$$E = -0.735 - 0.0591 \log [RS^-] \qquad (9)$$

Mixtures which were 5×10^{-4} *M* in RSSR, 10^{-3} *M* in RSH, 0.05 *M* in borax, 0.1 *M* in tartrate and which were 6.7×10^{-4} *M* and 2×10^{-3} *M* in ferrous iron gave only one reduction wave of cystine with half-wave potentials of -0.63 and -0.60 volt and zero current potentials of -0.58 and -0.55 volt, respectively.

From equation 9 we calculate a half-wave potential of -0.56 volt for a cysteine concentration of 10^{-3} *M*, which is in reasonable agreement with the experimental value of 0.60 for the above solution with the larger iron concentration, the experimental values becoming closer to the calculated ones as the iron concentration increases.

In order to exert the catalytic effect the oxidation potential of the iron in the system must be such that reaction (6) can take place to an appreciable extent and this reaction must be rapid. The half-wave potential of the ferrous–ferric couple in Versene at *p*H 9.2 is -0.234 volt while that of the couple in a cysteine solution is -0.54 volt. The oxidation potential of the system in the presence of Versene is not negative enough to give any appreciable reaction to the right in equation 6. The partial elimination of the catalytic reduction in the presence of much pyrophosphate appears to be attributable to the same cause as in the presence of Versene.

Whereas in the absence of iron the reversible oxidation potential corresponding to equation 1 of the RSSR–RSH couple is measured at the dropping electrode this should be no longer true in the presence of iron if our interpretation is correct. Actually the zero current potential of the couple was found more positive in the presence than in the absence of iron. For example, in a mixture of 5×10^{-4} *M* RSSR and 10^{-3} *M* RSH(*p*H 9) the zero current potentials were found to be -0.614 and -0.55 volt in the absence and presence of 2×10^{-3} *M* Fe(II).

Finally it should be mentioned that the sequence of reactions (2), (5), (3) and (4) can account equally well for the observed facts as reactions (6), (4) and (7). It is difficult to develop experimental conditions under which one sequence of reactions is conclusively favored over the other.

From the few experiments with dithiodiglycolic acid in the presence of iron it is found that iron has little effect on the prewave of this disulfide. The small effect is eliminated by tartrate which has no effect on the iron catalysis in the reduction of cystine. It might be inferred that reaction (6) with TSST instead of RSSR does not occur or occurs more slowly than with RSSR.

Acknowledgment.—This investigation was supported by a research grant (C-721, C_5) from the National Cancer Institute, U. S. Public Health Service. Part of the experimental work has been carried out with the assistance of Dr. R. C. Kapoor.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE PENNSYLVANIA STATE UNIVERSITY AND THE UNIVERSITY OF MICHIGAN]

Effect of Structure and Hydrogen Bonding on the Stereochemistry of Electrode Reactions. The α,α'-Dibromosuccinates

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The diastereoisomers (*meso* and racemic (*d,l*) forms) of α,α'-dibromosuccinic acid have been electrolyzed at a mercury cathode at controlled potentials over the *p*H range of 0.4 to 8.5. Fumaric acid was produced quantitatively from the *meso* form at all *p*H levels. The racemic form was converted entirely to fumaric acid at low (below 0.4) and high (above 6.9) *p*H levels; between these *p*H values, the *cis*-acid (maleic) also was formed, with a maximum yield (70 ± 3% of the products) at about *p*H 4.0. Diethyl *meso*- and *rac*-dibromosuccinates gave only diethyl fumarate on electroreduction. The data are interpreted with regard to steric factors and the effect of *p*H on these factors. A mechanism capable of explaining the nature of the reduction products produced by the elimination reaction is presented. Extended data on the polarographic behavior of diethyl fumarate and maleate also are given. Large scale and polarographic reductions of the compounds studied are compared.

Winstein, Pressman and Young[2a] studied the elimination of bromine from the 2,3-dibromobutanes, using iodide ion as the reducing agent, and found that the *meso* diastereoisomer formed 96% *trans*-2-butene while the racemic (*dl*) isomer formed 91% *cis*-2-butene. These facts, together with the observed second-order kinetics,[2b] were explained by assuming that the bromine atoms are *trans*[3] to each other prior to reduction and that the dehalogenation process is initiated by the removal of one of the bromine atoms by combination with iodide ion.[2a] The mechanism of the iodide reduction was considered to be a frontal attack on a bromine atom by an iodide ion forming a negatively charged carbon atom (carbanion) and BrI. The free electrons attack the carbon face opposite the remaining bromine atom, freeing bromide ion with an inversion of the carbon atom to form the olefin. In actual reaction, both steps were thought to proceed simultaneously.

