$[OH^-]/[ZNH_2]$. Introduction of the value of $[ZNH_2]$ into equation (12) leads to

$$\frac{dx}{dt} = \frac{k'K_2K_6[H_3O^+]a^2(f-x)}{[H_2O]^2\{[K_A/K_W)^2[H_3O^+]^2 + 2(K_A/K_W)[H_3O^+]C + C^2\}} \quad (16)$$

Since (K_A/K_W) $[H_3O^+]$ seems to be larger than C, the equation is simplified to

$$\frac{dx}{dt} = \frac{k'K_2K_6K_W\,a^2(f-x)}{[H_2O]^2K_A\{(K_A/K_W)[H_3O^+] + 2C\}} = k(f-x) \quad (17)$$

Hence, the reaction follows first-order kinetics with regard to $(f - x)$ in agreement with the experiment. The equation (17) may be expressed in the form

$$\left(\frac{k'K_2K_6K_W}{[H_2O]^2K_A}\right)\frac{a^2}{k} = (K_A/K_W)[H_3O^+] + 2C \quad (18)$$

where the value of C and the variation of it with

pH are relatively small. In agreement with equation (18), average values of a^2/k at each pH vary linearly with the concentration of the oxonium ion as Fig. 1 shows.

When the acidity of the reaction mixture was decreased (pH ca. 2–7), large amount of T precipitated according to the equation (4); hence, the formation of the resinous product was greatly retarded and the estimation of the accurate rate was difficult. Since the amount of free base of aniline in this range of pH is not negligible, the rate equation (12) will hold rather than equation (17). This expectation was confirmed by the observation that a maximum rate was found at about pH 5–6 at the very early stages of the reaction.

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KYOTO, JAPAN

Polarographic Behavior of Organic Compounds. IX. Iodoacetic Acid and the Bromoacetic Acids

BY PHILIP J. ELVING, ISADORE ROSENTHAL AND MARILYN KOLL KRAMER[1]

In the pH range of 1 to 12 iodoacetic acid gives one polarographic wave while tribromoacetic acid gives three waves, the most negative of which is identical in characteristics with the one wave of monobromoacetic acid and the more negative of the two waves of dibromoacetic acid. The intermediate tribromoacetate wave is identical in behavior with the more positive dibromoacetate wave. Each wave is irreversible with the possible exception of the most positive tribromoacetate wave. Each wave represents a two-electron current-producing process, which is due to the fission of a carbon–halogen bond.[3] The mechanism of reduction is the step-wise removal of halogen, e.g., tribromoacetic going to dibromoacetic and then to bromoacetic. There is an S-shaped relation between $E_{0.5}$ and pH; the pH value equal to the pK_a of the acid is located on the rising portion of the curve. The $E_{0.5}$ becomes more negative with increasing pH and may be pH-independent in portions of the acidic and basic regions.

The step-wise removal of halogen atoms from polyhalogenated compounds has been recently described in the case of the chlorinated methanes[2] and the chlorinated acetic acids.[3a] Reduction of the carbon–halogen bond has also been reported for α-bromopropionic acid.[3b] These compounds were studied in buffered solutions. Other organic compounds containing carbon–halogen bonds either have been studied in unbuffered solutions or have not been examined from the viewpoint of the variation of $E_{0.5}$ with pH[4]; the data in these papers is not readily susceptible to theoretical discussion.

It seems possible that by studying the ease of re-

(1) A portion of the material presented is based on the thesis submitted by Marilyn Koll Kramer for the M.S. degree at Purdue University in August, 1949.

(2) I. M. Kolthoff, T. S. Lee, D. Stocesova and E. P. Parry, *Anal. Chem.*, **22**, 521 (1950).

(3) (a) P. J. Elving and C. S. Tang, THIS JOURNAL, **72**, 3244 (1950); (b) E. Saito, *Bull. soc. chim. France*, 404 (1948).

(4) (a) R. Brdicka, *J. Gen. Physiol.*, **19**, 843 (1936); (b) G. Dragt, *Anal. Chem.*, **20**, 737 (1948); (c) H. Keller, M. Hochweber and H. V. Halban, *Helv. Chim. Acta*, **29**, 761 (1946); (d) J. J. Lingane, C. G. Swain and M. Fields, THIS JOURNAL, **65**, 1348 (1943); (e) M. B. Neiman, A. V. Ryabov and E. M. Sheyanova, *Doklady Akad. Nauk S. S. S. R.*, **68**, 1065 (1949); (f) R. Pasternak and H. V. Halban, *Helv. Chim. Acta*, **29**, 190 (1946); (g) K. Schwabe, *Z. Naturforsch*, **3**, 217 (1948); (h) G. K. Simpson, A. G. Johnsten and D. Trail, *Biochem. J.*, **41**, 181 (1947); (i) M. V. Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949); (j) M. V. Stackelberg, "Polarographische Arbeitsmethoden," Walter de Gruyter, Berlin, 1950, pages 212–214; (k) A. Winkel and G. Proske, *Ber.*, **69**, 693 (1936).

