served values were higher by 10%. This is attributed to the fact that the migration current has been markedly reduced by the higher relative concentration of indifferent electrolyte. The solubility of tetraethylammonium iodide, which was used in this investigation, is about four times as great as that of tetrabutylammonium iodide, which was used in the investigation of the alkali metal ions.

TABLE II

$E_{1/2}$ IN LIQUID AMMONIA AT −36° *versus* MERCURY POOL

Ion	C. mmole/l.	$E_{1/2}$, volts	Slope of $E_{d.e.}$ *vs.* log $\left(\frac{i_d - i}{i}\right)$
Ca	0.38	−1.96	0.058
Ca	.82	−1.96	.044
Sr	.37	−1.69	.061
Sr	.52	−1.68	.078
Sr	.78	−1.67	.117
Ba	.58	−1.54	.033
Ba	.63	−1.54	.040

Since the shape of a polarographic reduction wave, when the metal is soluble in mercury, is given by the expression[7]

$$E_{d.e.} = E_{1/2} + \frac{2.303RT}{nF} \log \frac{(i_d - i)}{i}$$

the slope of a plot of $E_{d.e.}$ *versus* log $(i_d - i)/i$ can be used as a test for reversibility. $E_{d.e.}$ is the potential of the dropping mercury electrode; $E_{1/2}$ is the half-wave potential; i_d is the diffusion current; and i is the current flowing at a potential $E_{d.e.}$. A reversible two-electron reduction would give a slope of 0.024.

In Table II are recorded values for the half-wave potentials of calcium, strontium and barium in liquid ammonia at −36° and also the slope of $E_{d.e.}$ *vs.* log $(i_d - i)/i$. The approach of the reduction to reversibility is not so close in the case of the alkaline earth ions as it is in the case of the alkali metal ions.[1] There is a parallel behavior between these ions and the alkali metal ions in that the largest ion is the most readily reduced to the amalgam. Insufficient data are available to calculate theoretical values of the half-wave potentials.

Summary

The diffusion currents of calcium, strontium and barium ions were measured and found to agree with those calculated by the Ilkovic equation.

The half-wave potentials were determined, and the reduction was found to be less reversible than in the case of the alkali metal ions.

PULLMAN, WASH. RECEIVED JULY 26, 1949

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(7) J. Heyrovsky and D. Ilkovic, *Coll. Czech. Chem. Commun.*, **7**, 198 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY AND THE PURDUE RESEARCH FOUNDATION]

Polarographic Behavior of Organic Compounds. I. The Maleate and Fumarate Species

BY PHILIP J. ELVING* AND CHARLES TEITELBAUM

Although extensive polarographic investigations of maleic and fumaric acids have been carried out, there was felt to be a need for a thorough study of the acids with a more careful control of the factors affecting polarographic reduction.

Insufficient attention was paid in much of the previous work[1] to such factors as buffering, electrolyte concentration, capillary characteristics, temperature control and concentration. The most thorough previous work is that of Vopicka,[1c] although the concentrations he used were somewhat high, capillary characteristics were not given, buffering at the ends of the *p*H range studied was not satisfactory, no measurements were made between *p*H 5.3 and 9.0, and no temperature control was attempted. He developed an equation to express the effect of *p*H on half-wave potential. Herasymenko[1e] interpreted Vopicka's results on the basis of a new equation, which gave slightly better agreement with the experimental results. The only previous work on the calculation of the "*n*" values (apparent electron change per molecule reduced) is that of Furman and Bricker[1k] for maleic acid where values of 1.17 and 1.22 were obtained. No clear relationship between diffusion current and *p*H has been established; Vopicka[1c] indicates a straight line relation between half-wave potential, $E_{0.5}$, and *p*H. No previous report has been found of the appearance of double waves in buffered solution. No previously reported polarographic investigation of the esters has been located.

