THE POLAROGRAPHIC BEHAVIOR OF GEOMETRICALLY ISOMERIC ACIDS

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According to Auwers and Wissebach's data [1], of two geometric isomers the trans-isomer, as a rule, is distinguished by a lower density and a smaller refractive index than the cis-isomer; however, the esters of tiglic and angelic acids show the opposite relationships. According to Langseth [2], trans-forms always have a higher melting point than the cis-forms. Stoermer and Heymann [3], stated that the trans-isomers of α-chloro-, β-chloro-, α-bromo- and dibromocinnamic acids melt at higher temperatures and are less soluble in water than the cis-forms and, at the same time, they noted that, on the contrary, the cis-forms of β-bromo-cinnamic and dichlorocinnamic acids are less soluble in water and have higher melting points than the trans-forms. In the same way, the melting point does not indicate either a cis- or a trans-configuration for the esters of halogen substituted cinnamic acids, as many of the trans-forms are compounds with lower melting points than those of the corresponding cis-forms [4].

Attempts were made to use spectographic data for determining the structure of crotonic acids. However, Auwers [5] considered that the configuration of stereoisomers could not be determined accurately from spectrographic investigations.

We decided to use the indices of the polarographic behavior of geometric isomers in investigating their structure, considering that the difference in the free energy of reduction of isomers must affect their capacity for reduction at an electrode. In passing, we determined the conditions for the quantitative analysis of mixtures of cis- and trans-isomers, which are, generally speaking, isolated with difficulty and, therefore, are difficult to analyze quantitatively by all the methods which require a separation of the mixture's components.

We used geometrically isomeric carboxylic acids of the ethylene series for our investigations. Of these, only maleic and fumaric acids had previously been subjected to a thorough polarographic investigation [6–13]. All the authors noted that maleic acid was reduced at a lower (in absolute value) potential than fumaric acid and in different media the difference in reduction potentials varied from 0.05 to 0.5 v.

Citraconic and Mesaconic acids

Citraconic acid was synthesized by Shriner, Ford and Roll's method [14]. Mesaconic was prepared from citraconic acid by boiling the latter with dilute nitric acid and subsequently evaporating the solution till the appearance of red vapor [15]. After recrystallization from water, the acid had m. p. 201°.

We used potassium chloride, disodium hydrogen phosphate, citric acid, boric acid, sodium hydroxide and hydrochloric acid of analytical purity as indifferent electrolytes. The dry salts were first recrystallized. The mercury for the dropping electrode was purified by the method described by Mislovitser [16]. McIlvain's buffer mixtures on 1 N potassium chloride solution were used to establish the effect of pH on the polarographic behavior of the acids.

The polarographic investigations were carried out with a visual polarograph M-7-2000. A saturated calomel electrode was used as the anode (all potential values are given in relation to this anode). The capillary characteristic (at m=1.12 mg/sec. and t=5 sec.) $m^{2/3} \cdot t^{1/6} = 1.41$ mg$^{2/3}$·sec$^{1/2}$. The galvanometer sensitivity was 1.37×10^{-8} A/mm. All determinations were carried out in a thermostat at 25 ± 0.2°.

Both the citraconic and mesaconic acids gave clear polarographic waves in the pH interval from 0.02 to 3.38. As backgrounds with pH from 3.38 to 6.62 each acid gave two waves; as the pH increased the first wave (at the more positive potential) decreased in height and finally disappeared; the second wave (at the more negative potential) increased in height and at pH > 6.62 only the second wave remained. Neither the citraconic or mesaconic acids were reduced at a dropping mercury cathode at pH = 9 and above.

As the pH of the medium increased, the half-wave potentials of both acids were displaced towards more negative values (Table 1). In all the range of pH values investigated, the half-wave potentials of both acids were found to be very close, so that when the two were present in the solution, the waves of both acids combined into one wave.

The coefficient of proportionality between the diffusion current and acid concentration in solutions of 0.1 N HCl was 4.46 μA/mmole/liter for citraconic and 6.40 μA/mmole/liter for the mesaconic acid.

The effect of substituting aqueous alcohol and alcohol media for the aqueous one is clearly seen from the data in Table 2. A 1 N hydrochloric acid solution was used as background for this series of experiments.