duction of halogenated compounds polarographically, data would be obtained on the relative reactivities of carbon–halogen bonds in given environments. Since the polarographic reduction of the compounds involves the fission of such bonds, it would be of interest to attempt correlation of the relative reactivity scale so prepared with the chemical reactivity of the carbon–halogen bonds in various types of reactions. Accordingly, a systematic study has been begun of halogenated organic compounds, in which an effort is being made to study the behavior of these compounds over a considerable range of pH. In the present paper no attempt is made to explain theoretically the various phenomena encountered or to attempt correlation with general reactivity, but the polarographic behavior of iodoacetic and of the three bromoacetic acids is described. It is felt that after the completion of work in progress on several types of related compounds, a valid basis for an explanation of the data will exist. However, the data for the four compounds studied will be correlated and the theoretical problems to be faced will be indicated.

Each wave obtained represents the cleavage of a carbon–halogen bond with a successive stepwise removal of the halogen atoms in the case of the polyhalogenated compounds. Of the three waves given by tribromoacetic acid, the two more negative ones coincide with the two waves of dibromo-

acetic acid, and the most negative wave of both di- and tribromoacetic acid coincide with the bromoacetic acid wave. This indicates that the first wave of tribromoacetic acid represents its conversion to dibromoacetic acid, that the second wave represents the conversion of dibromo to monobromo, and that the third wave is probably due to the conversion of monobromoacetic acid to acetic acid.[5] This conversion of a carbon–halogen bond to a carbon–hydrogen bond is not necessarily a reversible process, although the Br-3 wave may be reversible.

The reported lack of variation of half-wave potential, $E_{0.5}$, with pH,[2,3a,4f,i,j] at least for the halogenated acids, is apparently due to the fact that the compounds were investigated only over a limited range of pH. The dependence of $E_{0.5}$ on pH for the iodo- and bromoacetic acids follows an S-shaped relationship with the region of rapid increase of $E_{0.5}$ falling in the pH region where both the undissociated acid and the anion exist. $E_{0.5}$ may be independent of pH in the regions where the compound exists either as the undissociated acid or as the anion; in the intermediate pH region where both forms coexist, $E_{0.5}$ becomes more negative as the pH increases (Fig. 1). The fact that $E_{0.5}$ is more negative at high pH than at low pH is in conformity with the known polarographic behavior of acids in which the carboxyl carbonyl is conjugated, i.e., alpha to a double bond, in that the undissociated acid is more readily reducible than the corresponding anion.

The S-type of $E_{0.5}$–pH relationship found for the four acids studied is of a more general prevalence than is ordinarily supposed. It is found with maleic and fumaric acids,[6] with α-bromopropionic acid,[3a] probably with phthalic acid,[7] and with pyruvic acid and its homologs.[8] In the last two cases the authors did not explicitly indicate the possible S-shaped variation of $E_{0.5}$ with pH.

Experimental

Stock acid solutions were prepared using Eastman Kodak Co. white label grade bromoacetic and iodoacetic acids, a research sample of dibromoacetic acid furnished by the Dow Chemical Company to whom the authors wish to express their gratitude, and two samples of tribromoacetic acid supplied by the Sapon Laboratories, one of which was purified.

The buffer solutions used are listed in Table I. Potassium chloride was added to several of the buffers to increase their ionic strength. The concentration of the buffer and other base solution constituents is given in the tables of polarographic data for the different compounds. The ionic strength of the buffers used in the pH region 0.5 to 2 was 0.25; from 7 to 12, 0.5; and increased gradually from 0.25 to 0.50 at intermediate pH values. The variation in $E_{0.5}$ with ionic strength in the acid region was negligible over the ionic strength range of 0.25 to 0.50.
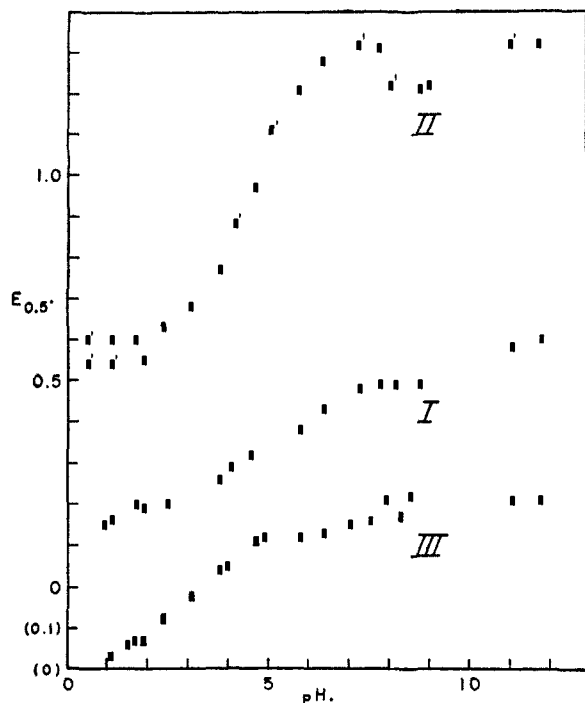