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(1) (a) Herasymenko, *Z. Elektrochem.*, **34**, 74 (1928); (b) Schwaer, *Chem. Listy*, **26**, 485 (1932); (c) Vopicka, *Coll. Czechoslav. Chem. Commun.*, **8**, 349 (1936); (d) Semerano and Bettinelli, *Gazz. chim. ital.*, **66**, 744 (1936); (e) Herasymenko, *Coll. Czechoslav. Chem. Commun.*, **9**, 104 (1937); (f) Miolati, *Mem. accad. Italia, Classe. sci. fis. mat. nat.*, **8**, 215 (1937); (g) Semerano and Bettinelli, *ibid.*, **8**, 255 (1937); (h) Miolati and Semerano, *Ricerca sci.*, **8**, II, 243 (1937); (i) Semarano and Rao, *Mikrochemie*, **23**, 9 (1937); (j) Semerano, *ibid.*, **24**, 10 (1938); (k) Furman and Bricker, THIS JOURNAL, **64**, 666 (1942); (l) Clark and Knopf, ACS, Abstracts of Papers, Meeting in Print, p. 3L, Sept., 1945; (m) Warshowsky, Elving and Mandel, *Anal. Chem.*, **19**, 161 (1947).

Experimental

Buffer solutions of varying *p*H (Table I) were prepared from reagent grade chemicals by weighing out one mole of the first named buffer constituent, diluting to approximately 800 ml., adding enough of the second component to reach the approximate *p*H desired, diluting to 1 liter and determining the exact *p*H.

Maleic acid (Pfanstiehl C. P., m. p. 133–136°) was used as received. Fumaric acid (Eastman Kodak Co. practical grade) was recrystallized three times from 1 *N* hydrochloric acid and decolorized with Norit; the white solid melted at 282–284° in a sealed tube. Solutions, 0.1 *M*, of the acids were prepared; 4 g. of sodium fluoride was added to each liter to inhibit mold growth. The diethyl maleate and diethyl fumarate were Eastman Kodak Co. White Label grade; diethyl maleate, $n^{20}{}_D$ 1.4400 (literature value[2] 1.4407) and diethyl fumarate, $n^{20}{}_D$ 1.4405 (literature value[3] 1.4410). The purified[4] 1,4-dioxane had $n^{20}{}_D$ 1.4221 in exact agreement with the literature value.[3] Since aqueous solutions of the esters would hydrolyze, 0.5 *M* stock solutions were prepared in 1,4-dioxane; only 1 ml. of stock solution was used in making 100 ml. of test solution. The absence of additional polarographic waves due to impurities supports the adequacy of the purity of the materials used.

TABLE I

BUFFER SOLUTIONS, 1 *M* IN MEASURED CONSTITUENT

No.	*p*H	Measured constituent	Unmeasured constituent
1	2.03	KCl	HCl
2	3.98	NaOAc	HOAc
3	4.89	NaOAc	HOAc
4	5.90	NaOAc	HOAc
5	6.98	HOAc	NH_4OH
6	7.90	NH_4Cl	NH_4OH
7	8.68	K_2HPO_4	.....
8	8.86	NH_4Cl	NN_4OH
9	9.87	NH_4Cl	NH_4OH

TABLE II

EFFECT OF CONCENTRATIONS OF BUFFER, ADDED ELECTROLYTE AND MALEIC ACID ON HALF-WAVE POTENTIAL OF MALEIC ACID IN SODIUM ACETATE–ACETIC ACID BUFFER SOLUTIONS

No.	Maleic acid *M* × 10⁴	KCl, *M*	NaOAc, *M*	Final *p*H	Half-wave potentials		
					Whole wave, volts	First wave, volts	Second wave, volts
1	5		0.1	4.50	....	−1.15	−1.63
2	5		.3	5.86	−1.13	−1.11	−1.30
3	5		.7	5.85	−1.13	−1.11	−1.25
4	5		.9	5.88	−1.12	....	....
5	5	*ca.* 0.6	.3		−1.12	−1.09	−1.27
6	5	*ca.* 1.2	.3		−1.11	−1.09	−1.25
7	2		.1	5.85		−1.12	−1.34
8	5		.1	4.50		−1.15	−1.63
9	2		.9	5.89	−1.12		
10	5		.9	5.88	−1.12		

A Sargent Polarograph Model XXI was used. Potential measurements were checked with a potentiometer. A Beckman Model G *p*H meter was used for all *p*H measurements. An H-type polarographic cell was used with a water-jacket around the sample leg and a saturated calomel electrode in the other half of the cell. Water at 25 ± 0.2° was circulated through the water-jacket.