TABLE 1

pH	Citraconic acid				Mesaconic acid			
	1st wave		2nd wave		1st wave		2nd wave	
	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)
0.02	—0.61	36.99	—	—	—0.68	41.11	—	—
1.14	—0.68	45.21	—	—	—0.72	57.54	—	—
2.55	—0.80	46.63	—	—	—0.88	54.80	—	—
3.38	—0.81	24.66	—1.01	21.92	—0.92	21.92	—1.15	28.77
5.42	—0.92	19.18	—1.17	28.77	—0.98	15.33	—1.22	23.29
6.62	—1.17	9.59	—1.42	31.51	—1.21	5.48	—1.45	11.64
7.50	—	—	—1.51	39.77	—	—	—1.45	3.08
8.00	—	—	—1.51	32.88	—	—	—1.45	3.56

TABLE 2

Alcohol concentration (in %)	Citraconic acid		Mesaconic acid	
	$E_{1/2}$	i_d (μA)	$E_{1/2}$	i_d (μA)
0	—0.62	37.88	—0.69	44.69
25	—0.68	22.26	—0.79	25.62
50	—0.72	26.28	—0.86	19.86
75	—0.75	24.25	—0.96	20.13
100	—0.77	23.29	—	—

The concentrations of the acids investigated were equal to $1 \cdot 10^{-3}$ M in all the experiments.

Polarographic investigations of citraconic and mesaconic acids in various media showed that citraconic acid was polarographed as well in aqueous as in aqueous alcohol and alcohol media, while mesaconic acid was readily polarographed in water, but was not polarographed at all in anhydrous alcohol.

The relation between diffusion current and concentration was determined for all aqueous alcohol backgrounds with 1 N hydrochloric acid (Table 3). In all cases direct proportionality was observed between the magnitude of the diffusion current and acid concentration.

TABLE 3

Medium	$\frac{i_d}{C}$ for acids $\left(\frac{\mu A}{\text{mmole} \cdot \text{liter}}\right)$	
	citraconic	mesaconic
Water	3.790	4.430
25% alcohol	2.386	2.491
50% alcohol	2.618	1.985
75% alcohol	2.469	2.116
100% alcohol	3.057	—

The data in Table 2 show that the half-wave potentials of both acids, in 1 N hydrochloric acid in 75% aqueous alcohol solution, differ by 0.2 v, which makes it possible to determine citraconic and mesaconic acids polarographically when they are present together. Under these circumstances, two definite waves were obtained, one of which (at the more positive potential value) was the citraconic acid wave and the other (with the more negative potential) was the mesaconic acid wave. The half-wave potentials did not depend on acid concentration.

In checking the method with standard preparations, quite satisfactory results were obtained: the errors in determination lay within the limits of ± 2.4% of the true amount of each acid in the mixture.

TABLE 4

pH	Cis-aconitic acid				Trans-aconitic acid			
	1st wave		2nd wave		1st wave		2nd wave	
	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)
0.02	—0.54	30.14	—	—	—0.59	32.88	—	—
1.14	—0.65	30.82	—	—	—0.68	35.62	—	—
2.35	—0.74	32.56	—	—	—0.78	36.30	—	—
3.45	—0.85	39.93	—	—	—0.90	40.41	—	—
5.44	—1.02	16.44	—1.32	15.07	—1.03	18.49	—1.40	15.75
6.31	—1.05	10.27	—1.35	12.53	—1.15	2.74	—1.45	11.64
7.70	—1.25	6.16	—1.54	8.22	—1.27	1.03	—1.73	10.96
8.50	—1.33	4.79	—1.66	7.53				

TABLE 5

Alcohol concentration (in %)	Cis-aconitic acid		Trans-aconitic acid	
	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)
0	—0.54	30.14	—0.59	32.88
25	—0.61	23.29	—0.77	25.34
50	—0.63	10.96	—0.82	17.81
75	—0.67	9.97	—0.88	15.09
	—0.59	10.96	—0.81	15.07

Cis- and Trans-Aconitic Acids

Trans-aconitic acid was prepared from citric acid by V. Bruce's method [14]. Its colorless crystals had m. p. 180°. Aconitic acid anhydride was prepared from the trans-aconitic acid by Anschutz and Bertram's method [17], and the cis-aconitic acid was prepared from the anhydride by Malakhovsky and Maslovsky's method [18]. Fine, needle-like crystals were obtained with m. p. 122°.