The *cis* effect in elimination reactions and stereochemical control of organic reactions has been reviewed recently.[2c]

In a polarographic study of *meso*[4a]-α,α'-dibro-

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[1] University of Michigan, Ann Arbor, Mich.

[2] (a) S. Winstein, D. Pressman and W. G. Young, THIS JOURNAL, **61**, 1645 (1939); (b) W. G. Young, D. Pressman and C. D. Coryell, *ibid.*, **61**, 1640 (1939); (c) D. Y. Curtin, *Record Chem. Prog.*, **15**, 111 (1954); (d) J. Hine and W. H. Brader, THIS JOURNAL, **77**, 361 (1955).

[3] In using the term *trans* with regard to the relative position of atoms or groups on two carbon atoms joined only by a single bond, we mean that the groups in question will be in, or close to, positions in which they will have the maximum possible separation from each other. The term *cis* is used in an opposite sense.

TABLE I

EFFECT OF *p*H, TEMPERATURE AND BUFFER NATURE ON THE MACRO SCALE REDUCTION OF *rac*-α,α'-DIBROMOSUCCINIC ACID

Cell conditions				Analysis of diluted reduced cell solution		
*p*H	Buffer	Applied potential, v.	Acid concn., m*M*	Maleic acid concn., m*M*	Fumaric acid concn., m*M*	Maleic acid formed, %
0.25	1	−0.40	5.98	0.039	0.52	7
1.10	1	− .40	5.98	.250	.57	29
1.90	1	− .40	5.98	.236	.35	40
2.90	3	− .50	5.82	.55	.51	52
3.43	3	− .50	5.82	.87	.54	62
3.72	3	− .50	5.82	.70	.34	68
4.25	3	− .55	5.82	.262	.14	70
4.25[a]	3	− .55	5.82	.271	.095	75
4.25	3[b]	− .55	5.82	.174	.116	62
4.54	3	− .60	5.82	.40	.202	67
5.05	3	− .60	5.82	.290	.132	69
5.65	3	− .75	5.82	.50	.90	36
6.15	3	− .75	5.82	.198	.79	20
6.90	3	− .75	5.82	...	.65	0.0
3.70	4	− .60	3.91	.184	.079	70
3.70[a]	4	− .60	3.91	.224	.082	73
3.70[c]	4	− .60	3.91	...	...	...
4.20	4	− .60	3.91	.79	.278	72
5.05	4	− .60	3.91	.48	.34	68
6.13	4	− .85	3.14	.073	.250	22
8.20	5	− .80	4.39	...	.41	0.0
8.53	5	− .80	4.39	...	.33	0.0

[a] Run at 2.0°. All other runs were at 25° except as noted. [b] Solution was 2.0 *M* in KCl. [c] Run at 35°. Decomposition of the original acid was noted.

mosuccinic acid,[4b] the reduction product was shown to be fumaric acid. Two two-electron waves were found, the first of which marked the over-all elimination of the two bromine atoms to form fumaric acid, and the second the reduction of the fumaric acid to succinic acid. The evidence for the formation of only fumaric acid as the reduction product was based on polarographic runs made at *p*H values greater than 5.5, in which *p*H range the possible presence of maleic acid could be polarographically detected. The data agreed with the work on the 2,3-dibromobutanes. In a continuation of this study the *rac*[4a]-acid was examined polarographically[5] at *p*H 8.2 and, contrary to what was expected, fumaric acid was again the reduction product. This led to a closer examination of the possible internal orientations of the *rac*-acid and the postulation that under certain *p*H conditions the carboxyl groups could play a determining role in deciding the preferred orientation and, consequently, the nature of the reduction products.[5]

In order to investigate the reduction products in the low *p*H region, it was necessary to reduce a mass of the *meso*- or *rac*-acid in buffered solution at a massive mercury cathode by coulometric technique[6]; the reduction products were then examined polarographically at *p*H *ca.* 8.2 where mixtures of maleic and fumaric acids can be analyzed readily with relatively good accuracy.[7] The present paper deals with the results of this study and necessary allied investigations.

The modifying terms, coulometric and coulometer, will be used in subsequent discussion to distinguish experiments performed using a large stirred mercury electrode. Where the coulometric data were actually calculated, they supported the *n* values calculated from the Ilkovic equation. The reduction of either the racemic or *meso*-acid to maleic or fumaric acid is a two-electron process; the reduction of maleic or fumaric acid to succinic acid is also a two-electron process. The same values were found for the esters.

Experimental Results

Acids.—Data for the reduction of the racemic acid at a massive mercury cathode are given in Table I and Fig. 1. The amounts of maleic and fumaric acids were determined individually, using I $(= i_d/Cm^{2/3}t^{1/6})$ values from the literature,[4b,5,7] and were reproducible to ±3%. No maleic acid was found in coulometric runs made with the *meso*-acid at *p*H 0.25, 1.10, 1.90, 2.90, 4.25, 5.05, 6.15, 8.20 and 8.53. The possible interconversion or side reactions of all active species due to chemical action under coulometer conditions were investigated by allowing the solutions to stand in the coulometer cell with an applied potential less than that necessary to cause reduction; no significant production of bromide ions was noted.