The operations involved in the measurements were the usual ones used in polarographic studies. All solutions were degassed by a stream of oxygen-free nitrogen. The *p*H was determined after the solution had been degassed and the curves determined so that any effect of the degassing on the *p*H would not be ignored.

Calculation of the resistance through the cell with the concentrations of buffers used indicated that any correction for the potential drop would be within the experimental error. Confirmation for this view was received in the polarographing of solutions of cadmium chloride in 0.1 *M* potassium chloride where satisfactory agreement with the literature values was obtained. Since the buffers used had a higher conductivity than 0.1 *M* potassium chloride, no correction was considered necessary. The accuracy of the potential measurements were periodically checked by measurement of cadmium chloride solutions.

Experiments and Data

The "*m*" value for the capillary into distilled water was 2.17 mg. per second.

The effect of buffer concentration on the polarographic waves for maleic acid was determined at *p*H 5.9, where very clear waves were obtained. In solutions of low buffer concentration two waves were obtained; as the concentration of buffer was increased, the two waves gradually merged (Table II, Nos. 1 to 4). Where a reasonable distinction could be made, the $E_{0.5}$ values of both waves and of the whole, composite wave were measured. Although the significance of $E_{0.5}$ for a whole wave is perhaps doubtful in those cases where the waves consist of two separate and distinct parts, such values are included for comparison with the cases where the waves were not resolvable and were reported as one wave. To test whether the effect was due to the change in buffer capacity or to the change in ionic strength, varying concentrations of potassium chloride were added to a fixed concentration of buffer (Table II, nos. 5 and 6). Finally, to test the constancy of $E_{0.5}$ at varying concentrations of reducible species and to demonstrate further the optimum concentration of buffer, the concentration of maleic acid was varied in two buffer concentrations (Table II, nos. 7 to 10).

The effect of *p*H on $E_{0.5}$ of maleic acid was studied over the *p*H range of 2 to 9 using buffer solutions which were 0.1 *M* or 0.9 *M* in the major buffer constituent. The values obtained in 0.1 *M* solution showed an irregular relation between $E_{0.5}$ and *p*H; the values for 0.9 *M* solution are given in Table III. Similar studies on fumaric acid and the diethyl esters in solutions of varying concentration of buffer constituent and reducible

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[2] Knops, *Ann.*, **248**, 193 (1888).

[3] Lange, "Handbook of Chemistry," 6th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1946.

[4] Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 369.

TABLE III

POLAROGRAPHIC BEHAVIOR OF 0.5 mM. MALEIC ACID IN SOLUTIONS 0.9 *M* IN BUFFER

Buffer	Final *p*H	No. of waves[a]	Half-wave potential, volts	Drop time, sec.	Diffusion current, microamp.
1	2.43	2	−0.73	3.1	4.23
2	4.00	2	−0.89	3.1	2.90
3	4.89	1 or 2	−0.96	3.0	3.76
4	5.88	1	−1.12	...	4.01
5	6.93	1	−1.27	2.7	3.99
6	7.80	1	−1.34	2.6	2.46
7	8.72	1	−1.43	2.4	2.88
8	8.60	1	−1.37	2.5	2.79
9	9.63	1	−1.42	2.5	0.96

[a] At higher *p*H values, a second wave may have escaped observation due to an irregular diffusion current. $E_{0.5}$ refers to the value for the first wave where two waves were obtained; to the whole wave where only one wave was apparent.

species indicated that low concentrations of buffer constituent such as 0.1 *M* are inadequate but that 0.9 *M* is adequate. The results for fumaric acid and the two esters in the latter type solution are given in Tables IV, V and VI. The effect of the dioxane from the stock solutions of the esters was shown to be negligible by taking equal quantities of diethyl maleate with and without dioxane; the curves obtained were identical within the experimental accuracy. A second wave was obtained for both esters in buffer 9 (Table VII). The relation between $E_{0.5}$ and *p*H for all compounds studied is shown in Fig. 1.

