Polarographic Behavior of Cinnamic-, Styrylacetic- and Crotonic- Acids⑴

By Shin-ichi ONO and Tadao HAYASHI

(Received December 20, 1952)

Introduction

Several authors have already measured the reduction potentials of cinnamic acid⑵ and crotonic acid⑶ in various solutions.

In connection with the electrolytic reduction of cinnamic acid,⑷ the authors have undertaken the polarographic observation of cinnamic-, styrylacetic- and crotonic acids, in order to know the relation between the reducibility and the structure of molecules and also the reduction of carbon-carbon double bond in these acids at a dropping mercury electrode.

Experimental

Dioxane-water mixture containing 50% dioxane was used as a solvent, with several types of supporting electrolytes. Since the decomposition potential of buffer-solutions was found to be less negative than the reduction potential of the double bond in these acids, special care was taken for the selection of supporting electrolytes. In the experiments which will be discussed, unbuffered electrolytes were usually used. The supporting electrolytes used were as follows:

(a) Acid media
  (1) HCl—0.1N LiCl System
  (2) HCl—0.1N $SrCl_2$ 〃
  (3) HCl—0.1N $CaCl_2$ 〃
(b) Neutral media
  (1) $(CH_3)_4NBr$ (0.1N), $(CH_3)_4NI$ (0.05N)
  (2) LiCl. KCl, NaCl, NH_4Cl (0.1N)
  (3) $CaCl_2$, $SrCl_2$, $BaCl_2$ (0.1N)
(c) Alkaline media
  (1) LiOH (0.1N)

The dropping mercury electrode had the following characteristics. At a pressure of 50 cm of mercury, the droptime in 50% Dioxane-0.1N $(CH_3)_4NBr$ was 3.98 sec. (Open circuit). The value of m was 1.01 mg. $sec.^{-1}$, with a calculated value of $m^{2/3}t^{1/6}$ of 1.267 $mg.^{2/3}t^{-1/2}$ (Open circuit).

Table 1

Half-wave Potentials and Diffusion Currents of Polarographic Waves of Styrylacetic and Crotonic Acids. (50% Dioxane)

Sample (mol.)	Electrolyte	Half-wave Potential (volt vs. S. C. E.)	I_l (μA.)	I_l/C.
Styrylacetic acid				
4×10^{-3}	0.1N $(CH_3)_4NBr$	−1.70	4.56	1.14
1 〃	〃	−1.64	1.06	1.06
2 〃	0.05N $(CH_3)_4NI$	−1.69	2.40	1.20
1 〃	〃	−1.64	1.16	1.16
2 〃	0.1N LiCl	−1.65	2.40	1.20
2 〃	0.1N $SrCl_2$	−1.64	2.80	1.40
2 〃	0.1N $CaCl_2$	−1.60	2.20	1.10
2 〃	0.1N LiOH	—		
Crotonic acid				
5×10^{-3}	0.1N $(CH_3)_4NBr$	−1.73	9.12	1.82
2 〃	〃	−1.70	3.38	1.69
2 〃	0.1N LiCl	−1.66	3.04	1.52
2 〃	0.1N $SrCl_2$	−1.65	2.72	1.31
2 〃	0.1N LiOH	—		

⑴ This paper was presented at the Annual meeting of the Chemical Society of Japan, held in Tokyo, on April 1952. This paper shall be "Part IV of Electrolytic Reduction of Aromatic Carboxylic Acids".

⑵ (a) L. Schwaer, *Collection Czechoslov. Chem. Commun.*, **7**, 326, (1935).

(b) G. Semerano and A. Chisini, *Gazz., Chim. Ital.*, **66**, 510, (1936).

(c) S. Wauzonek, S. C. Wang and P. Lyons, *J. Org. Chem.*, **15**, 593, (1950).

⑶ (a) K. Shoji, *Sc. P.* (*Japanese*), **9**, 69, (1930).