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[4] (a) Henceforth, the terms *meso* and racemic will be used to denote the respective forms of α,α'-dibromosuccinic acid. (b) I. Rosenthal and P. J. Elving, THIS JOURNAL, **73**, 1880 (1951).

[5] I. Rosenthal, "Mechanism of Electrochemical Carbon–Halogen Bond Fission," Ph.D. Thesis, The Pennsylvania State College, State College, Pa., 1951, pp. 60–67.

[6] J. J. Lingane, THIS JOURNAL, **67**, 1916 (1945).

[7] B. Warshowsky, P. J. Elving and J. Mandel, *Anal. Chem.*, **19**, 161 (1947); P. J. Elving, A. J. Martin and I. Rosenthal, *ibid.*, **25**, 1082 (1953).

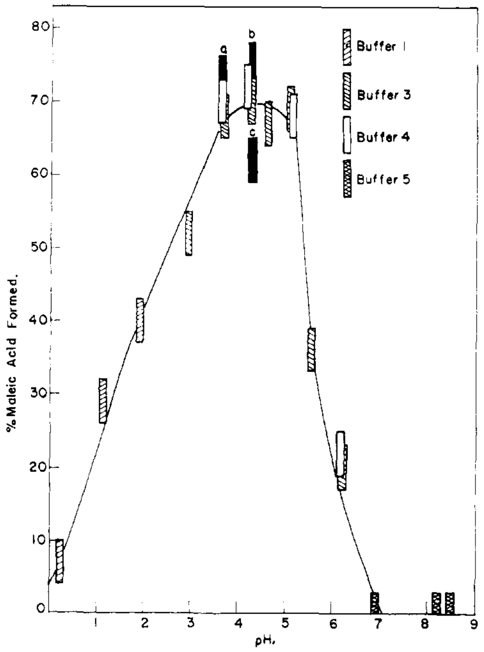

Fig. 1.—Relation of percentage maleic acid formed to *p*H in the macro scale reduction of *rac*-dibromosuccinic acid. Data are at 25° except that *a* represents a run in buffer 4 at 2.0°; *b*, buffer 3, 2.0°; *c*, buffer 3 made 2.0 *M* with KCl, 25.0°. Points are drawn to show a possible ±3% deviation in determination of maleic acid formed, and ±0.05 unit deviation in *p*H.

Reduction of the *meso*-acid yielded only fumaric acid over the *p*H range of 0 to 8, while the *rac*-acid gave varying amounts of maleic and fumaric acids depending on the *p*H; the maximum yield of maleic acid (70%) occurred at about *p*H 4. The *rac*-acid tended to give slightly higher percentages of maleic acid in acetate buffer than in MacIlvaine buffer though the difference is within experimental error. Higher percentages of maleic acid were produced from the *rac*-acid in two runs at 2° than at 25°.

Data on the polarographic behavior of the dibromosuccinic acids are given in Table II and Figs. 2 and 3. The acids show the general S-shape behavior observed for other acids with the exception that the acidic portion of the *meso* curve is not *p*H-independent in the *p*H region examined. Similar behavior has been found and discussed in the case of trichloroacetic acid.[8]

Esters.—Data for the polarographic behavior of the diethyl esters of the *rac*- and *meso*-acids are given in Table III. The first polarographic waves for the esters are not clearly developed due to presence of the mercury oxidation wave in many of the buffered solutions used. The following information, however, was obtained in spite of this interference by using a sulfate medium at 2°.

(1) Both esters reduce to the fumarate. It was established by direct polarographic analysis that no diethyl maleate was produced below *p*H 4.4. This was verified for the entire *p*H range by reducing the dibromoesters coulometrically and then analyzing the products at *p*H 0.4 where there is a 0.15-volt difference between the $E_{1/2}$ values of maleate and fumarate.