TABLE IV

POLAROGRAPHIC BEHAVIOR OF 0.5 mM. FUMARIC ACID IN SOLUTIONS 0.9 *M* IN BUFFER

Buffer	Final *p*H	Half-wave potential, volts	Drop time, sec.	Diffusion current, microamp.
1	2.56	−0.79	3.2	3.99
2	4.00	−0.94	3.1	4.00
3	4.89	−1.06	2.9	3.49
4	5.83	−1.21	2.9	0.91
5	6.87	−1.48	2.1	3.88
6	7.81	−1.55	2.1	4.33
7	8.78	−1.71	2.0	3.98
8	8.41	−1.58	2.4	3.74
9	9.50	−1.58	2.6	3.56

TABLE V

POLAROGRAPHIC BEHAVIOR OF 0.5 mM. DIETHYL MALEATE IN SOLUTIONS 0.9 *M* IN BUFFER

Buffer	Final *p*H	Half-wave potential, volts	Drop time, sec.	Diffusion current, microamp.
1	2.20	−0.87	3.9	3.36
2	3.98	−0.95	3.8	2.40
3	4.88	−0.99	3.6	2.89
4	5.86	−1.04	3.3	2.74
5	6.96	−1.03	4.0	2.82
6	7.90	−1.03	3.9	3.13
7	8.68	−1.05	4.1	2.25
8	8.65	−1.03	4.1	3.02
9	9.70	−1.05	3.5	1.83

TABLE VI

POLAROGRAPHIC BEHAVIOR OF 0.5 mM. DIETHYL FUMARATE IN SOLUTIONS 0.9 *M* IN BUFFER

Buffer	Final *p*H	Half-wave potential, volts	Drop time, sec.	Diffusion current, microamp.
1	2.16	−0.75	3.8	1.87
2	3.97	− .84	3.4	2.43
3	4.86	− .86	3.6	2.55
4	5.90	− .93	3.6	2.57
5	6.94	− .97	...	3.09
6	7.62	−1.01	4.0	1.77
7	8.66	−1.07	3.5	0.89
8	8.62	−1.62	3.6	1.68
9	9.63	−1.15	3.1	2.48

Calculations for the "*n*" values were made by plotting $\log i/(i_D - i)$ *vs.* E[5] (Table VIII).

TABLE VII

SECOND POLAROGRAPHIC WAVE OF 0.5 mM. DIETHYL ESTERS OF MALEIC AND FUMARIC ACIDS IN BUFFER OF *p*H 9.87 AND 0.9 *M* BUFFER

Reducible species	Final *p*H	Half-wave potential, volts	Diffusion current, microamp.
Diethyl maleate	9.70	−1.46	0.92
Diethyl fumarate	9.63	−1.37	1.32

TABLE VIII

ELECTRON CHANGES (*n* VALUES) FOR 0.5 mM. CONCENTRATION OF REDUCIBLE SPECIES AND 0.9 *M* CONCENTRATION OF BUFFER

Reducible species	Buffer no.	Final *p*H	"*n*" value
Maleic acid	4	5.88	1.03
Fumaric acid	4	5.83	1.02
Diethyl maleate	1	2.20	0.44
	2	3.98	.68
	4	5.86	.81
	6	7.90	.87
	9	9.70	1.17[a]
Diethyl fumarate	4	5.90	1.37
	6	7.62	1.04

[a] Slope of line from first part of curve only used for calculation.