Fig. 1.—Variation of $E_{0.5}$ with pH: I, I-1 wave (Table II); II, Br-1 wave (Table III, primed points and Table IV, unprimed points); III, Br-2 wave (Table IV). To separate the points, those for the Br-2 wave (III) are plotted on a separate $E_{0.5}$ coördinate.

TABLE I

BUFFER SOLUTIONS

Buffer	pH range	Composition[9]
1	0.5–2.0	HCl with added KCl
2	0.5–2.0	HCl with added KCl and citric acid
3	2.2–7.8	Na_2HPO_4 with added citric acid
4	3.5–5.5	Sodium acetate with added acetic acid
5	7.0–8.8	NH_4Cl with added NH_4OH
6	10.4–12.0	Na_2HPO_4 with added NaOH

A Model XXI Sargent Polarograph and a calibrated Fisher Elecdropode were used. Potential measurements were checked with a potentiometer. A Beckman Model G pH meter was used for pH measurements. The capillaries used for the dropping electrode were prepared from Corning marine barometer tubing; m values for the two capillaries used were 1.70 and 1.05 mg./sec. at open circuit in distilled water. Two different H-type cells were used; each contained a saturated calomel electrode and a potassium chloride–agar–fritted glass disk salt bridge. In one cell the entire H was water-jacketed; in the other only the sample leg was jacketed. Water at 25.0 ± 0.1° was circulated through the jacket. All potential measurements are versus the saturated calomel electrode at 25°. Nitrogen used for degassing was deoxygenated by bubbling through either chromous acetate or alkaline pyrogallol solutions. The nitrogen was then conditioned by passage through distilled water and a portion of the solution examined.

Procedure.—The sample solution was prepared by mixing measured volumes of the stock standard acid solution and the buffer base solution. The resulting solution had essentially the same pH as the buffer used. The solution was degassed for 20 min. and then electrolyzed, using a constant height of the mercury column for the dropping mercury cathode; the nitrogen atmosphere was maintained throughout the electrolysis. $E_{0.5}$ was determined from the curve obtained by subtracting the residual current from the limiting current. Where necessary, the i_d values of second and third waves were corrected for the electrocapillary effect.

(5) The waves which result from the cleavage of carbon-halogen bonds, will be designated as follows: The wave resulting from the removal of the first halogen atom from a carbon atom containing n halogen atoms will be designated by the chemical symbol followed by n, and analogously for the other halogen atoms in the carbon atoms, e.g., in tribromoacetic acid the most positive wave would be the Br-3 wave; the second wave, the Br-2 wave; and the third wave, the Br-1 wave. For dibromoacetic acid the most positive wave would be the Br-2 wave, and for iodoacetic acid the wave would be the I-1 wave.

(6) P. J. Elving and C. Teitelbaum, THIS JOURNAL, 71, 3916 (1949).

(7) N. H. Furman and C. E. Bricker, ibid., 64, 660 (1942).

(8) R. Brdička, Coll. Czechoslov. Chem. Communs., 12, 212 (1947).

(9) H. T. S. Britton, "Hydrogen Ions," Chapman and Hull, London, 1942.