TABLE II

EFFECT OF *p*H AND BUFFER NATURE ON POLAROGRAPHIC BEHAVIOR OF *rac*- AND *meso*-α,α′-DIBROMOSUCCINIC ACIDS

*p*H	Buffer	Wave I $-E^1/_2$, v.	Wave I *I*		Wave II $-E^1/_2$, v.	Wave II
rac-α,α′-Dibromosuccinic acid						
1.1	1	0.09[a]	2.7		0.61	3.4
1.9	1	.12[a]	2.8		.70	3.5
1.13	2	.05[a]	2.2		.60	2.3
1.80	2	.05[a]	1.9		.65	2.1
2.40	3	.16	3.2			
2.98	3	.19				
3.80	3	.22	3.3			
4.52	3	.31	3.3			
5.47	3	.43	3.2			
3.92	4	.13	2.3		.88	2.7
4.0	4	.16	2.1		.88	2.7
4.4	4	.20	2.3		.92	2.7
5.6	4	.38	3.0	I	1.17	2.0
				II	1.43	1.4
5.7	4	.33	2.7	I	1.18	2.1
				II	1.49	2.3
5.8	4	.34	2.9	I	1.22	2.3
				II	1.54	2.4
8.47	5	.51	3.7		1.58	4.9
9.43	5	.49	3.2		1.58	
meso-α,α′-Dibromosuccinic acid						
1.13	2	0.10[a]	2.2		0.60	3.7
1.80	2	.07[a]	4.2		.69	3.9
2.03	1	.06	3.6		.89	2.9
3.80	3	.16	1.6		.75	2.7
4.05	3	.23	2.6		.89	2.9
5.81	3	.55	2.8	I	1.20	1.8
				II	1.47	2.1
8.13	5	.55	3.8		1.56	3.7
8.71	5	.55	3.8		1.57	3.8

[a] Concentration of acid was 0.2 m*M* in these experiments and 0.5 m*M* in the others.

(2) The racemic ester is reduced in a two-electron step to the fumarate at an $E_{1/2}$ of about +0.05 v.; over the restricted *p*H range available, $E_{1/2}$ was *p*H-independent. The *meso*-ester also is reduced to the fumarate in a two-electron step; $E_{1/2}$ is more positive than that for the racemic form and can be estimated at +0.12 v.

(3) The esters are reduced more easily than the free acids as was found with the α-haloalkanoic acids.[8]

In order to identify the reduction products of the diethyl dibromosuccinates, the diethyl esters of maleic and fumaric acids were studied polarographically under identical temperature and buffer conditions (Table IV and Fig. 4). The second wave shown in Table IV is due to the free acid formed by hydrolysis at higher *p*H values; this does not affect the value of $E_{1/2}$ for the remaining ester. In general, the results followed a pattern similar to that previously found.[9] A greater *p*H range was covered, however, in a greater variety of buffers,

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(8) P. J. Elving and C. S. Tang, THIS JOURNAL, **74**, 6109 (1952); I. Rosenthal, C. S. Tang and P. J. Elving, *ibid.*, **74**, 6112 (1952).

(9) P. J. Elving and C. Teitelbaum, *ibid.*, **71**, 3916 (1949).

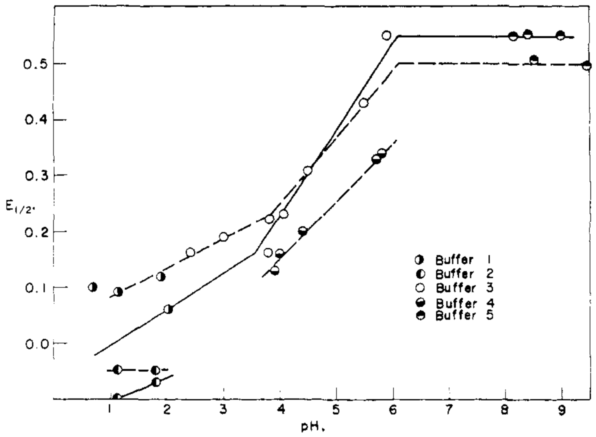

Fig. 2.—Variation of $E_{1/2}$ with *p*H for *rac*- and *meso*-dibromosuccinic acids. The solid line is based on experimental data taken from reference 4b on the *meso* acid; plotted points represent experimental values obtained in the present study. The broken line represents data found for the racemic acid.

TABLE III

EFFECT OF *p*H AND BUFFER NATURE ON POLAROGRAPHIC BEHAVIOR OF *rac*- AND *meso*-DIETHYL α,α'-DIBROMOSUCCINATES AT 2°

*p*H	Buffer	$-E_{1/2}$,[a,b] v.	*I*
	rac-Diethyl α,α'-dibromosuccinate		
0.40	1	0.55	1.57
1.20	1	.63	1.47
1.78	1	.68	1.44
4.33	4	.80	1.46
4.95	4	.84	2.42
5.75	4	.90	2.68
4.40	3	.89	2.00
6.45	3	.99	2.02
	meso-Diethyl α,α'-dibromosuccinate		
0.40	1	0.52	1.60
1.78	1	.67	2.34
4.33	4	.83	1.74
4.95	4	.85	1.80
5.75	4	.91	1.90
4.40	3	.87	2.00
6.45	3	.98	1.97

[a] There was definite evidence of a preceding wave but its constants could not be calculated with the buffers used due to interference caused by mercury oxidation; this wave is discussed in the text. [b] Ester concentration was 0.5 m*M*.

which enabled one to differentiate *p*H effects from buffer effects. Thus, instead of a definite crossover of ester $E_{1/2}$ values previously reported[9] at about *p*H 8, both esters tend to level off at about the same $E_{1/2}$ value in this *p*H region; the reported cross-over is probably due to buffer and hydrolysis effects.

