[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Polarographic Behavior of Organic Compounds. III. The Chloroacetic Acids

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Organic acids are not polarographically reducible unless two carboxyl groups are adjacent or an ethylene linkage is located on the α-carbon to the carboxylic group. The polarographic reduction of iodoacetic acid[3] was considered due to removal of the iodine. Winkel and Proske[4] claimed that the introduction of halogen made possible the reducibility of the carbonyl group in acetone; iodo-, bromo- and chloroacetone, and *sym*-dichloroacetone can be reduced polarographically while acetone itself cannot be; consideration of the data indicates that the reduction might be not that of the carbonyl group but of the halogen on the α-carbon to the carbonyl group. Without giving experimental details or data, Pasternak and Halban[5] stated that benzyl bromide and chloride give waves, whose $E_{0.5}$ is independent of *p*H and whose reduction, based on the height of the wave, involves a two-electron process. Based on this independence of $E_{0.5}$ of *p*H they stated that, contrary to Winkel and Proske,[3] the halogen, not the carbonyl, is being reduced in the haloacetones. They also ascribed one of the waves in the reduction of ω-bromoacetophenone and of dibenzoyl mono- and dibromomethane to the reduction of the halogen bond. Recent observations on the reducibility of organic halogen compounds are summarized by Wawzonek.[6,6a]

TABLE I

ELECTROCAPILLARY CURVE IN AMMONIUM CHLORIDE–AMMONIUM HYDROXIDE BASE SOLUTION OF *p*H 8.2

Applied potential, v.[a]	−0.00	−0.20	−0.40	−0.56	−0.80	−1.00	−1.30	−1.60	−1.90
Drop-time, sec.	5.20	5.60	5.80	5.90	5.73	5.40	4.83	3.87	2.80

[a] Potential difference between the dropping mercury cathode and the mercury pool; the potential *vs.* the S.C.E. is more positive by 0.04 v. Solution is 0.5 *M* in buffer.

Since the three chloroacetic acids contain different numbers of chlorine atoms, it was considered that the polarographic behavior of this homologous series might show the manner of reduction of the halogen bond. From the data obtained, the reduction of the polychlorinated acetic acids is found to involve the successive removal of halogen atoms. This mechanism for the reduction of the polychlorinated acetic acids is formally similar to certain chemical reactions of the latter with cuprous ion and with metallic copper and zinc.[7]

Experimental

Solutions of the acids were prepared from reagent grade chemicals; the exact concentration was determined by titration. Buffer solutions of *p*H 6.8 to 8.8 were prepared by adding concentrated NH_4OH solution to 0.1, 0.5 or 1.0 *M* solutions of NH_4Cl. Buffers of *p*H 4.0 and 10.4 were prepared by adding acetic acid to 0.5 *M* sodium acetate solution and NaOH to 0.5 *M* KH_2PO_4. The concentrations of the electrolytes were great enough so that the buffer solutions could act as base solutions.

A calibrated Fisher Elecdropode was used. Potential measurements were checked with a potentiometer. A Beckman Model G *p*H meter was used for the measurement of *p*H. The capillary used for the dropping electrode was prepared from Corning marine barometer tubing. In 0.5 *M* buffer solution, *p*H 8.2, m at open circuit was 1.59 mg.

TABLE II

EFFECT OF *p*H, CONCENTRATION, TEMPERATURE, AND BUFFER CONCENTRATION ON THE $E_{0.5}$ AND i_d OF DICHLOROACETIC ACID

Curve	*p*H	Cl_2CH-COOH concn., mM.	Temp., °C.	Buffer concn., *M*	$E_{0.5}$, v.	i_d, μa	*n*
1	3.89	0.495	25	0.5	No wave ob.; see text		
2	6.79	.495	25	.5	−1.572	3.91	
3	7.65	.495	25	.5	−1.570	3.80	
4	8.19	.495	25	.5	−1.568	4.06	
5	8.79	.495	25	.5	−1.567	4.06	
6	10.41	.495	25	.5	−1.571	4.06	
7	8.19	.101	25	.5	−1.570	0.83	2.19
8	8.19	.495	25	.5	−1.573	4.06	2.08
9	8.19	.917	25	.5	−1.578	7.46	2.07
10	8.19	2.036	25	.5	−1.578	14.17	2.04
11	8.19	0.495	0	.5	−1.615	2.56	
12	8.19	.495	20	.5	−1.577	3.71	
13	8.19	.495	25	.5	−1.570	4.06	
14	8.19	.495	30	.5	−1.566	4.17	
15	8.19	.495	25	.1	−1.677	3.14	
16	8.19	.495	25	.5	−1.571	4.06	
17	8.19	.495	25	1.0	−1.541	4.13	

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[2] The material presented is based on a portion of the thesis submitted by Miss Tang for the degree of Master of Science, February, 1949.