(b) M. v. Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118, (1949).

⑷ S. Ono and T. Hayashi, This Bulletin, **26**, 11, (1953).

The electrolytic cell was a simple cylindrical shape with a mercury pool anode, and was provided with side arms for anode connection and for admission of hydrogen for the removal of dissolved oxygen.

The anode potential was measured against a saturated calomel electrode (S.C.E.). The current-voltage curve was photographically recorded with A Model SH Shimazu Polarograph, which has a current scale calibrated in microamperes (Sensibility ; 8.0×10^{-3}microamp./mm./m.). All the experiments were carried out at room temperature. (15° ± 1°C).

All samples were prepared by the usual method, and purified by recrystallization. Cinnamic acid, m.p. 133—133.5°C, styrylacetic acid, m.p. 87—87.5°C, crotonic acid, m.p. 71—72°C.

Dioxane was purified by refluxing with sodium for 12 hours and by distillation.

The purified samples were dissolve in dioxane to the concentration of 1×10^{-2}mol/1, as a stock solution.

Polarographic results

(1) Electroreduction in neutral and alkaline solutions.—Both styrylacetic acid and crotonic acid gave a single wave, corresponding to the deposition of hydrogen ion in neutral solution, whereas they gave no polarographic (reduction) wave in alkaline solution. Table 1 shows the observed half-wave potentials and diffusion currents of styrylacetic and crotonic acids.

On the other hand, cinnamic acid gave a well-defined two-step polarographic wave in neutral solutions, and the first wave diminished by the addition of alkali.

Typical polarograms are given in Fig. 1, using a 0.05N $(CH_3)_4NI$ solution as a supporting electrolyte.

Table 2 shows a summary of the observed half-wave potentials and diffusion currents of cinnamic acid. In the presence of NH_4Cl, KCl, or NaCl as a supporting electrolyte, the second wave of cinnamic acid overlapped the decomposition potentials of these cations; therefore, it was difficult to distinguish "the real reduction wave" of the carbon-carbon double bond. However, if we used solutions of LiCl, $SrCl_2$, $CaCl_2$, $(CH_3)_4NI$, or $(CH_3)_4NBr$, as a supporting electrolyte, cinnamic acid gave a well-defined two-step reduction wave.

It was an interesting fact that the half-wave potentials of the second wave became more positive by 0.12 volt for $SrCl_2$ and by 0.15 volt for $CaCl_2$ than those for $(CH_3)_4NBr$.

We found, when $(CH_3)_4NBr$ was used, that the half-wave potentials of cinnamic acid were independent of the concentration of cinnamic acid,

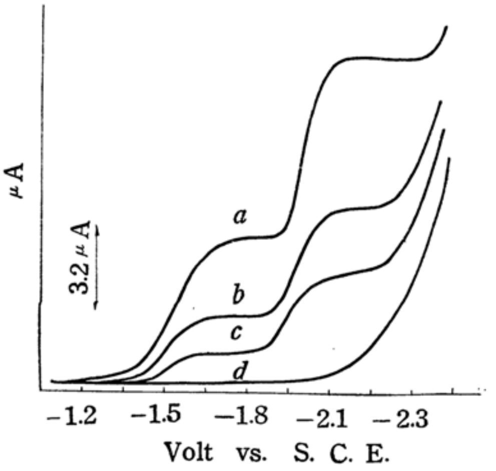

Fig. 1.—A typical polarograme of Cinnamic acid in 0.05 N $(CH_3)_4NI$ (containing 50% Dioxane, 0.001% gelatine)
(a) 4×10^{-2}M. of sample. (b) 2×10^{-3}M. (c) 1×10^{-3}M. (d) Residual Current.