Relation between *p*H and Percentage Maleic Acid Formed

The polarographic and the macro scale reductions of *meso*-dibromosuccinic acid and the diethyl *meso*- and *rac*-dibromosuccinates do not give any detectable yield of maleate species. However, the racemic acid does yield varying amounts of maleic acid over the *p*H range of 1 to 7. These results can only be explained in terms of a hydro-

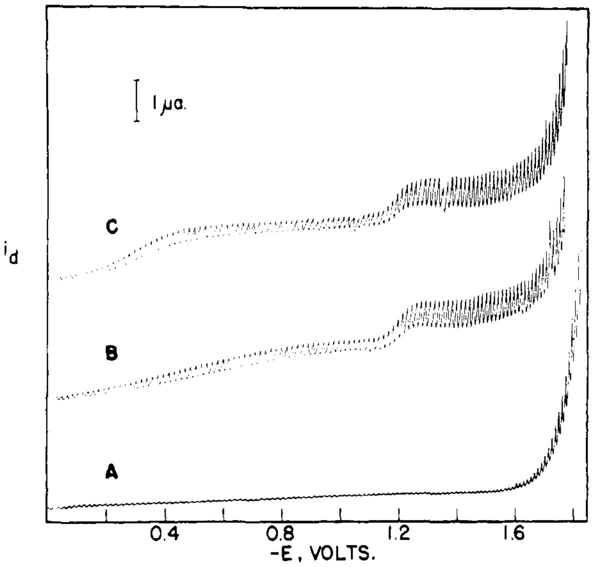

Fig. 3.—Polarograms for (A) background solution (0.48 *M* sodium acetate adjusted to *p*H 5.56 with acetic acid), (B) *meso*-dibromosuccinic acid (0.261 m*M*), and (C) *rac*-dibromosuccinic acid (0.255 m*M*).

TABLE IV

EFFECT OF *p*H AND BUFFER NATURE ON POLAROGRAPHIC BEHAVIOR OF DIETHYL FUMARATE AND DIETHYL MALEATE AT 2°

		Wave I		Wave II	
*p*H	Buffer[a]	$-E_{1/2}$, v.	*I*	$-E_{1/2}$, v.	*I*
		Diethyl Fumarate[b]			
0.40	1	0.54	1.73		
1.13	1	.61	1.74		
1.78	1	.68	1.74		
4.40	3	.86	1.68		
6.45	3	.98	1.68		
7.85	3	1.02	1.65		
4.33	4	0.82	1.32		
4.95	4	.85	1.35		
5.75	4	.91	1.50		
8.10	5	.99	1.77	1.22	0.020
8.75	5	.99	1.73	1.27	0.034
9.70	5	1.01	1.69	1.31	1.020
10.30	6	1.03	0.84	1.41	0.796
11.10	6	1.06	0.54	1.43	1.020
		Diethyl Maleate[b]			
0.40	1	0.69	1.89		
1.13	1	.77	1.93		
1.78	1	.83	1.95		
4.40	3	.97	2.03		
6.45	3	1.04	2.04		
7.85	3	1.05	2.02		
4.33	4	0.97	1.55		
4.95	4	0.99	1.70		
5.75	4	1.02	1.76		
8.10	5	1.02	2.33		
8.75	5	1.01	2.16		
9.70	5	1.02	2.05		
10.30	6	1.08	1.22	1.71	0.450
11.10	6	1.09	1.89	1.68	0.014

[a] Solutions contained 4% dioxane. [b] Fumarate concentration was 0.46 m*M*; maleate concentration was 0.48 m*M*.

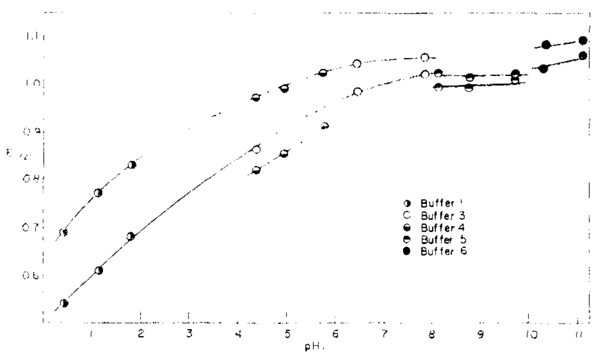

Fig. 4.—Variation of $E_{1/2}$ with pH for diethyl maleate and diethyl fumarate. The solid line represents data for diethyl fumarate, the broken line for diethyl maleate.

gen bonding whose strength is influenced by pH and steric factors, regardless of the mechanistic route proposed. In considering the influence of pH and steric factors on hydrogen bonding in the dibromosuccinic acids, it is convenient to divide the pH scale into three regions: (a) where both carboxyl groups are undissociated, (b) where one carboxyl group is ionized, and (c) where both carboxyl groups are ionized.