TABLE II

EFFECT OF pH, CONCENTRATION, BUFFER NATURE AND TEMPERATURE[a] ON $E_{0.5}$ AND i_d OF IODOACETIC ACID

Curve	Buffer	Buffer component concn., M	pH	Added constituent concn., M	CH₂ICOOH concn., mM	$E_{0.5}$, v.	i_d, μa.	$\dfrac{i_d}{cm^{2/3}t^{1/6}}$	n^b
1	1	0.25	0.9		0.204	0.15^d	1.11	3.9	0.65
2	1	.25	1.1		.21	$.16^d$	1.13		.64
3	2	.25	1.1	0.2^c	.204	$.15^d$	1.08	3.8	.76
4	1	.25	1.1	$.2^k$	.204	.16	1.10	3.9	.73
5	2	.25	1.7	$.2^c$	.204	$.20^d$	1.10	3.9	
6	1	.25	1.9		.21	$.19^d$	1.2		.90
7	3	.11	2.5	$.2^k$	.204	$.20^d$	1.13	4.0	.87
8	3	.14	3.8	$.2^k$	.21	$.26^d$	1.1		.75
9	4	.50	4.1		.98	$.29^d$	5.3	2.9	.97
10	3	.15	4.6	$.2^k$	.408	$.32^d$	2.16	3.8	.80
11	3	.16	5.8	$.2^k$	.21	$.38^d$	1.0		.73
12	3	.17	6.4	$.2^k$	.204	$.43^d$	1.10	3.8	.67
13	5	.50	6.7		.98	.47	6.6	3.6	.58
14	3	.19	7.3	$.2^k$	.408	$.48^d$	2.06	3.7	.64
15	5	.50	7.4		.98	.49	6.3	3.5	.58
16	3	.20	7.8	$.2^k$	.204	$.49^d$	1.06	3.8	.57
17	5	.10	8.0		.98	.55	6.2	3.4	.36
18	5	.50	8.1		4.9	.54	32.9	3.6	.60
19	5	1.00	8.1		0.98	.50	6.4	3.5	.58
20	5	0.50	8.2		.98	.52	6.4	3.5	.53
21	5	.50	8.2		.098	$.49^d$	0.68	3.7	.40
22	5	.50	8.2		.49	.50	3.3	3.6	.62
23	5	.50	8.2		.98	.53	5.7	3.1	
24	5	.50	8.2		.98	.52	6.6	3.7	
25	5	.50	8.6	$.2^n$	.204	.48	1.04	3.7	.60
26	5	.50	8.8		.408	$.49^d$	2.17	3.7	.58
27	5	.50	8.8		.98	.52	6.2	3.5	.55
28	6	.50	10.4		.98	.56	5.4	3.3	.53
29	6	.25	11.1	$.2^k$	.204	$.58^d$	1.02	3.7	.68
30	6	.33	11.8	$.1^k$	.204	$.60^d$	1.00	3.6	.72

[a] Measurements for No. 23 are at 20° and for No. 24 at 30°. Significant figures are given to indicate the drift. [c] Citric acid.   [b] Calculated from relation $E_{0.25} - E_{0.75} = 0.058/n$; two significant figures. [d] Plotted in Fig. 1.   [k] KCl.   [n] Na₂HPO₄.

Discussion

Iodoacetic Acid.[10]—The polarographic data[11] are given in Table II. One well-defined cathodic wave was obtained in the pH range of 0.9 to 11.8. At concentrations of the iodoacetic acid greater than about 0.5 mM_1 maxima developed. As the concentration of the acid was reduced, the position of the maximum shifted to a more negative potential, resulting in a retrogressive phenomenon. At concentrations of about 0.2 mM the maximum was reduced to a point where it was hardly noticeable. In general the magnitude of the maximum and retrogressive effect was greatest in the acid region; but these effects were present throughout the pH region investigated. The n values, determined from the slope of the wave, tended to decrease as the pH increased with an apparent maximum at pH 2.4 and another increase at 11. The n value found in the acetate buffer is higher compared to other n values in this pH region. However, at both ends of the pH range the potential–current curves showed a change of slope in the region of rapid increase of the current, e.g., in No. 29 the apparent n value is 0.3

(10) Based only on the linear relation of wave height and concentration in 0.06 M sodium carbonate and in borate buffers of pH 8 to 13, Brdicka[8] postulated that the polarographic reduction of sodium iodoacetate is due to the conversion of the latter to acetate ion due to removal of the iodine as iodide ion.

(11) 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.

until $i = 0.33i_d$, then the n value changes to 0.7. The n values determined by means of the Ilkovic equation are 2 in all cases.

With increasing pH of the medium (no. 1–16, 20, 25–30) $E_{0.5}$ increases in an S-shaped manner (Fig. 1). The diffusion current constant shows a decrease in its average value of about 8% as the pH increases; the main portion of the decrease occurs in pH region 6.5 to 8.0. At pH 8.2 (no. 18, 20–22) and 8.8 (no. 25–27) i_d/c is a constant, with an average deviation from the mean of about 1.5%. As the concentration of iodoacetic acid is increased, $E_{0.5}$ increases (no. 20–22, 25–27).