Table 2

Half-wave Potentials and Diffusion Currents of Cinnamic Acid in Neutral or Alkaline Solution. (50% Dioxane, with 0.001% gelatin)

Cinnamic acid (mol.$\times10^{-3}$)	Electrolyte	First wave $\pi_{1/2}$ (Volt vs. S. C. E.)	First wave I_l (μA.)	First wave I_l/C.	Second wave $\pi_{1/2}$ (Volt vs. S. C. E.)	Second wave I_d (μA.)	Second wave I_d/C.
5.0	$(CH_3)_4NBr$	−1.53	5.76	1.15	−2.03	9.28	1.86
4.0	〃	−1.52	4.08	1.02	−2.02	7.20	1.80
2.0	〃	−1.50	2.16	1.08	−2.01	3.68	1.84
1.0	〃	−1.49	1.05	1.05	−1.98	1.85	1.85
4.0	$(CH_3)_4NI$	−1.56	4.16	1.04	−2.05	6.88	1.72
2.0	〃	−1.52	2.16	1.08	−2.01	3.52	1.76
1.0	〃	−1.55	1.10	1.10	−1.99	1.78	1.78
2.0	LiCl	−1.54	2.24	1.12	−1.99	5.84	2.92
2.0	$SrCl_2$	−1.55	2.40	1.20	−1.89	3.52	1.76
2.0	$CaCl_2$	−1.53	2.24	1.12	−1.86	3.52	1.76
4.0	LiOH	—			−1.97	11.00	2.75
2.0	〃	—			−1.96	5.40	2.70
1.0	〃	—			−1.95	2.80	2.80

and the height of waves increased linearly with the concentration.

It was made clear that lithium cinnamate gave a single wave corresponding to the reduction of cinnamate anion, by using 0.1N LiOH solution.

(2) **Electroreduction in acid solution.**—In the case of 0.1N HCl solution as a supporting electrolyte, cinnamic-, styrylacetic- and crotonic-acids gave no reduction waves of carbon-carbon double bond, owing to the decomposition potential of hydrogen ion in the bulk of HCl solution. (Decomposition potential of hydrogen ion was measured at ca. −1.16 volt. vs. S. C. E.)

Another attempt was made to investigate the polarographic behavior of cinnamic acid in some unbuffered acid solutions.

Table 3 shows a summary of the observed half-wave potentials and diffusion current of cinnamic acid in acid solution. The second wave (I_d) which corresponds to the reduction of carbon-carbon double bond, was diminished linearly with the increase of the concentration of HCl, while the first wave (I_l) grew remarkably large, owing to the decomposition of hydrogen ion.

(3) **Electroreduction of ethyl cinnamate.**—We have undertaken the polarographic observation of ethyl cinnamate in neutral and also alkaline solutions.

Ethyl cinnamate gave a single wave which might correspond to the reduction of carbon-carbon double bond in a neutral solution (0.1N $(CH_3)_4NBr$), whereas it gave a double wave in

Table 3

Half-wave Potentials and Diffusion Currents of Cinnamic Acid in Acid Solution. (50% Dioxane, 0.004—0.005% gelatin)