Both geometrically isomeric acids gave definite polarographic waves in the range of pH values from 0.02 to 5.44; at pH from 5.44 to 8.5 each of the acids gave two waves; as the pH increased the first wave (more positive) decreased in height; the second also decreased as regards absolute height, although it remained greater than the first. As the pH of the medium increased the half-wave potentials of both acids were displaced towards more negative values (Table 4). Over all the range of pH values investigated, the values of the half-wave potentials were found to be very close, with the cis-isomer being reduced at a somewhat more positive potential than the trans-isomer. When both isomers were present in the solution, their waves combined into one overall wave.

TABLE 6

pH	Cis-cinnamic acid		Trans-cinnamic acid	
	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)
0.02	Not polarographed		—1.21	4.66
1.14	Not polarographed		—1.29	5.82
2.00	—0.80	0.19	—1.37	6.03
3.00	—0.96	0.22	—1.38	6.03
4.00	—1.18	0.44	—1.41	6.99
5.00	—1.50	1.44	—1.56	4.93
6.05	—1.56	1.03	—1.59	4.66
6.90	—1.61	0.62	—1.66	3.70
8.20	—1.67	0.19	—1.67	1.37

TABLE 7

Alcohol concentration (in %)	Cis-cinnamic acid		Trans-cinnamic acid	
	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)
0	—1.42	1.44	—1.40	2.88
25	—1.42	0.96	—1.40	1.58
50	—1.51	0.79	—1.56	1.85
75	Not	polarographed	—1.55	2.06
100	„	„	—1.60	3.49

TABLE 8

Alcohol concentration (in %)	Isocrotonic acid		Crotonic acid	
	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)
0	—1.57	2.329	—1.60	2.466
25	—1.43	2.329	—1.45	1.781
50	—1.40	0.822	—1.45	1.370
75	—1.39	0.959	—1.45	1.165
100	—1.42	0.411	Not polarographed	

Cis-aconitic acid was not reduced at a dropping mercury cathode at pH 9 and above, while trans-aconitic acid stopped being polarographed at pH 8.5.

Table 5 gives the values of half-wave potentials of both isomers in relation to the alcohol content in a background, 1 N with hydrochloric acid. The separate determination of cis- and trans-aconitic acids was possible when both were present in 50% alcohol, as their $E_{1/2}$ differed by 0.2 v. In solutions with higher alcohol concentrations, the proportionality between diffusion current and acid concentration was upset, making their quantitative determination difficult.

Our experiments showed that in 1 N hydrochloric acid in 50% alcohol with both cis- and trans-aconitic acids present, two waves were actually produced, the first belonging to cis-aconitic and the second to trans-aconitic acid. The half-wave potentials did not depend on acid concentration.

The diffusion currents were proportional to the concentrations of these acids in the mixture. The proportionality coefficient was equal to 1.067 ± 0.025 μA/mmole/liter for the cis-acid and 1.749 ± 0.058 μA/mmole/ /liter for the trans-acid.

We checked the polarographic method of determining cis- and trans-aconitic acids when both were present in solution, with artificially made up mixtures of definite composition. The error in determination lay within the limits of ± 2.6%.

Cis- and Trans-Cinnamic Acids

Normal cinnamic acid, which is a trans-isomer, was polarographed by Semerano and Cisini [19] in a 0.1 N solution of NH_4Cl in 50% alcohol. The reduction potential was found to be 1.46 v. The latest and quite thorough work devoted to the polarographic behavior of cinnamic acid is that of Ono Shikata and Hayasi Tadao [20]. They polarographed cinnamic acid in 50% aqueous dioxane solutions at various pHs in the presence of alkali and alkaline earth metal chlorides. In neutral solutions cinnamic acid gave two waves with $E_{1/2} = -1.5$ and -2.0 v. The height of the first wave decreased when alkali was added. One wave was observed in a 0.1 N solution of lithium chloride and the authors considered that it corresponded to the reduction of the cinnamic acid anion. Cinnamic acid was not reduced in 0.1 N HCl but in 0.01 and 0.001 N HCl it again gave two waves, the first, according to the authors, corresponding to the reduction of the cinnamic acid anion, increased greatly with increase in HCl concentration while, at the same time, the second wave, corresponding to the reduction of the $C=C$ bond, decreased. We consider that such an explanation of the behavior of cinnamic acid is improbable: the degree of dissociation of weak cinnamic acid ($K=3.6 \cdot 10^{-5}$) must fall rapidly with an increase in HCl concentration, and the wave, corresponding to anion reduction, must decrease rather than increase.

We found no data in the literature on the polarographic behavior of cis-cinnamic acid.

