60 ml. of dry ether proceeded readily without external heating. After one-half hour, the mixture was refluxed for 2 hours and then allowed to stand overnight. All of the magnesium dissolved and the mixture separated into two layers. The lower layer gave no Gilman test for Grignard reagent. The mixture was poured onto ice, the ether layer separated and washed with dilute hydrochloric acid and water. The ethereal solution was dried over calcium sulfate and the ether removed. The residue amounted to 4.2 g., contained iodine (by sodium fusion test) and was polymeric in nature. About 1.5 g. of material, b.p. 100–190° (6–7 mm.), was obtained on distillation before the residue began to decompose. The volatile product was purified by evaporative distillation for analysis.

Anal. Calcd. for $(C_4H_{10}Si)_{20}I_2$: C, 48.59; H, 10.19; I, 12.83. Found: C, 48.14; H, 10.41; I, 12.43.

The combustion analysis gave fair agreement for structure I with $x = 20$. Actually, the material is probably a mixture of $(C_4H_{10}Si)_n$ and I with values of n and x small enough to give the observed b.p. range.

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Polarographic Behavior of Organic Compounds. VIII. The System *meso*-α,α'-Dibromosuccinic Acid–Fumaric Acid

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Previous work on the α-halogenated acids[1,2] has shown that the polarographic reduction of these compounds involves the fission of the carbon–halogen bond and the formation of the saturated acid. This behavior is in accord with the chemical reduction of carbon–halogen linkages. In the case of α,β-dibromides both chemical reduction[3,4] and polarographic reduction[5] result in formation of the olefin. The polarographic work[5] on 1,2-dibromoethane and the preparative electrolysis[5] on 2,3-dibromobutane, unfortunately, was done at only one set of conditions in unbuffered solution. No attempt was made to identify the configuration of the olefin produced, which is of primary interest with regard to any mechanism proposed for the reduction. It was therefore felt to be of interest to study this phenomenon under suitable conditions, with a view to investigating the nature of the process and to see if the isomers formed as reduction products were analogous to those formed chemically. The compound chosen for study was *meso*-α,α'-dibromosuccinic acid whose olefinic reduction product would be either fumaric or maleic acid, either of which could be identified polarographically. In addition, the dibromosuccinic acid with its two equivalent carbon–halogen bonds held promise of shedding additional light on the mechanism of polarographic reduction of symmetrical linkages and of carbon–halogen bonds.

The work done on fumaric acid was primarily to aid in identifying the second polarographic wave obtained with the dibromosuccinic acid. At the same time it was possible to extend previous work on fumaric acid.[6]

Experimental

The experimental conditions, procedures and apparatus are the same as elsewhere described[2] except that a new capillary was used, whose m value was 1.027 mg./sec. at open circuit, into distilled water, with a head of 50 cm. and a drop-time of 6.0 seconds. The buffers used are given in Table I and are analogous to those previously used in the fumaric acid study.[6] All measurements were made at 25.0 ± 0.1°.

TABLE I

BUFFER SOLUTIONS

Range	Concentration of components
0 to 2	0.9 M in KCl with added HCl
4 to 6	0.9 M in NAOAc with added HOAc
8 to 9	0.9 M in NH_4Cl with added NH_4OH

Fumaric acid (Eastman Kodak Co. practical grade) was recrystallized three times from 1 N hydrochloric acid. *meso*-α,α'-Dibromosuccinic acid, prepared according to "Organic Syntheses,"[7] was purified by repeated washing with water and by recrystallization from ethyl ether. By means of solubility tests in ethyl ether it was shown that the amount of fumaric acid present as impurity was less than 3 mole %.

Discussion and Conclusions[8]

The polarographic data for dibromosuccinic acid, fumaric acid, and mixtures of the two are given in Table II. Two well-defined cathodic waves were obtained for dibromosuccinic acid over the *p*H range 2 to 9 except at *p*H 5.9 where three waves were obtained. The first of these waves marks the reduction of the dibromosuccinic acid to fumaric acid and the remaining wave (two waves at *p*H 5.9) is due to the reduction of the fumaric acid thus formed to succinic acid (no. 4 to 6 and 8 to 11). The identity of the second wave is shown by comparing the curves of dibromosuccinic acid with the waves produced with fumaric acid and fumaric–dibromosuccinic acid mixtures (no. 3 and 4; 5 and 6; 7 and 8; 9 and 10); in all cases the $E_{0.5}$ and i_d/c values agree. In calculating the i_d/c values for the second waves of the fumaric acid–dibromosuccinic acid mixture, the concentration values used were the sum of the fumaric acid and the dibromosuccinic acid concentrations. At *p*H 5.9 the reduction of fumaric acid involves two waves and, consequently, the reduction of dibromosuccinic acid at this *p*H results in three waves (no. 7 and 8). While the diffusion current constants for the reduction of the two acids are similar at any one *p*H, they vary considerably among themselves at different *p*H values. This behavior in the diffusion currents has been previously noted.[6]

A plot of $E_{0.5}$ *vs.* *p*H for the dibromosuccinic acid

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(7) H. S. Rhinesmith, in "Organic Syntheses," Vol. 18, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 17.

(8) Although reference is made to the acids throughout the paper, it should be remembered that the behavior of the anions was being observed under many of the conditions used.