Examination of the molecular model of the *meso*-acid shows that it is possible for both the bromine and carboxyl groups to be essentially *trans* at the same time, *i.e.*, to have nearly maximum separation to their respective counterparts. Thus, in the first and third pH regions, pH variation should have no effect. In the second case, however, there exists a possibility of interaction between the dissociated and undissociated carboxyl groups.[10] Such bonding would necessitate that the bromine groups be very close (*cis*) to one another, and, since the energy of repulsion is probably much greater than that due to the carboxyl group interaction in a seven-membered ring, the cyclic bound form will not occur to any appreciable extent.

With the racemic acid the same three species exist, but with obviously different spatial arrangements of the bromines and carboxyl groups to one another. In this case, if either the bromines or the carboxyl groups have maximum spatial separation (*trans*) to their respective counterparts, the other pair will tend toward minimum separation (*cis*). Thus, in the third pH case one would expect that due to the repulsion between the negative charges on the carboxyl groups, these groups would approach maximum separation even if this involved proximity of the bromine atoms. In the second pH cases, where the possibility of interaction between dissociated and undissociated carboxyl groups is again present, interaction is favored by the fact that, when the carboxyl groups are close together, the bromines approach maximum separation. In the first pH case the relative positions are somewhat more difficult to establish *a priori* but the two main possibilities are (a) the completely staggered form[11] with the hydrogen of each asymmetric carbon atom midway between the bromine and carboxyl groups of the other carbon and (b) the two hydrogens essentially *cis* with the bromine and carboxyl groups on one asymmetric carbon atom, respectively, adjacent to the carboxyl and bromine groups on the other asymmetric carbon atom.

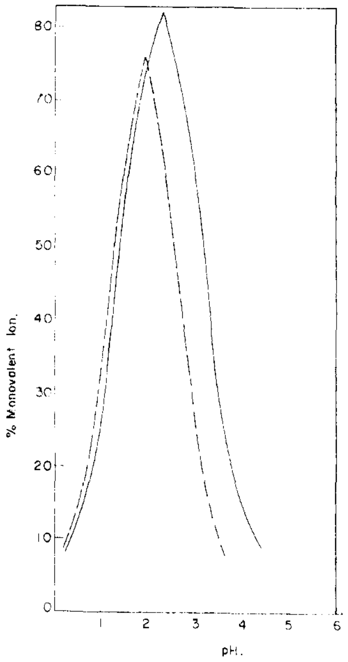

Fig. 5.—Variation of percentage monovalent ion present with pH in solutions of racemic dibromosuccinic acid. The solid line is plotted from calculations made using the ionization constants given by H. Bode and K. Petersen, *Ber.*, **71B**, 871 (1938), assuming unit activity; the broken line represents similar calculations using activities calculated for an ionic strength of 1.0.

Therefore, out of the six possibilities with the two acids, there is only one species (singly ionized racemic acid) in which the charge and steric factors combine energetically to favor hydrogen bond (cyclic) formation. The stability of this cyclic form should not be surprising in view of the fact that the steric factors alone tend to keep both *meso*- and *rac*-2,3-dibromobutane[12] in the *trans* position. This, coupled with the added energy of interaction between the hydroxyl hydrogen and the carboxylate ion, should lead to a relatively stable configuration.

If this description of hydrogen bond formation is accepted, it can then be seen that, all other considerations notwithstanding, there will be an additional force in the bonded form tending to keep the carboxyl groups *cis* during reduction. Added evidence for a cyclic form is given by the fact that both increasing the temperature from 2 to 25° and increasing the ionic strength lead to lower yields of maleic acid.

If the hypothesis of hydrogen bonded racemic acid yielding maleic acid is correct, then the amount of maleic acid formed should be proportional to the amount of singly dissociated acid present over the pH range, since the hydrogen bonding is dependent

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(10) G. E. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 116.

(11) W. G. Young, Abstracts of Papers, Eighth National Organic Chemistry Symposium, American Chemical Society, St. Louis, Mo., December, 1939, pp. 92–95.