Where two or more buffers were used at the same pH, $E_{0.5}$ was not changed if the ionic strengths of the buffers were the same. Increasing the ionic strength of the buffer in the alkaline region caused $E_{0.5}$ to decrease while i_d/c remains constant (no. 17, 20, 19). The temperature coefficient of i_d is 1.6% per degree which is of the magnitude expected for a diffusion-controlled process.

Bromoacetic Acid.—The polarographic data are given in Table III. One well-defined cathodic wave (Br-1) was obtained in the pH range of 0.5 to 11.8. At concentrations of the bromoacetic acid greater than about 1 mM maxima developed of greatest magnitude in the acid region. The n values based on the slope of the wave remain essentially constant at 0.4 with a greater value in acetate buffer; n calculated from the Ilkovic equation is 2.

TABLE III

EFFECT OF pH, CONCENTRATION, BUFFER NATURE AND TEMPERATURE[a] ON $E_{0.5}$ AND i_d OF BROMOACETIC ACID

Curve	Buffer	Buffer component concn., M	pH	Added constituent concn., M	$CH_2BrCOOH$ concn., mM	$E_{0.5}$, v.	i_d, μa.	$\dfrac{i_d}{cm^{2/3}t^{1/6}}$	n[b]
1	1	0.25	0.5	0.2[k]	0.195	0.54[d]	1.06	3.9	0.49
2	2	.25	0.5	.2[k] / .2[c]	.195	.60[d]	1.05	3.8	.43
3	1	.25	1.1		.48	.54[d]	2.54		.44
4	2	.25	1.1	.2[c]	.195	.60	1.05	3.8	.42
5	1	.25	1.9		.48	.55	2.56		.44
6	3	.11	2.4	.2[k]	.195	.64	1.05	3.8	.44
7	3	.14	3.7	.2[k]	.19	.72	1.01		.39
8	4	.50	4.0		.87	.88	5.3	3.3	.73
9	3	.14	4.2	.2[k]	.36	.88[d]	1.54		.35
10	3	.15	5.1	.2[k]	.15	1.11[d]	0.83		.37
11	3	.16	5.8	.2[k]	.15	1.20	0.91		.41
12	5	.50	6.3		.87	1.21	5.9	3.8	.36
13	3	.19	7.2	.4[k]	.195	1.30	0.90		.44
14	3	.19	7.3	.2[k]	.195	1.32[d]	0.90	3.7	
15	5	.10	7.9		.87	1.33	5.55	3.6	.37
16	5	.50	8.0		.96	1.22	6.7	3.9	.37
17	5	.50	8.1		4.00	1.21	26.6	3.8	.48
18	5	.50	8.1		0.087	1.23	0.68	4.4	.40
19	5	.50	8.1		.44	1.22[d]	3.1	4.1	.41
20	5	1.00	8.2		.87	1.18	6.3	4.2	.39
21	5	0.50	8.3		.83	1.22	4.8	3.3	.21
22	5		8.3		.83	1.21	5.8	4.0	
23	5	.33	8.6	.1[n]	.210	1.24	1.03	3.6	.51
24	5		8.6	.2[n]	.195	1.21	0.90	3.5	.49
25	5	.50	8.7		.87	1.22	5.7	3.7	.43
26	6	.50	10.3		.87	1.28	5.0	3.9	.39
27	6	.25	11.1	.2[k]	.195	1.32[d]	0.92	3.6	.43

[a] Measurements for No. 21 are at 20° and for No. 22 at 30°. [b] Calculated from relation $E_{0.25} - E_{0.75} = 0.058/n$. [c] Citric acid. [d] Plotted in Fig. 1. [k] KCl. [n] Na_2HPO_4.

The $E_{0.5}$–pH relation (no. 3–16, 25–27) is S-shaped (Fig. 1). The i_d-constant decreases about 8% as the pH increases, mostly in the range of pH 6.5 to 8.0 (no. 3, 5–7, 9–11, 13, 14, 27); this set of runs was made with the same concentration of bromoacetic acid. Runs made with a different sample of the acid average about 3% higher, which is probably due to a small difference in purity. The ratio, i_d/c, varies inversely with the concentration (no. 16–19) with a 15% variation over a 50-fold concentration range. Over the same range $E_{0.5}$ remains constant.

Where two or more buffers with the same pH and ionic strength were used, significant variations in $E_{0.5}$ were found in some cases. The data on this effect will be discussed in connection with the Br-1 wave of dibromoacetic acid, since the effects are the same for both waves. Increasing the ionic strength of the buffer in the alkaline region causes $E_{0.5}$ to decrease while i_d/c tends to increase (no. 15, 16, 20). The temperature coefficient of i_d was 2.1% per degree with little variation of $E_{0.5}$ with temperature (no. 15, 16, 20).