TABLE II

POLAROGRAPHIC DATA AT DIFFERENT *p*H VALUES FOR *meso*-α,α'-DIBROMOSUCCINIC ACID, FUMARIC ACID AND MIXTURES OF BOTH

				Dibromosuccinic acid or mixture											
				Wave I				Wave II				Fumaric acid			
Curve	Dibromosuccinic acid, m*M*	Fumaric acid, m*M*	*p*H	$E_{0.5}$, v.	i_d/c, μa./m*M*	$\frac{i_d}{cm^{2/3}t^{1/6}}$	*n*[b]	$E_{0.5}$, v.	i_d/c, μa./m*M*	$\frac{i_d}{cm^{2/3}t^{1/6}}$	*n*[b]	$E_{0.5}$, v.	i_d/c μa./m*M*	$\frac{i_d}{cm^{2/3}t^{1/6}}$	*n*[b]
1		0.520	0.6									0.56	5.2	4.0	2.0
2		.520	1.1									.62	5.2	4.0	1.8
3		.520	2.0									.72	5.1	3.9	1.3
4	0.501		2.0	0.06	4.7	3.6	1.1	0.72	5.3	4.1	1.1				
5	.501		4.0	.23	3.5	2.6	0.4	.89	3.8	2.9	1.0				
6	.450	.520	4.0	.22	3.5	2.6		.89	3.8[a]	2.9					
7		.520	5.9									I 1.19	1.9	1.4	
												II 1.46	1.9	1.4	
8	.501		5.9	.53	3.4	2.5	.5	I 1.19	2.1	1.6	1.5				
								II 1.47	1.8	1.4	0.8				
9	.501		8.1	.55	5.1	3.8	.4	1.56	4.9	3.7	1.0				
10	.450	.520	8.1					1.56	4.8[a]	3.7					
11	.501		8.7	.55	5.2	3.8	.3	1.57	4.8	3.8					

[a] Concentration of fumaric acid used in calculating i_d/c is 0.970, *i.e.*, the sum of the original concentrations of dibromosuccinic and fumaric acids. [b] Calculated from the equation, $E_{0.75} - E_{0.25} = -0.058/n$.

shows an S-shaped relationship similar to that elsewhere described,[2] with the acid end unexplored because the wave starts to merge with the chloride wave. The *n* values calculated by means of the equation, $E_{0.75} - E_{0.25} = -0.058/n$, are constant at about 0.4 except that at *p*H 2 it rises to 1.1.

The remote possibility that the first wave observed was due to the reduction of bromofumaric acid formed by the dehydrohalogenation of the dibromosuccinic acid has been investigated. A solution of the dibromosuccinic acid, 10 m*M*, upon standing for 48 hr. showed less than 1% decomposition as shown by tests for the formation of bromide ion. Since the solutions prepared were used within 24 hr. and since in order to account for the i_d/c results obtained there would have to be almost complete conversion to the bromofumaric acid, the possibility that the more positive wave was due to the latter substance is eliminated.

The studies of fumaric acid at the lower *p*H values (No. 1 to 3) extend earlier work.[6] The existence of two waves at *p*H 5.9 (no. 7) explains the very low value of the diffusion current previously obtained.[6] The $E_{0.5}$ then obtained for fumaric acid was 1.21 which agrees with the value of 1.19 obtained in the present study for the more positive of the two waves due to fumaric acid. Another interesting phenomenon is the gradual increase in *n* value in the low *p*H region from 1 to 2. It has been established (*cf.* reference 1[6]) that the reduction of fumaric acid is a two-electron process. From the present investigation it is seen that in the reduction of dibromosuccinic acid both waves have similar diffusion current constants. It follows from this and the similarity between the dibromosuccinic acid and the fumaric acid that the reduction of the dibromosuccinic acid to fumaric acid is likewise a two-electron process.

The data obtained indicate that *meso*-α,α'-dibromosuccinic acid is reduced in a one-step two-electron process to fumaric acid. The formation of fumaric rather than maleic acid is in line with the evidence found for analogous chemical reactions, in which *trans*-elimination of the bromine atoms takes place.[4,9,10] Typical results are shown by the action of aqueous iodide solution at 90° upon the 2,3-dibromobutanes.[4] The *meso* form gives a butene which is 96% *trans;* the racemic gives a butene which is 91% *cis.* Similar work[10] on *meso*-α,α'-dibromosuccinic acid also indicates *trans*-elimination with the formation of fumaric acid.

The conversion attained polarographically is greater than 98% since no maleic acid wave was obtained even at *p*H 8.2 where the $E_{0.5}$ of maleic acid[6] is 0.2 v. lower than the $E_{0.5}$ of fumaric acid and, therefore, easily detectable.

It is unfortunately impossible on the basis of the present work to distinguish between a simultaneous one-electron attack on each of the carbon–halogen bonds and an unsymmetrical two-electron attack on one of the two carbon–halogen bonds with a subsequent rearrangement of the free electron pair and the displacement of the second bromine atom as a bromide ion. However, the chemical evidence[4] seems to favor the latter alternative.

The type of polarographic reduction encountered with the dibromosuccinic acid may be of a general nature and may take place wherever two adjacent halogens occur whose removal will lead to a stable double or triple bond.[5] Further work along these lines is continuing.

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The Reaction of Propylene Oxide with Thiophenol

BY ROBERT D. SCHUETZ

During the course of an investigation in this Laboratory on the syntheses of tertiary amines