(12) D. P. Stevenson and V. Schomaker THIS JOURNAL, **62**, 3173 (1939).

on the presence of the one charged carboxyl group. Figures 1 and 5 give this comparison. The general agreement is good with the one exception that maleate production peaks at about *p*H 4, while the monoanion concentration peaks at about *p*H 2. The difference can be explained on an analogous basis to that used for the character and location of the split polarographic waves of maleic and fumaric acids.[13]

The single maleic acid wave found in the low *p*H region becomes a double wave at about *p*H 5.5. The height of the second wave increases with *p*H while the original wave decreases; the total of the two remains essentially constant. At about *p*H 6.5 the first wave disappears completely and at *p*H 8.2 the second wave starts to repeat the splitting phenomena; only in this case the more negative of the split waves is hidden beyond the background-electrolyte discharge. At about *p*H 10, the original second wave disappears. The original first wave (low *p*H) is identified with the reduction of undissociated acid even though at *p*H 4, for example, there should be present only very minute amounts of this species. However, it is known[14] that the anion can recombine with hydrogen ion in an effort to attain equilibrium by replenishing the concentration of undissociated acid which is reduced at a less negative potential than the anion. If this process is sufficiently rapid, all of the anion will be reduced in the form of undissociated acid. As *p*H is increased, the rate of recombination decreases, and, eventually, becomes controlling and so slow that some of the anion is reduced directly. When this occurs with maleic acid, the wave splits since a wave due to the direct reduction of anion is observed. As the *p*H is increased, the second ionization stage becomes significant, and the process is repeated. The net effect is to shift the *p*H–reduction current curve of any ionized species to higher *p*H values than the static equilibrium concentration curve would indicate. The extent of the shift depends on the association rate. Therefore, the difference in peak values for maleic acid production can be ascribed to the effect of rates of equilibration between the different species.

Relation between Polarographic and Macro Scale Reduction Products

The discussion on acid–anion interconversion indicates that reduction at a massive mercury electrode could be different from that at a micro dropping mercury electrode, especially when questions of rates are involved. There is a check in the alkaline region where both the *meso* and racemic acids give only fumaric acid under both coulometric and polarographic conditions. It was considered necessary to demonstrate the polarographic production of mixtures of maleic and fumaric acids in that *p*H region where macro scale reduction of the racemic acid yields a similar mixture. Demonstration of the polarographic formation of fumaric acid by reduction of the racemic acid was difficult because of the small separation of the maleic and fumaric acid waves in the lower *p*H regions. However, by taking advantage of the splitting[13] of fumaric and maleic acid waves at about *p*H 5.7 as well as the unequal shifts of these waves with changes in buffer concentration and ionic strength,[9] it was possible to demonstrate unequivocally the polarographic production of maleic and fumaric acids. The best base solution for this was buffer 4 at *p*H 6.0 and ionic strength of 0.1. The percentages of maleic acid formed were equal to or slightly higher than those found coulometrically. The identity of the waves was verified by adding separately maleic and fumaric acids to the racemic acid test solution and showing that the postulated waves (for maleic and fumaric acids from the racemic acid) were increased proportionally in i_d with no shift in $E_{1/2}$.

Mechanism of Reduction

In considering a mechanism for the electrochemical reduction of carbon–halogen bonds, there is some experimental evidence for a carbanion[15] mechanism and other evidence that indicates a free-radical mechanism.[15] The present experimental work is a case in point. Any attempt to fit all the data into a strict carbanion or free-radical mechanism would lead at best to a forced picture. It is believed that the reason for this is the essentially dual nature of the reduction process. The following mechanistic picture is proposed as being the best explanation of known carbon–halogen reduction phenomena.

The initial action is the displacement of the halogen by a single electron followed by step A or B: (A) The discrete existence of a trigonal free radical which will undergo a typical radical reaction, *e.g.*, addition of a second electron or dimerization. (B) The immediate addition of a second electron.

The question of whether the displacement is completed by step A or B depends on which route requires the less activation energy, *i.e.*, on the difference in free energy of the transition states. In the case of the *meso*-acid at all *p*H values and the racemic acid at intermediate *p*H values, step B is followed. In all these cases the conformation of the molecule is such that the bromine atoms are essentially *trans* and coplanar so that, as a pair of electrons is added (with a bromide ion leaving), a rearward displacement of the second bromine atom and the formation of a double bond could all take place simultaneously. This type of action, suggested for the chemical reduction of similar compounds,[2] would have a relatively low activation energy. However, in the case of the *racemic* acid at high and also probably at low *p*H values, the preferred configuration has bromine atoms constrained in a *cis* position, and single step elimination of the rearward type is not possible. In these cases it is postulated that step A is followed; a planar free radical is formed and then the second electron is added in such a manner that the remaining bromine can be displaced at the same time.

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[13] P. J. Elving and I. Rosenthal, *Anal. Chem.*, **26**, 1454 (1954); V. Hanus and R. Brdicka, *Chem. Listy*, **44**, 291 (1950).