Dibromoacetic Acid.—Two cathodic waves (Br-2 and Br-1) were obtained in the pH range 1.0 to 11.8 (Table IV); the more negative (Br-1) was essentially identical in behavior with the one wave (Br-1) of bromoacetic acid (Table III). Both Br-1 waves showed a significant variation of $E_{0.5}$ with the nature of the buffer. $E_{0.5}$ values found in an HCl–KCl buffer (Clark–Lubs) (Table III: no. 4, 5; Table IV: no. 1, 5, 6, 8) are increased by 0.01 v.

on adding to a similar HCl–KCl buffer 0.04 mM per ml. of citric acid (Sörenson buffer). Increasing the citric acid concentration to 0.2 M caused $E_{0.5}$ values to increase by 0.05 v. or about 9%. The latter values fit smoothly the curve obtained using MacIlvaine buffer, which in the low pH region is essentially a citrate buffer. The effect of the citric acid was not an ionic strength effect since making the solution 0.2 M in potassium chloride caused no significant increase of $E_{0.5}$. In the basic region $E_{0.5}$ values determined with NH_4OH–NH_4Cl buffers were 0.1 v. more positive than those found using MacIlvaine buffers of similar ionic strength. The addition of Na_2HPO_4 to NH_4Cl–NH_4OH buffers causes significant changes in the ionic strength of the buffer, which is not the case with the addition of citric acid to HCl–KCl buffers. From Table III no. 13–16, 20, and Table IV no. 22, 24, 27, an approximate value of a 0.015 v. decrease in $E_{0.5}$ is obtained for each 0.1 increase in ionic strength. On this basis the corrected $E_{0.5}$ values for no. 23 and 24 of Table III are 1.26 and 1.30 v., respectively. This shows that the addition of increasing amounts of Na_2HPO_4 causes increases in $E_{0.5}$ after ionic strength effects are taken into account. The $E_{0.5}$ values obtained with acetate buffers agree with those obtained with MacIlvaine buffers.

In the case of the less negative (Br-2) wave of dibromoacetic acid, at concentrations of the acid exceeding 0.5 mM, maxima developed at all pH values, whose magnitude was greatest in the acid region. The n values decrease from 1.1 to 0.5 over