We used trans-cinnamic acid of analytical purity with m. p. 132°. Cis-cinnamic acid was prepared from the trans-cinnamic. For this purpose, it was brominated, then the HBr was carefully split off giving, as a result, phenylpropiolic acid with m. p. 137°. By hydrogenating the phenylpropiolic acid on a palladium catalyst, we obtained cis-cinnamic acid. For purification it was converted into the aniline salt which was recrystallized from acetone and decomposed with hydrochloric acid. It had m. p. 68° [21].

The investigation of the polarographic behavior of both geometric isomers of cinnamic acid in aqueous buffer solutions in a range of pH values from 0.02 to 9 gave the following results: cis-cinnamic acid was not reduced at a dropping mercury cathode at a pH less than 1.14; neither the cis- nor the trans-cinnamic acids gave polarographic waves at pH = 9 or higher; both acids were reduced at other pH values; the cis-form was reduced at much more positive values of half-wave potentials in acidic media up to pH 4 than the trans-form; the half-wave potentials of both acids became very close at pH = 5 and higher (Table 6). As the pH of the medium increased, the half-wave potentials of both acids were displaced towards more negative values.

With equal concentrations in the solutions ($1 \cdot 10^{-3}$ m), trans-cinnamic acid gave much higher waves than cis-cinnamic acid over all the range of pH values that were checked. Due to this, even in the pH range of 2 to 4 in which the half-wave potentials of the two isomers differed by 0.23 –0.57 v, and would have, it seemed, made it possible to determine them quantitatively together, this was, however, actually impossible due to the small values of the diffusion current for cis-cinnamic acid.

The effect of substituting aqueous alcohol and alcohol media for the aqueous medium on the polarographic behavior of cinnamic acids was investigated in 0.1 N solutions of NH_4Cl, as the cis-cinnamic acid was not reduced in hydrochloric acid media. The data obtained for $1 \cdot 10^{-3}$M solutions are given in Table 7. With an increase in alcohol content, the half-wave potentials of both isomers were displaced towards negative values. The diffusion current for cis-cinnamic acid decreased evenly with increase in alcohol content so that at an alcohol % of 75–100 it did not give any diffusion waves. Proportionality between diffusion current and concentration was observed only in those solutions where the alcohol concentration in the background was not less than 50%. We established with special experiments that even with both isomers present together in a solution, the proportionality between diffusion current and concentration was maintained by each of them.

A determination of the concentration of both isomers in mixtures was carried out in the following way. The trans-isomer concentration was determined by taking polarograms in 0.1 N NH_4Cl and 100% alcohol. Under these conditions, we found that the proportionality coefficient was equal to 3.51± 0.07 μA/mmole/liter.

Then a polarogram was taken in 0.1 N NH_4Cl in 50% alcohol. An overall wave was thus obtained for both isomers. Under these conditions, $\frac{i_d}{C} = 1.849 \pm 0.055$ for trans-cinnamic and $\frac{i_d}{C} = 0.808 \pm 0.018$ for cis-cinnamic acid. The conversion coefficient from one background to another was equal to 1.849: 3.51 = 0.526, for trans-cinnamic acid.

Multiplying the value i_d, found for a solution in 100% alcohol, by 0.562 and subtracting the product from the value of i_d, found for a solution in 50% alcohol, we obtained the i_d for the cis-isomer, by which we determined its concentration in the solution.

The range of concentrations determined lie within the limits of $1 \cdot 10^{-2}$ to $5 \cdot 10^{-4}$ M.

The above method was checked with a series of artificially prepared mixtures of definite composition. The error in determination lies within the limits of ± 2.0 %.

Cis- and Tarns-Crotonic Acids

Crotonic acid was synthesized from malonic acid by Auwer's method [5]. Its m. p. was 71°. From it we prepared the dibromide [22] and from the latter – tetrolic acid [23]. By hydrogenating the tetrolic acid on a palladium catalyst in an alcohol medium [20], we obtained liquid isocrotonic acid with a solidification temperature of 15°.

Crotonic acid is considered to have a trans-configuration and the isocrotonic– a cis-configuration.

Neither the crotonic or isocrotonic acids were reduced at a dropping mercury cathode in the range of pH values from 0 to 10 (in citrate-phosphate and borate buffer solutions). Both crotonic acids gave clear polarographic waves in 0.1 N NH_4Cl in water, 25, 50 and 75% aqueous alcohol solutions. Only the isocrotonic acid was reduced in 100% alcohol and 0.1 N NH_4Cl. The data obtained for solutions with $1 \cdot 10^{-3}$ M concentration are given in Table 8. In all solutions the proportionality between diffusion current and acid concentrations was maintained.