Discussion

Effect of Buffer Concentration.—Low concentrations of buffer were definitely indicated as not adequate. Ordinarily, it is expected that a molar ratio of buffer to reducible species of 100:1 is adequate for the desired constancy of *p*H throughout the solution. Considering that the usual concentration of reducible species used was 0.5 mM, a buffer concentration of 0.05 *M* should be adequate. However, the inadequacy of buffer solutions of low electrolyte concentration becomes more understandable if we consider the role of the buffer in the reduction. The reduction of the acids may be written as

$$C_4H_4O_4 + 2H^+ + 2e \longrightarrow C_4H_6O_4$$

Since the reaction tends to use up hydrogen ions and make the solution more basic, only the acidic

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(5) Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, p. 145.

component of the buffer is effective in maintaining a constant *p*H. In the case of the sodium acetate–acetic acid buffer of *p*H 5.9, only the basic component, sodium acetate, was measured. The approximate concentration of the acidic form, acetic acid, can be calculated from the known *p*H and the concentration of the acetate.[6] Such a calculation indicates that the ratio of sodium acetate to acetic acid is approximately 18:1. Hence, the 0.1 *M* concentration of buffer gives a ratio of acidic form of buffer to reducible species of only 56:1; the 0.3 *M*, 160:1; the 0.7 *M*, 390:1; and the 0.9 *M*, 500:1. These facts explain the $E_{0.5}$ data for fumaric acid at *p*H 5.9 at different buffer concentrations: −1.242 (0.1 *M*), −1.224 (0.3 *M*), −1.213 (0.7 *M*), and −1.210 (0.9 *M*). This would indicate that there is inadequate buffering at the lower values and that, in this case, the minimum sufficient concentration of sodium acetate is between 0.3 and 0.7 *M*. In terms of the ratio of the acid component of the buffer to reducible species, a ratio of between 160:1 and 390:1 is required. The $E_{0.5}$ would be expected to be constant at varying concentrations of reducible species only if there were adequate buffering. The data for maleic acid in 0.1 *M* concentrations of measured buffer constituent give a very irregular relation when $E_{0.5}$ is plotted against *p*H while the relation for the 0.9 *M* buffer is quite regular; the former, apparently, is due to the irregularly inadequate buffering. It may be noted that Vopicka[1c] used a sodium acetate–acetic acid buffer at *p*H 9, in which the concentration of acidic form must have been negligible.

The foregoing comments on buffering capacity have applied only to buffer 4 which had the highest *p*H of any of the acetic acid buffers (2, 3 and 4) and thus the smallest concentration of acetic acid. If a 0.9 *M* concentration in measured constituent of this buffer was sufficient, then a similar concentration of the other buffers should most certainly be sufficient since the concentration of the acid component of the other buffers would be still higher. For buffer 5, the concentration of acetic acid is 0.9 *M*, which should be sufficient. For buffers 6 to 9, the acidic form, ammonium chloride or potassium hydrogen phosphate, is also fixed at 0.9 *M*. In buffer 1, the buffering capacity is admittedly dubious but since the results obtained were consistent with the others, it may be concluded that either the buffering was adequate or that good buffering was not necessary in this *p*H range.

An anomaly which seems difficult to interpret is the effect of buffer concentration on the polarographic waves of maleic acid. Two waves are obtained at *p*H 5.90 when low concentrations of buffer are used; these waves gradually merge as the concentration of buffer is increased. The addition of a presumably inert electrolyte, such as potassium chloride, has, to some degree, the same effect as the increase of buffer concentration. Two waves appear only at low *p*H. As previously noted, incomplete buffering should lead to more basic conditions. The appearance of two waves only at a low concentration of buffer of *p*H 5.9 might indicate that a high *p*H favors the appearance of two waves; however, two waves appear only in buffers of low *p*H. To explain the effect of the addition of a presumably inert electrolyte, one can only postulate that the phenomenon observed is at least partially caused by an ionic strength effect and that the appearance of two waves is not an indication of a varying ratio of different dissociated forms. The polarographic reduction of fumaric acid yielded only one wave in all buffers.