TABLE IV

EFFECT OF pH, CONCENTRATION, BUFFER NATURE AND TEMPERATURE[a] ON $E_{0.5}$ AND i_d OF DIBROMOACETIC ACID

Curve no.	Buffer no.	Buffer component concn., M	pH	Added constituent concn., M	CHBr₂-COOH concn., mM	$E_{0.5}$, v.	First wave, Br-2 i_d, μa.	$\overline{\dfrac{i_d}{cm^2/t_i^{1/6}}}$	n[b]	Second wave, Br-1 $E_{0.5}$, v.	i_d, μa.	$\overline{\dfrac{i_d}{cm^2/t^{1/6}}}$	n[b]
1	1	0.25	1.1		0.20	0.03^d	1.08		1.0	0.53	1.11		0.43
2	1	.25	1.1	0.2^k	.182	.03	0.90	3.6	1.1	.54	0.98	3.9	.46
3	2	.25	1.1	$.2^c$	.182	.03	.88	3.5	1.2	$.60^d$	.97	3.8	.38
4	2	.25	1.2	$.04^c$	.182	.03	.90	3.6	1.2	.56	.99	3.9	.43
5	1	.25	1.2		.182	.03	.91	3.6	1.2				
6	1	.25	1.5		.091	$.06^d$	.93	3.6	1.0				
7	2	.25	1.7	$.2^c$	.182	$.07^d$	.89	3.5	1.0	$.60^d$	0.97	3.9	.39
8	1	.25	1.9		.20	$.07^d$	.99		0.94	$.55^d$	1.03		.43
9	1	.25	1.9	$.2^k$	.182	.10	.94	3.6	1.0	.55	0.99	3.9	.45
10	2	.25	1.9	$.04^c$	.182	.07	.93	3.6	0.97	.57	.98	3.9	.45
11	3	.11	2.4	$.2^k$	.182	$.12^d$	.89	3.5	.80	$.63^d$	.93	3.6	.45
12	3	.12	3.1	$.2^k$	.182	$.18^d$	.88	3.4	.66	$.68^d$	.91	3.6	
13	3	.14	3.8	$.2^k$	.20	$.24^d$	.96		.57	$.77^d$	1.04		.39
14	4	.50	4.0		.92	$.25^d$	5.5	3.2	.33	.88	5.6	3.4	.34
15	3	.15	4.7	$.2^k$	.182	$.31^d$	0.90	3.5	.53	$.97^d$	0.89	3.6	.33
16	3	.15	4.9	$.2^k$	.182	$.32^d$	0.91	3.5	.52	1.00^d	0.90	3.6	.36
17	3	.16	5.8	$.2^k$	.20	$.32^d$	1.0		.49	1.21^d	1.1		.39
18	3	.17	6.4	$.2^k$	.182	$.33^d$	0.90	3.5		1.28^d	0.88	3.5	
19	5	.50	6.7		.92	.37	6.5	3.8	.50	1.20	6.7	4.1	.41
20	3	.19	7.3	$.2^k$	.182	$.35^d$	0.88	3.4		1.30	0.88	3.5	
21	3	.20	7.8	$.2^k$	.182	$.36^d$	0.82		.73	1.31^d	0.97		
22	5	.10	7.9		.92	.42	6.0	3.5	.61	1.35	6.1	4.2	.37
23	5	.50	8.1		4.59	.46	35.1	4.2	.72	1.20	33.1	4.1	.50
24	5	1.00	8.1		.92	.40	6.5	3.8	.64				
25	5	0.50	8.2		.46	.38	3.1	3.7	.64	1.21	3.0	4.1	.44
26	5	.50	8.2		.092	.36	0.65	3.8	.54	1.24	0.77	5.0	.43
27	5	.50	8.2		.92	$.41^d$	6.7	3.9	.64	1.20	6.7	4.1	.44
28	5	.50	8.2		.92	.42	6.3	3.7		1.23	6.4	4.3	
29	5	.50	8.2		.92	.39	7.4	4.3		1.22	7.8	5.3	
30	5	.50	8.6		.182	.37	0.95			1.21^d	1.02		
31	5	.50	8.6	$.2^k$	.182	$.37^d$	0.90	3.5	.70	1.20	0.91	3.6	.43
32	5	.50	8.8		.92	$.42^d$	6.5	3.8	.61	1.22^d	6.4	4.3	.48
33	6	.50	10.5		.92	.46	5.3	3.1	1.0	1.25	5.1	3.5	.36
34	6	.25	11.1	$.2^k$	.182	$.41^d$	0.90	3.5	1.0	1.31	0.91	3.6	.38
35	6	.33	11.8	$.1^k$	.182	$.41^d$	0.92	3.5	1.0	1.32^d	0.91	3.6	

[a] Measurements for no. 28 are at 20° and for no. 29 at 30°. [b] Calculated from relation $E_{0.25} - E_{0.75} = 0.058/n$. [c] Citric acid. [d] Plotted in Fig. 1. [k] KCl.

the pH range 1 to 7, increase slightly near pH 7 to 0.7 and hold an average value of 0.7 over pH 7 to 9; between pH 9 and 10, there is another increase to 1.0, which value is constant to pH 11.8. The n value calculated from the Ilkovic equation is 2 over the whole pH range. In the pH region around 11, current–potential relations show a change of slope in the region of rapid increase of i_d, e.g., a change from an apparent n value of 0.3 to one of 1.0 at $i = 0.33\ i_d$ (no. 34).

With increasing pH of the medium, $E_{0.5}$ varies as shown in Fig. 1; the difficulty of working in the pH region less than 1 under the conditions used prevented further exploration of the S-shaped curve expected. While the i_d-constant is essentially the same over the whole pH region for one concentration, i_d/c has a slight tendency to increase as the concentration increases (no. 23, 25-27).

When curves in the pH region of 7 to 9 were corrected for the residual current and the effect of the electrocapillary curve on the second wave, the two current steps obtained were identical within the experimental measurements. Curves in other pH regions were not similarly corrected; however, the method of determining i_d by the geometric technique corrected for the residual current and largely for the electrocapillary effect. The fact that in the acidic region the diffusion current constants for the second Br-1 wave are somewhat greater than those calculated for the Br-2 wave in the same sample may be ascribed to the difference in properties of the dibromoacetate and monobromoacetate species in controlling reactions at the electrode. However, the Br-1 waves of the two acids are identical in behavior.

$E_{0.5}$ increases with concentration (no. 23, 25-27); however, the values at any one concentration give the same slope of $E_{0.5}$ vs. pH (cf. no. 14, 19, 27, 32, 33 vs. 18, 20, 21, 30, 34, 35). At the same pH value and similar ionic strength $E_{0.5}$ seemed to be independent of the nature of the buffer. Increasing the ionic strength caused $E_{0.5}$ to decrease slightly (no. 22, 24, 27) while i_d/c shows a possible tendency to decrease at the lowest ionic strength. The temperature coefficient of i_d is 1.7% per degree.

