\text{HA}_C + \text{A}_C^-)$ (Scheme 1) is the reversible hydrolysis step (I):



Steps II and III are in equilibrium. Despite the presence of steps II and III, it can be shown that Scheme (16) is described by the second-order equation of a reversible reaction [7] under the condition of substitution of the alcohol concentration ($[A1]$) into this equation:

$$k_{1+} = \frac{2.3[A^1]_{eq}}{t(2C_F^0 - [A^1]_{eq})} \cdot \lg \frac{C_F^0[A^1]_{eq} + [A^1] \cdot (C_F^0 - [A^1]_{eq})}{C_F^0([A]_{eq} - [A^1])} \quad (17)$$

On the basis of (3)-(6), (10), and (12) and considering that $C_E^0 \gg C_E^0 - [Al]_{eq}$ for the investigated system, we find from (17) at constant pH $[Al]_{eq} = (3.5-3.8) \cdot 10^{-4}$ M):

$$\lg (\bar{i}_{11m}^{\text{eq}} - \bar{i}_{11m}) = \text{const} - \frac{(2C_E^0 - [Al]_{\text{eq}})\bar{k}_{i+}}{2.3[Al]_{\text{eq}}} t. \quad (18)$$

Thus, the investigated process (16) is formally described by the first-order equation of a reversible reaction. It should be noted that this conclusion remains in force if one also takes into account the presence of a certain amount of ethyl alcohol (as well as L and HA + A⁻) in the starting ester (Fig. 4). In this case, because [Al]_{eq} ≫ [Al]_{in} ([Al]_{in} = [0.8–1.9] · 10⁻⁵ M) in our experiments, Eq. (18) remains unchanged [8]. The subscript "in" pertains to time t = 0.

Equation (18) is confirmed by the experimental data (Fig. 5) — by the linear dependence of $\log (\bar{i}_{\text{lim}}^{\text{eq}} - \bar{i}_{\text{lim}})$ on t at constant pH. The hydrolysis rate constant was found from the slope of these lines (Table 1).

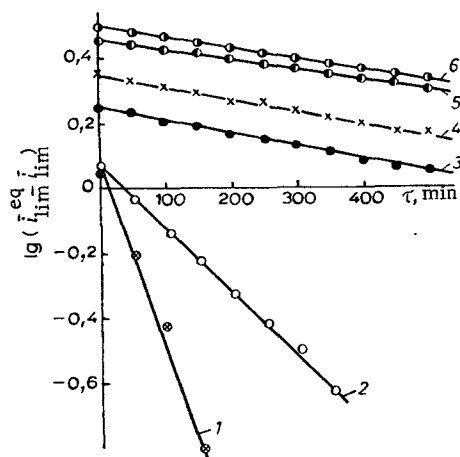


Fig. 5. Verification of Eq. (18) at the following pH values: 1) 0.00; 2) 1.00; 3) 2.09; 4) 2.56; 5) 3.29; 6) 3.78.

2-10. An LP-60 electronic polarograph (Czechoslovakia) and a thermostated (at $25 \pm 0.2^\circ\text{C}$) cell with a capillary ($m = 3.03 \text{ mg/sec}$ and $t = 2.78 \text{ sec}$ when $E = -1.0 \text{ V}$ relative to an external saturated calomel comparison electrode) were used. The oxygen was removed by bubbling purified nitrogen through the solutions. The concentrations of the compounds in the polarographic cell were as follows: C_{E^0} and $C_{HA_t^0} = 4.0 \cdot 10^{-4} \text{ M}$, and $C_L^0 = 3.76 \cdot 10^{-4} \text{ M}$. The $(i_{\text{lim}}^0)_{HA_t}$ value was $3.60 \mu\text{A}$.

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The constancy of the rate constant at pH 2.1-3.8 indicates compensation for the effects of a change in the concentrations of the basic and acidic catalysts (the components of the buffer mixture) as the pH of the solution changes. At pH < 2, specific acid catalysis has a stronger effect.

EXPERIMENTAL

The ester was synthesized by the method in [9], and samples from the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR were also used. The purity of the ester was monitored by means of IR spectroscopy. The trans form of FAA and the lactol were obtained by the method in [1].

The study of the polarographic characteristics of HA_c and HA_t and the investigation of the kinetics (by recording the polarograms at different times) and of the equilibrium of the reaction (Scheme 1) were performed in 1 M HCl, 0.1 M HCl + 1 M KCl, and in universal buffer solutions (+1 M KCl) with pH