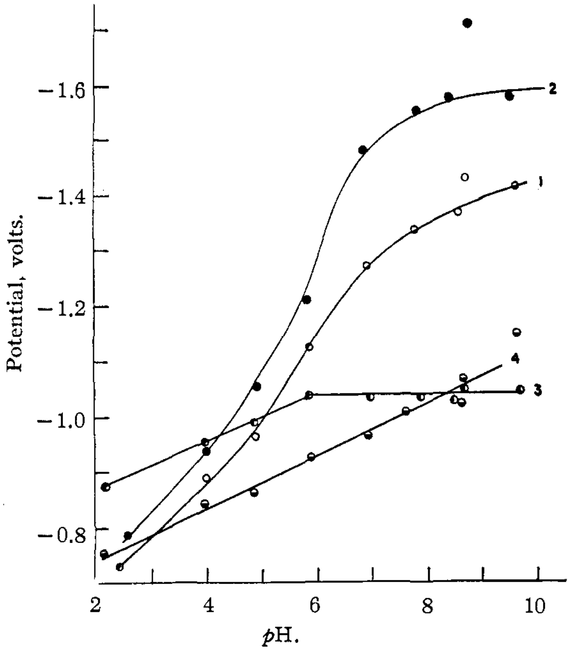

Fig. 1.—Variation of half-wave potential with *p*H: 1, maleic acid; 2, fumaric acid; 3, diethyl maleate; 4, diethyl fumarate.

Polarography of the Esters.—Freshly prepared stock solutions of diethyl fumarate gave curves with a distinct maximum while solutions which had been allowed to stand for some time did not. Since the addition of very small amounts of fumaric acid also suppressed the maximum, its disappearance was attributed to the slow partial hydrolysis of the ester in the stock solution by traces of water.

The appearance of two waves in the reduction of the diethyl esters can only be attributed to a two-step reduction since only one form of the reducible species exists. This might, by analogy, indicate that the two waves for maleic acid might be due to a two-step reduction and not to the reduction of two different forms. However, in the

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[6] Clark, "The Determination of Hydrogen Ions," 3rd ed., Williams and Wilkins Co., Baltimore, Md., 1928, p. 220.

case of the esters two waves occur only at high pH values while for the maleic acid it happens only at low pH, indicating a fundamental difference in the two phenomena. It certainly indicates that a proof by analogy would be dubious.

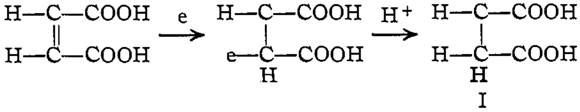
Interpretation of $E_{0.5}$–pH Curves for Maleic and Fumaric Acids.—The curves for maleic and fumaric acids, relating $E_{0.5}$ to pH, are of similar flattened S-shapes (Fig. 1). The fumaric acid curve is more negative at all points. The greater thermodynamic stability of fumaric acid would lead us to expect it to have the more negative $E_{0.5}$ values since the more stable of two compounds yielding the same product on reduction would be expected to be the less easily reduced. The facts, that at most pH values a single wave is obtained for the reduction and that a smooth curve is obtained when $E_{0.5}$ is plotted against pH, lead to the assumption that we may treat the curve as representing the composite behavior of the three possible forms of the acid: undissociated, half-dissociated and fully dissociated. The observed $E_{0.5}$ is a function of the ease of reduction of all of the forms present and their relative concentrations; the effect of pH on half-wave potential will be considered in this light.

The fact that maleic acid becomes still less stable at high pH values may be due to the electrostatic repulsion of the two negatively charged carboxylate groups in close proximity to one another. In the first ionization stage, maleic ($K_{a_1} = 1.5 \times 10^{-2}$) is a stronger acid than fumaric ($K_{a_1} = 1 \times 10^{-3}$); on the other hand, in the second ionization stage, maleic ($K_{a_2} = 2.6 \times 10^{-7}$) is a much weaker acid than fumaric ($K_{a_2} = 3 \times 10^{-5}$). This may be explained as being due to the difficulty of removal of the second positively charged proton in such close proximity to the negative charge of the carboxylate group. Roberts and Kimball[7] account for the anomalous *cis*-addition of bromine to maleic acid in basic solution on the basis of rupture of the three-membered ring of the primary addition product and rotation to the fumaroid configuration in which configuration the electrostatic repulsion is considerably less because of the wider separation of charge. This evidence also indicates that the close proximity of the two carboxylate groups causes a decreased stability of the doubly-charged maleate ion. These lines of evidence agree with the observations of this study, that the difference in stability between fumaric and maleic acids, as reflected by their $E_{0.5}$ values, is greatest at high pH values.