[14] R. Brdicka, *Collection Czechoslav. Chem. Communs.*, **12**, 212 (1947); R. Brdicka and K. Wiesner, *ibid.*, **12**, 138 (1947); J. Koutecky and R. Brdicka, *ibid.*, **12**, 337 (1947).

[15] See summary article by P. J. Elving, *Record Chem. Prog.*, **14**, 99 (1953).

The fact that the more stable double-bonded compound, ethyl fumarate, is formed from both the *meso* and racemic esters may indicate a non-stereospecific reaction at the electrode which proceeds by a free radical mechanism. A similar mechanism may apply to the *meso* and racemic acids except where the acid carboxyl groups in the racemic acid are kept *cis* by hydrogen bonding. Such a brief statement of the mechanism does not, however, clearly indicate why both bromines are eliminated in a two-electron process to form an olefin, whereas in the case of two or more halogens on the same carbon atom, each halogen requires a two-electron process for its removal and replacement by hydrogen in a *p*H-independent process[15]; neither does it satisfactorily indicate what happens when maleic acid is formed from the racemic acid.

Experimental

Apparatus.—A water-jacketed coulometer essentially as described by Lingane[6] was used for the macro scale reductions. The potential of the stirred mercury cathode was maintained within ±0.05 v. of the desired potential by a S.C.E.-potentiometer circuit. Constant voltage to the electrolysis electrodes was applied from storage batteries through a slide-wire potentiometer. A Weston milliammeter, properly shunted, was used to measure current in the coulometer circuit. A KCl salt-bridge with sintered glass discs on both ends connected the electrolysis cell to a vessel containing the silver-wire anode in 1 *M* KCl solution. Before making a coulometric run, both solutions were stirred and deoxygenated with purified and conditioned nitrogen.

The temperature of the coulometer and the polarographic cell[16] was controlled to ±0.1° at 25° and ±0.5° at 2°. The dropping mercury electrode had a capillary constant, $m^{2/3}t^{1/6}$, of 1.61 g.$^{2/3}$ sec.$^{-1/2}$ at open circuit (h = 50 cm.) at 25° into distilled water.

A Sargent model XXI Polarograph was used to analyze the coulometric reduction products of the acids and a Leeds and Northrup model E Electro-Chemograph was used for the ester products. *p*H was determined with a Beckman model G *p*H meter.

Chemicals.—Reagent grade chemicals were used for buffer preparation (Table V) after polarographic analysis at high sensitivity revealed no interfering impurities.

The *rac*-α,α'-dibromosuccinic acid was prepared and then purified by recrystallization from water and ethyl ether.[17] Solubility tests showed less than 2 mole % of maleic acid present. The *meso*-α,α'-dibromosuccinic acid[19] was purified by repeated washing with water and by recrystallization from ethyl ether; solubility tests showed less than 3 mole % of fumaric acid present. Bromination of diethyl fumarate and maleate led, respectively, to the *meso* and racemic forms of diethyl dibromosuccinate[20]; the former was purified by recrystallization from alcohol and the latter by vacuum distillation.

TABLE V

DESIGNATION, *p*H RANGE AND COMPOSITION OF BUFFERS

Buffer	*p*H range	Composition
1	0–2	1.0 *M* KCl with added HCl
2	1–2	1.0 *M* K_2SO_4 with added H_2SO_4
3	2–7	Na_2HPO_4 + citric acid + KCl[a]
4	3.7–6	1.0 *M* NaOAc with added HOAc
5	8.2–9.7	1.0 *M* NH_4Cl with added NH_3
6	10–12	0.2 *M* Na_2HPO_4 with added NaOH

[a] This buffer was made up according to Britton[18] with KCl added to bring the ionic strength to 1.0.

Procedure for Macro Scale Reduction.—Two hundred ml. of buffer (ionic strength of 1.0, Table V) was deoxygenated and electrolyzed until the current was less than 1 ma. (In polarographic and coulometric runs with esters, the solutions contained 4% purified dioxane to increase their solubility.) Enough material then was added to make the solution 3 to 15 m*M* in active species; experiments showed the concentration not to be critical. The cathode potential applied was determined from the polarographic study of the compounds (Tables II and III; Figs. 2 to 4) and references 4b and 5, and was less than the value at which reduction of the olefinic product occurred. As the reduction proceeded, 5.00-ml. samples were withdrawn from the coulometer cell and generally diluted to 50.0 ml. with 1.0 *M* ammonia buffer (in the case of the acids) so that the final *p*H of the test solution was between *p*H 8.2 and 9.2, where the maleic and fumaric acid waves are easily distinguished; the solutions then were analyzed polarographically. With the esters, the coulometer samples usually were diluted with 1.0 *M* KCl–HCl buffer to a final *p*H of 0.3 to 0.4 where the diethyl maleate and fumarate can be distinguished. The macro scale coulometric reductions were continued until a current of less than 1 ma. was flowing.

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