Cinnamic acid (mol.)	HCl (N.×10^{-3})	Electrolyte	First wave $\pi_{1/2}$ (Volt vs. S. C. E.)	First wave I_l (μA.)	First wave I_l/C.	Second wave $\pi_{1/2}$ (Volt vs. S. C. E.)	Second wave I_d (μA.)	Second wave I_d/C.
2×10^{-3}	0.5	0.1N $CaCl_2$	−1.55	3.2	1.60	−1.89	2.9	1.45
〃	1.0	〃	−1.50	4.5	2.25	−1.89	1.5	0.75
(c. f.	1.0	〃	−1.47	2.5)				
5×10^{-3}	—	0.1N $CaCl_2$	−1.55	5.2	1.04	−1.87	7.8	1.54
〃	0.5	〃	−1.55	6.0	1.20	−1.87	6.8	1.36
〃	1.0	〃	−1.50	7.2	1.44	−1.88	5.8	1.16
〃	5.0	〃	−1.49	22.2	4.44	−1.77	3.4	0.68
(c. f.	5.0	〃	−1.53	24.4)				
5×10^{-3}	—	0.1N $SrCl_2$	−1.55	5.4	1.08	−1.90	9.4	1.88
〃	0.5	〃	−1.54	6.4	1.28	−1.90	8.6	1.72
〃	1.0	〃	−1.50	8.2	1.64	−1.92	7.4	1.28
〃	5.0	〃	−1.47	25.4	5.08	−1.79	5.6	1.12
(c. f.	5.0	〃	−1.51	25.5)				
1×10^{-2}	—	0.1N $SrCl_2$	−1.57	12.8	1.28	−1.97	18.0	1.80
〃	1.0	〃	−1.54	14.8	1.48	−1.96	16.4	1.64
〃	2.0	〃	−1.53	20.4	2.04	−1.97	13.2	1.32
〃	5.0	〃	−1.48	33.2	3.32	−1.86	10.4	1.04
〃	10.0	〃	−1.47	99.6	9.96	−1.86	6.8	0.68
(c. f.	1.0	〃	−1.55	3.2)				

Table 4

Half-wave Potentials and Diffusion Currents of Ethyl Cinnamate. (50% Dioxane)

Sample (mol.)	Electrolyte	First wave* $\pi_{1/2}$ (Volt vs. S. C. E.)	First wave* i_d (μA.)	Second wave $\pi_{1/2}$ (Volt vs. S. C. E.)	Second wave i_d (μA.)
5×10^{-3}	0.1N $(CH_3)_4NBr$	−1.69	13.1	—	—
1×10^{-3}	〃	−1.68	2.6	—	—
4×10^{-3}	0.1N LiOH	−1.65	……**	−1.97	……**
2×10^{-3}	〃	−1.66	……	−1.96	……
1×10^{-3}	〃	−1.67	……	−1.96	……

* This first waves have different meaning for those of Table 2.

** i_d value are omitted, because they are changeable with the lapse of hydrolysis.

alkaline solution (0.1N LiOH).

Table 4 gives the observed half-wave potentials and diffusion currents of ethyl cinnamate. Comparing the results obtained from both cinnamic acid and its ester in the same supporting electrolyte, it was clear that the half-wave potential of ethyl cinnamate was more positive than that of cinnamic acid. The appearance of the double wave in the reduction of the ethyl cinnamate in alkaline solution can be attributed mainly to the reduction of two different forms, that is, ethyl cinnamate and cinnamic acid resuling from hydrolysis. Fig. 2 shows a polarograme for the hydrolysis of ethyl cinnamate. The first wave was observed to have diminished by the hydrolysis. The total wave heights were constant and they were twice as large as the height of cinnamic acid in the same concentration. Detailed discussion on this phenomenon will be presented in another paper.

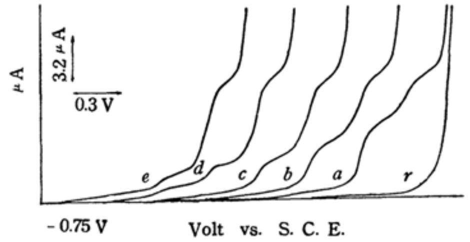

Fig.—2.—A polarogram for the hydrolysis of Ethyl Cinnamate. (Supporting media: 50% Dioxane 0.1N LiOH, Sample: 1.5×10^{-3}M.) (R) Residual Current. (a) Initial state, (b), (c), (d), (e) states after the lapse of respectively 40 min., 80 min., 120 min., 160 min., from (a).

Discussion

It has been pointed out that the electroreducibility of a carbon-carbon double bond was closely related to the nature of the conjugated system of the double bond in the study of polarographic reduction of several unsaturated acids.(2a)

It was found in the present experiment that cinnamic acid gave only the polarographic wave corresponding to the reduction of carbon-carbon double bond. The electroreduction of cinnamic acid gave two-step polarographic waves in neutral solution. Under these conditions, there would be neutral molecules, dissociated cinnamate anions and hydrogen ions in the vicinity of the electrode surface and these species would contribute to the potential determining step. The following characteristic kinds of behavior were observed;

(1) Well-defined two-step reduction wave was obtained in a neutral solution.