This explanation says nothing about the $E_{0.5}$ of each acid individually; the curve for each acid is difficult to interpret because there is involved in the effect of pH upon $E_{0.5}$ not only the activity of hydrogen ion but also the presence of three different forms of the reducible species and three different forms of the presumed product of reduction, succinic acid. However, one would predict that the change in the difference in $E_{0.5}$ should be greatest at the same pH as where the greatest change in the concentration of the doubly-charged maleate ion occurs. If the first ionization of maleic acid, which is very largely complete at the pH values considered, is neglected, it is found that $pH = pK_{a_2} + \log [A^=]/[HA^-]$, so that the ratio, $[A^=]/[HA^-]$, changes one hundred-fold when the pH changes from $(pK_{a_2} + 1)$ to $(pK_{a_2} - 1)$. This, then, is the pH region (5.3 to 7.3) where one would expect to find the greatest change in concentration of doubly-charged maleate ion and, correspondingly, the greatest difference in $E_{0.5}$ values. That this prediction is at least roughly realized is shown in Fig. 1. The presence of the points for buffer 7 above the rest of the curve suggests the possibility of some sort of complex formation between the phosphate and the acid.

The calculated electron changes (Table VIII) involved in the reduction of both acids gave values of close to one. The wide variance of the diffusion current in varying pH led to the conclusion that calculations of the n value by the Ilkovic equation would be meaningless.

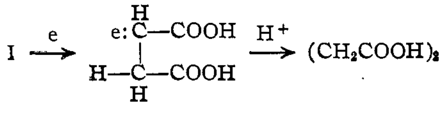
The previously mentioned interpretation of the $E_{0.5}$–pH curve stated that the difference in $E_{0.5}$ is explicable by the difference in thermodynamic stability. If this explanation is valid, then it seems likely that the potential-determining step in both cases leads to the same product, for the differences in energy of the two acids can have significance only if they are referred to a common standard. An electron change of one in the potential-determining step indicates that succinic acid cannot be the product of the potential-determining step since formation of succinic acid involves a two-electron change. The production of nascent hydrogen does not seem likely as the step since this should give a $E_{0.5}$–pH relationship unaffected by the nature of the acid and the two acids should give identical $E_{0.5}$ values. What seems more likely as the potential-determining, probably reversible step is the formation of a radical ion which would, perhaps simultaneously, acquire a proton



$$\begin{array}{c}\text{H—C—COOH}\\ \|\\ \text{H—C—COOH}\end{array} \xrightarrow{e} \begin{array}{c}\text{H—}\dot{\text{C}}\text{—COOH}\\ |\\ \text{e—C—COOH}\\ \text{H}\end{array} \xrightarrow{H^+} \begin{array}{c}\text{H—}\dot{\text{C}}\text{—COOH}\\ |\\ \text{H—C—COOH}\\ \text{H}\end{array}$$

I

I would be expected to have free rotation about the central bond and thus be the same for maleic and fumaric acids. The pH dependence of the reduction seems to indicate a proton being added before the second step. The further reduction of I would then not be potential-determining and would proceed as follows



$$\text{I} \xrightarrow{e} \begin{array}{c}\text{H}\\ \text{e:C—COOH}\\ |\\ \text{H—C—COOH}\\ \text{H}\end{array} \xrightarrow{H^+} (CH_2COOH)_2$$

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[7] Roberts and Kimball, THIS JOURNAL, 59, 947 (1937).

Interpretation of $E_{0.5}$–pH Curves for Diethyl Maleate and Diethyl Fumarate.—The diethyl esters were chosen for study in the belief that the factors influencing the polarographic reduction would be simplified. Since the ethyl groups are not as labile as protons and the hydrolysis of the esters is relatively slow, one need only consider one form of the reducible species and one form of the reduced product. The expectation that the curves of $E_{0.5}$ *vs.* pH would be considerably simpler to interpret, was not realized. Generally, the change in $E_{0.5}$ with varying pH is smaller for the esters than for the acids, but the variations in this change are actually less easily understandable for the esters than for the acids.