Tribromoacetic Acid.—Three cathodic waves (Table V) were obtained at pH 3.7 and 7.7. Addition of dibromoacetic acid increased the i_d of the two more negative (Br-1 and Br-2) waves by the same amount, while additional tribromoacetic acid did the same for all three waves. The most positive wave (Br-3) was characterized by reproducible drops which, however, did not follow the usual parabolic increase of current. The first sample of tribromoacetic acid studied was brownish, and melted with decomposition over the range of 120–130°; at pH 7.7 the two more positive waves (Br-2 and Br-3) whose $E_{0.5}$ values are about 0.1 v. apart appeared as one. The acid was purified by extraction with purified hexane. Since drying the sample over a period of several hours led to further decomposition and brown coloration, the sample was reextracted but not dried; this probably accounts for the low i_d-constant values obtained as compared to those for mono- and dibromoacetic acids. The purified acid had a melting point range of 130–133° and a colorless needle-like crystalline form. The $E_{0.5}$ of the most negative wave agreed with the values found for the Br-1 wave of the other two bromoacetic acids. For the second wave, $E_{0.5}$ at pH 3.7 likewise agreed with that obtained with the Br-2 wave of dibromoacetic acid. However, at pH 7.7 the second wave was 0.03 v. more negative than the

corresponding value for dibromoacetic acid at the same concentration as calculated by extrapolation, or about 0.01 v. greater than experimental error. The latter is probably due to the difficulty in plotting the wave which at this point is only 0.1 v. removed from the most positive wave. The i_d/c values for the three waves agree fairly well with each other. The n values of the Br-1 wave agree with those obtained with the corresponding waves of the other bromoacids; those for the Br-2 wave are higher than the values for the corresponding wave of dibromoacetic acid; the n values for the Br-3 wave at pH 3.7 and 7.7 as calculated from the slope of the wave were 2.3. It is also interesting to note that $\Delta E_{0.5}/\Delta pH$ equals 0.060 for the Br-3 wave. This figure and the n value of 2.3 indicate the possibility that the Br-3 wave is reversible.

Relation of $E_{0.5}$ to pH.—The variation of $E_{0.5}$ with pH for all four compounds (Fig. 1) is similar in that there is a region of rapid increase of $E_{0.5}$, designated as the region of primary pH-dependence, which region includes the pK_a of the reducible acid. As a corollary of this statement it follows that the regions of primary pH dependence are in the same order as the pK_a values of the acids, which is the experimental fact. The limiting portions of the $E_{0.5}$ vs. pH curve for bromoacetic acid seem to be pH-independent. For iodoacetic acid in both the acidic and alkaline regions of the $E_{0.5}$ vs. pH curve and for the alkaline region of the Br-2 wave, there are possible regions of pH-independence changing to a pH-dependent region. In the case of the first wave of tribromoacetic acid, the data only permit one to say that there is at least one region of pH-dependence. The average rates of increase of $E_{0.5}$ with pH in the region of primary pH dependence is 0.07 v. per pH unit for the I-1 wave, 0.08 for the Br-2 wave, and 0.27 for the Br-1 wave.

The n values based on the slope of the wave increase from 0.4 for the Br-1 wave to 2.3 for the Br-3 wave. For the I-1, Br-1 and Br-2 waves $E_{0.5}$ decreases as the ionic strength increases in the alkaline region; only the Br-1 wave shows definite variation of $E_{0.5}$ when different buffers at the same ionic strength are used. All waves showed a tendency to develop maxima at concentrations of the reducible acid exceeding about 0.5 to 1.0 mM.

TABLE V

$E_{0.5}$ AND i_d OF TRIBROMOACETIC ACID AT pH 3.7 AND 7.7

Curve	Buffer	Buffer component concn., M	pH	Added constituent concn., M	CBr_3COOH concn., mM
1	3	0.14	3.7	0.2^k	0.43
2	3	.20	7.7	$.2^k$	.43
3	3	.20	7.7	$.2^k$	.43

First wave, Br-3

Curve	$E_{0.5}$, v.	i_d, $\mu a.$	$\dfrac{i_d}{cm^{2/3}t^{1/6}}$	n^a
1	0.08	1.42	2.4	2.4
2	.32	1.42	2.4	2.3
3	.32	1.49	2.4	2.4

Second wave, Br-2

1	0.21	1.42	2.4	1.1
2	.42	1.42	2.4	0.82
3	.41	1.49	2.4	0.72

Third wave, Br-1

| 1 | 0.79 | 1.65 | 2.5 | 0.43 |
| 2 | 1.31 | 1.65 | 2.6 | 0.36 |

^{a} Calculated from relation $E_{0.25} = E_{0.75} = 0.058/n$.
^{k} KCl.

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