To determine quantitatively the content of both isomeric acids in mixtures, a polarogram was taken in 100% alcohol and the isocrotonic acid concentration was determined by the height of the wave (the proportionality coefficient was equal to 0.418). Then a second polarogram was taken in an aqueous 0.1 N NH_4Cl solution and the height of the wave of the overall diffusion current was determined. Knowing i_d for isocrotonic acid, we multiplied this value by the ratio of the proportionality coefficients in water and in 100% alcohol, i. e., by 5.574, and by subtracting the value obtained from the height of the overall wave, we obtained a remainder which corresponded to the diffusion current of crotonic acid; from this, knowing the proportionality coefficient $\frac{i_d}{C} = 2.535$, we could calculate the concentration of crotonic acid in the solution. The concentrations determined lay within the range $1 \cdot 10^{-2}$ to $5 \cdot 10^{-4}$ M.

The method was checked with artificially made up mixtures. The errors in determination lay within the limits of ± 4.7%.

Discussion of Results

Certain definite rules were found in the behavior of the four pairs of geometrically isomeric acids investigated by us when reduced at a dropping mercury cathode.

1. Cis-isomers were always reduced at a more positive potential, i. e., more readily than trans-isomers. This was to be expected as cis-isomers are less stable and have a greater reserve of free energy which finds expression in higher molar values of heats of combustion and in smaller heats of formation than those of trans-isomers.

This rule in polarographic analysis was observed by many authors before us, using maleic and fumaric acids as examples [6, 10-13, 24].

2. It was established for all acids investigated (except for the crotonic acids which were not reduced in the buffer backgrounds we used) that with an increase in the alkalinity of the medium the half-wave potential was displaced towards more negative values. This relation is expressed by a straight line with a 0.06–0.08 v change in $E_{1/2}$ per unit of pH (except for cis-cinnamic acid), which approximately corresponds to a reduction process, proceeding by the addition of two electrons.

We calculated the theoretical values of $E_{1/2}$ by the equation $E_{1/2} = E_0 - 0.0591\ \mathrm{pH}$, where E_0 is the half-wave potential in the reduction of the given acid at pH = 0 (in 1 N hydrochloric acid). $E_{1/2} = -0.61$ v for citraconic acid, −0.68 v for mesaconic, −0.54 v for cis-aconitic, −0.59 v for trans-aconitic and −1.21 v for trans-cinnamic acid (cis-cinnamic acid was not reduced in 1 N hydrochloric acid).

We found that the calculated values for $E_{1/2}$ agreed quite well with those found experimentally for citraconic and mesaconic acids (Table 9) at pH < 6; the calculated half-wave potentials for both isomeric aconitic acids were quite close to the experimental ones only at pH < 3. With further increase in the pH of the background, theoretically calculated $E_{1/2}$ differed increasingly from those found practically, apparently due to the fact that in neutral and especially in alkaline media, the equilibrium

$$\text{acid} \rightleftarrows \text{anion}' \rightleftarrows \text{anion}''$$

is displaced considerably to the right and the concentration of undissociated acid becomes less and less.

The formation of two waves by citraconic and mesaconic acids in the range of pH values from 3.38 to 6.62 and by cis- and trans-aconitic acids from 5.44 to 8.50 may be explained by the dissociation of the acid with simultaneous reduction at the cathode both as an undissociated molecule and a singly charged anion, though, of course, at different potentials. With further increase in pH value, the first wave disappeared as the amount of undissociated molecules became insignificant.

TABLE 9

pH	Citraconic acid		Mesaconic acid	
	$E_{1/2}$ theor.	$E_{1/2}$ exp.	$E_{1/2}$ theor.	$E_{1/2}$ exp.
0.02		−0.61		−0.68
1.14	−0.65	−0.68	−0.72	−0.72
2.55	−0.76	−0.80	−0.83	−0.88
3.38	−0.81	−0.81	−0.88	−0.92
5.42	−0.93	−0.92	−1.00	−0.98
6.62	−1.00	−1.17	−1.07	−1.21
7.50	−1.05		−1.12	
8.00	−1.08		−1.15	

This is one explanation of the phenomenon. On the other hand, this phenomenon may be explained by a different mechanism of hydrogen addition to an organic molecule in acidic and alkaline media [25].