The curve of $E_{0.5}$ *vs.* pH for diethyl maleate consists of two straight lines (Fig. 1), intersecting at pH 5.8 and crossing the single straight line for diethyl fumarate at pH 8.4. As in the case of the acids, the greater stability of the fumarate should cause it to have the more negative $E_{0.5}$ value; this expectation is realized at high pH values.

The distinct break in the $E_{0.5}$–pH curve for diethyl maleate indicates two distinct mechanisms for the polarographic reduction, a pH-dependent mechanism at low pH and a pH-independent mechanism at high pH. It seems clear that the mechanism for the reduction of diethyl maleate at high pH differs from the mechanism for diethyl fumarate. At low pH values, the similarity of mechanisms for both esters seen in the parallel lines of the $E_{0.5}$–pH curve, whose slope lies between that expected for a reaction involving one proton and one involving two protons.

The "*n*" values calculated for diethyl maleate (Table VIII) seem to indicate an irreversible reaction at low pH values and a possible electron change of one for the potential-determining step at high pH values. The "*n*" values calculated for diethyl fumarate imply a mechanism of reduction similar to the acids, that is, a potential-determining reduction to a radical ion simultaneously with or immediately followed by a proton addition. Another electron and another proton would then be added to complete the reduction. This is supported by the appearance of a double wave at high pH values, indicating a two-step reduction.

There are two observed anomalies for which possible causes should be discussed, the higher $E_{0.5}$ of the less stable diethyl maleate at low pH and the change in mechanism of its reduction. Price[8] has explained anomalous effects in the reactivity of the two esters in copolymerization on stereochemical grounds. Based on relative stabilities diethyl maleate should copolymerize more readily than diethyl fumarate. However, the reactivity of the latter toward copolymerization is almost 12.5 times that of the former. On the other hand, the reactivity of maleic anhydride is almost 10 times that of diethyl fumarate. Price postulates that at some step in the copolymerization one of the intermediates is stabilized by resonance which requires a copolar configuration. Construction of molecular models indicates that there is steric strain involved in the assumption of a coplanar configuration by diethyl maleate but no such strain for diethyl fumarate or maleic anhydride. If one assumes that a planar intermediate is involved in the potential-determining step of the pH-dependent mechanism but not in the pH-independent mechanism, the two anomalies mentioned become understandable. For the similar pH-dependent mechanisms of the two esters, the steric strain in the intermediate makes the diethyl maleate more difficultly reducible. This does not necessarily mean that the product of the addition of the first electron is not the same but may merely imply that a higher energy barrier must be crossed in the change from diethyl maleate to the first product than in the case of diethyl fumarate. As the pH is raised, the reduction becomes more difficult. Finally, the reduction becomes so difficult by the pH-dependent mechanism as the hydrogen ion activity is decreased that another mechanism is favored. This does not happen for diethyl fumarate because there is no steric strain to make the pH-dependent mechanism a difficult one and also because the increased thermodynamic stability of the fumarate would make the pH-independent mechanism more difficult for it as opposed to diethyl maleate.

Acknowledgment.—This work was made possible by the award of a Frederick Gardner Cottrell Grant by the Research Corporation to whom the authors wish to express their gratitude.

Summary

The polarographic curves for maleic acid, fumaric acid, diethyl maleate and diethyl fumarate have been determined over a pH range of 2 to 9. A concentration of major buffer constituent exceeding 0.5 *M* was found necessary for adequate buffering action. Mechanisms of reduction consistent with the half-wave potential–pH curves and other related data have been proposed.

Maleic acid gave two waves at low pH in solutions of low concentration of buffer; increase in concentration of buffer constituents caused gradual merging of the waves into one. The same effect could be caused by adding potassium chloride to a fixed concentration of buffer, indicating the cause of the merging of the two waves to be probably a change in ionic strength and excluding as the cause of the two waves the successive reduction of different dissociated forms of the acid.

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(8) Price, "Mechanisms of Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, pp. 98–100.

(9) Original manuscript received January 14, 1949.