[3] Brdicka, *J. Gen. Physiol.*, **19**, 843 (1936).

[4] Winkel and Proske, *Ber.*, **69**, 693 (1936).

[5] Pasternak and Halban, *Helv. Chim. Acta*, **29**, 190 (1946).

[6] Wawzonek, *Anal. Chem.*, **21**, 61 (1949).

[6a] After the present paper had been submitted for publication, Stackelberg and Stracke, *Z. Elektrochem.*, **53, 118** (1949), reported some $E_{0.5}$ values in 0.05 *M* tetraethylammonium bromide solution containing 75% dioxane or 90% butanol: acetic acid, −1.99 v.; chloroacetic, −1.70; dichloroacetic, −1.19 and −1.64; and trichloroacetic, −0.8 and −1.66. Neiman, Ryabov and Sheyanova, *Doklady Akad. Nauk S. S. S. R.*, **68**, 1065 (1949) (*Chem. Abstr.*, **44**, 1360 (1950)), found over the potential range of 0 to −2.5 the following $E_{0.5}$ values in 0.1 *N* NaOH: chloroacetic −1.6, dichloroacetic −1.14, and trichloroacetic 0.4, with each wave corresponding to the formation of one halogen ion.

[7] Doughty, *et al.*, THIS JOURNAL, **39**, 2685 (1917); **41**, 1129 (1919); **44**, 636 (1922); **47**, 1091 (1925); **51**, 852 (1929); **53**, 1594 (1931).

TABLE III

EFFECT OF *p*H, CONCENTRATION, TEMPERATURE AND BUFFER CONCENTRATION OF THE $E_{0.5}$ AND i_d OF TRICHLOROACETIC ACID

					First wave			Second wave		
Curve	Final *p*H	Cl_3COOH concn., mM.	Temp., °C.	Buffer concn., *M*	$E_{0.5}$, v.	i_d, a.	*n*	$E_{0.5}$, v	i_d, a.	*n*
1	3.98	0.444	25	0.5	−0.894	2.17		No wave obtained; see text		
2	6.79	.444	25	.5	−0.849	3.56	2.05	−1.572	3.49	2.00
3	7.65	.444	25	.5	−0.847	3.55	2.04	−1.570	3.40	1.99
4	8.19	.444	25	.5	−0.844	3.67	2.11	−1.568	3.63	2.08
5	8.79	.444	25	.5	−0.843	3.68	2.11	−1.568	3.63	2.08
6	10.41	.444	25	.5	−0.841	3.69	2.11	−1.567	3.33	
7	8.19	.089	25	.5	−0.839	0.75	2.15	−1.568	0.74	2.19
8	8.19	.444	25	.5	−0.842	3.67	2.11	−1.574	3.63	2.08
9	8.19	.864	25	.5	−0.845	7.07	2.09	−1.575	7.01	2.07
10	8.19	1.729	25	.5	−0.846	14.12	2.05	−1.575	13.86	2.04
11	8.19	0.444	0	.5	−1.045	2.24		−1.608	2.34	
12	8.19	.444	20	.5	−0.873	3.39		−1.572	3.34	
13	8.19	.444	25	.5	−0.842	3.67		−1.565	3.63	
14	8.19	.444	30	.5	−0.818	3.84		−1.560	3.75	
15	8.19	.864	25	.1	−1.141	6.96	2.06	−1.671	5.48	
16	8.19	.864	25	.5	−0.844	7.12	2.09	−1.575	6.99	2.07
17	8.19	.864	25	1.0	−0.733	7.19	2.33	−1.527	7.28	2.15

Values of $m^{2/3}\,t^{1/6}$ were determined from the electrocapillary curve (Table I).

Procedure.—A 2-ml. aliquot of the stock standard acid solution and 20 ml. of buffer base solution were added to a thermostated cell; the resulting solution had essentially the same *p*H as the buffer used. The solution was electrolyzed, using a quiet mercury pool as the anode and a constant height of the mercury column (43.3 cm.) for the dropping mercury cathode. All measurements, unless otherwise specified, were made at 25 ± 0.1°. The potential of the D. M. E. was converted to a potential *vs.* the saturated calomel electrode; correction for the resistance of the cell was made. $E_{0.5}$ values were determined by the intersecting point method; i_d was determined by subtracting the residual current from the limiting current. The i_d for the second wave was corrected for the effect of the electrocapillary curve.

Trichloroacetic Acid.—The polarographic data[8] are given in Table III. Two cathodic waves were obtained in the *p*H range of 6.8 to 10.4; the potential range covered extended from 0.4 to −2.0 volts where the ammonium ion gave a wave.