The calculated half-wave potentials of trans-cinnamic acid agree quite well with those found experimentally in all the pH range investigated (Table 10). This fact may be explained by the reduction of cinnamic acid molecules and not of its anions, due to the low value of the dissociation constants of the acid ($3.6 \cdot 10^{-5}$) at all pHs.

3. The graphs of the ratio of $\lg \frac{i}{i_d - i}$ to E are straight lines with lg $\alpha = 0.59$ for citraconic, 0.73 – for mesaconic, 0.65 – for cis-aconitic, 0.53 – for trans-aconitic, 0.36 – for cis-cinnamic, 0.125 – for trans-cinnamic, 0.14 – for isocrotonic and 0.36 – for crotonic acid.

Thus, $\alpha < 1$ for all the acids investigated, which indicates the irreversibility of their reduction at a dropping mercury cathode. The values for $E_{1/2}$ found graphically correspond quite well with those found experimentally (Table 11).

4. Although the processes investigated were, apparently, irreversible, we made the assumption that two electrons participated in the reduction of the acids (based on the dependence of $E_{1/2}$ on pH), i. e., the processes proceeded by the scheme

$$R + 2e + 2H \rightarrow RH_2.$$

In this case, substituting all the values found experimentally and $n = 2$ in Ilkovich's equation

$$i_d = 605\, nD^{1/2}\, cm^{2/3} t^{1/6},$$

we were able to calculate the diffusion coefficients of these acids.

TABLE 10

pH	Trans-cinnamic acid	
	$E_{1/2}$ theor.	$E_{1/2}$ exp.
0.02		—1.21
1.14	—1.28	—1.29
2.00	—1.38	—1.37
3.00	—1.39	—1.38
4.00	—1.45	—1.41
5.00	—1.51	—1.56
6.05	—1.57	—1.59
6.90	—1.62	—1.66
8.20	—1.69	—1.67

TABLE 11

Acids	$E_{1/2}$ graph (V)	$E_{1/2}$ exp. (V)
Citraconic	—0.755	—0.75
Mesaconic	—0.965	—0.96
Cis-aconitic	—0.625	—0.63
Trans-aconitic	—0.820	—0.82
Cis-cinnamic	—1.480	—1.51
Trans-cinnamic	—1.550	—1.56
Isocrotonic	—1.550	—1.57
Crotonic	—1.620	—1.60

TABLE 12

Acids	Indifferent electrolyte	Solvent	$D \cdot 10^6$ cm$^2 \cdot$ sec^{-1}
Citraconic	1 N HCl	75% alcohol	2.02
Mesaconic	1 N HCl	75 „ „	1.25
Cis-aconitic	1 N HCl	50 „ „	0.61
Trans-aconitic	1 N HCl	50 „ „	1.63
Cis-cinnamic	0.1 N NH_4Cl	50 „ „	0.31
Trans-cinnamic	0.1 N NH_4Cl	50 „ „	1.74
Isocrotonic	0.1 N NH_4Cl	Water	2.79
Crotonic	0.1 N NH_4Cl	„	3.13

We obtained the values given in Table 12. These values are quite probable if one considers the effect of the electrolyte and solvent present. For a comparison we should note that the diffusion coefficients, determined by other methods in a pure aqueous medium, according to the literature data, were found to be equal to: $8.2 \cdot 10^{-6}$, for succinic, $6.6 \cdot 10^{-6}$ for tartaric, $4.8 \cdot 10^{-6}$ sec^{-1} for citric acid, i.e., they have values of the same order as those of the coefficients we found.

SUMMARY

1. We investigated the polarographic behavior of four pairs of geometrically isomeric organic acids in relation to the background pH and the nature of the solvent. It was established that the polarographic behavior of the acids was considerably affected by the substitution of aqueous alcohol and alcohol media for the aqueous medium: the half-wave potential and diffusion current changed with this substitution and the changes were of an individual character. We explained the formation of two waves on the polarographic curves in a certain range of pH values of citraconic, mesaconic and both aconitic acids. We concluded that the reduction of the acids investigated was irreversible and that two electrons participated in it. The diffusion coefficients for these acids were calculated.

2. It was established that cis-isomers were reduced more readily at a dropping mercury cathode, i. e., at a less negative potential than trans-isomers.

3. We proposed methods for the quantitative polarographic determination of cis- and trans-isomers when both are present in solution.

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