(2) The first wave was observed to diminish by addition of alkali.

(3) Lithium cinnamate gave a single wave either in neutral or in alkaline solution.

(4) The heights of the first wave and the heights of the second wave were both proportional to the concentration of samples.

(5) Total wave heights of both the first and the second waves remained constant when alkali was introduced into a neutral solution.

In the initial stage of waves (first wave), therefore, this phenomenon may be considered as being due to the discharge of hydrogen in the bulk of solution. This is true because at such pH values (pH>6) the concentration of the undissociated acid becomes negligibly small and the cinnamate anion may be reduced directly on the electrode surface.

Another interesting result which was obtained was that the half-wave potentials of the carbon-carbon double bond, in the case of divalent cations as a supporting electrolyte, were shifted and became less negative than in the case of the monovalent cation. (Table 5) The effect of divalent cations can be explained by the ionic activity of these cations that form the metal complex with carbonyl anion and tend to diffuse to the electrode surface by the electrostatic interaction.

It has been mentioned that(4) the electrolytic reduction of cinnamic acid in acid solution with mercury cathode, gave rise to bimolecular compounds, which were produced by the dimerization of free radicals, $Ph\text{-}\dot{C}HCH_2COOH$ obtained from cinnamic acid. But in alkaline solution, no bimolecular compounds were produced; that is, only hydrocinnamic acid was given.

If we assume that the polarographic reduction process will take place in the same manner as in the case of so-called electrolytic reduction, it may be expected that there will be considerable change in the polarograms obtained from acid

Table 5

Effect of Cations on the Half-wave Potentials of Cinnamic acid. (50% Dioxane)

Sample (2.0×10^{-3} mol.)	Cation	Electrolyte	Half-wave Potential (Volt vs. S. C. E.)	I_d (μA.)	I_d/C.
Li cinnamate	$(CH_3)_4N^{\cdot}$	0.1N $(CH_3)_4NBr$	−1.98	6.0	3.00
〃	$Li^{\cdot}$	0.1N LiCl	−1.93	8.5	4.25
〃	$Sr^{\cdot\cdot}$	0.1N $SrCl_2$	−1.88	5.8	2.90
〃	$Ca^{\cdot\cdot}$	0.1N $CaCl_2$	−1.84	5.5	2.75
Ba cinnamate	$Ba^{\cdot\cdot}$	0.1N $(CH_3)_4NBr$	−1.92	5.8	2.90
Ca cinnamate	$Ca^{\cdot\cdot}$	〃	−1.90	5.7	2.85

solution, compared with that in neutral or alkaline solution. But, in the present experiments, no clear effect of hydrogen ion concentration could be established, since the half-wave potential of carbon-carbon double bond was observed to be more negative than the decomposition potential of hydrogen ion.

Summary

1) In neutral solution, both styrylacetic acid and crotonic acid gave a single wave (ca. —1.6——1.7 *v.*), on the other hand cinnamic acid gave a well-defined two-step polarographic wave (ca. —1.5 *v.* and ca. —2.0 *v.*) corresponding to the reduction of carbon-carbon double bond. The half-wave potentials of cinnamic acid were shifted by the presence of divalent cations.

2) Ethyl cinnamate gave a single wave (ca. —1.7 *v.*) in neutral solution, but in alkaline solution it gave two waves (ca. —1.7*v.* and ca. —2.0 *v.*). The first wave was observed to diminish by the hydrolysis in alkaline solution.

The authors wish to express their thanks to Dr. I. Tachi of the Univ. of Kyoto, and his collaborator for the discussion of the results.

Department of Chemistry,
Faculty of Education, Naniwa University, Osaka