The *p*H of the medium (nos. 1 to 6) had no effect upon the $E_{0.5}$ in *p*H range 6.8 to 10.4. The i_d values of both waves showed a slight but linear increase of 4 to 5%. At *p*H 4.0 the waves were considerably distorted in the sense of extension along the potential direction. The $E_{0.5}$ of the first wave was slightly more negative while the i_d decreased by one-third; the uncorrected $E_{0.5}$ was 1.27 v. The second wave could not be distinguished when 2 v. had been applied. Based upon the experimental data and curves, the optimum *p*H for further study was considered to be 8.2.

At *p*H 8.2 i_d values for both waves were directly proportional to concentration (nos. 7 to 10); at concentrations exceeding 2 m*M*, the galvanometer readings became unsteady but the i_d values were reproducible and linear at least up to 4 m*M*. The $E_{0.5}$ values *vs.* S. C. E. were constant at *p*H 8.2 and 25° at −0.843 ± 0.003 for the first wave and −1.573 ± 0.003 v. for the second wave. The temperature coefficient for i_d (nos. 11 to 14) was 2.5% for both waves; the $E_{0.5}$ values became less negative with increasing temperature in the range of 0 to 30°, approximately straight-line relations being obtained for both waves. These facts are in good agreement with normal behavior for a diffusion-controlled current.

Increase in buffer concentration (nos. 15 to 17) increased i_d; the first wave showed greater variation. It is possible that the diffusion coefficients of the substances producing the two waves vary in different magnitude with the concentration of buffer solution. $E_{0.5}$ became less negative with increasing buffer concentration. The best defined curve was obtained in 0.5 *M* buffer solution.

Dichloroacetic Acid.—The polarographic data are given in Table II. One cathodic wave was obtained in the *p*H range of 6.8 to 10.4. The behavior of this wave was identical in every respect with that shown by the second, more negative wave of trichloroacetic acid.

Chloroacetic and Acetic Acids.—Using 0.5 *M* buffer solutions, no waves were observed in 1 m*M* solutions of acetic and chloroacetic acids over *p*H range 6.8 to 8.8, and potential range of 0.4 to −2.0 v.

Analysis of the Data

Calculation of *n* by the Ilkovic Equation.—Values for *n*, the number of faradays required per mole of the reactive substance in the controlling reaction, were calculated using the Ilkovic equation. The diffusion coefficients of undissociated trichloroacetic and dichloroacetic acids can be approximated[9a] as 1.00 ± 0.03 × 10^{-5} cm.^{2} sec.$^{-1}$; similar values are calculated for the corresponding anions using the equivalent conductances.[9b] Since i_d varied relatively slightly with *p*H, and since the square root of the diffusion coefficient is used, the error is probably not appreciable when these coefficients are used to calculate *n*. The *n* values for both waves of trichloroacetic acid and for the one wave of dichloroacetic acid were calculated as being approximately 2 in all cases.

Calculation of *n* as a Measure of Reversibility.—The following equation, derived from the usual equation for the polarographic wave at 25°, $E_{0.75} - E_{0.25} = -0.058/n$, was suggested[10]

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

[9] (a) Thovert, *Ann. Phys.*, **2**, 369 (1914); (b) "International Critical Tables," Vol 6, p. 261, McGraw-Hill Book Co., New York, N. Y., 1929.

[10] Tomes, *Coll. Czechoslov. Chem. Commun.*, **9**, 12, 81, 150 (1937).

as a criterion of reversibility; where n is less than one, the electrode reaction is usually irreversible. From a typical polarogram of trichloroacetate (Table III, no. 4) n was calculated to be 0.2 for the first wave and 0.4 for the second wave. Apparently, the potential-determining steps in the reduction of trichloroacetic acid are irreversible. Similarly, n for dichloroacetate was found to be 0.4 (Table II, no. 4).

Discussion

In pH 6.8 to 10.4, trichloroacetate ion shows two reduction waves; dichloroacetate shows only one wave. This indicates a two-step reduction process for trichloroacetate and a one-step process for dichloroacetate. Chloroacetate and acetate ions show no reduction in the potential range 0.4 to −2.0 v. It is probable that the first reduction step for trichloroacetate ion involves the transformation of the ion to dichloroacetate which reaction proceeds more readily, *i. e.*, at less negative potential, than the second reduction process involving the conversion of dichloroacetate to chloroacetate. In the case of the dichloroacetate ion only the latter process can occur.

Brdicka[3] postulated for the polarographic reduction of sodium iodoacetate in 0.08 N sodium carbonate solution

$$ICH_2COOH + H^+ + 2e = CH_3COOH + I^- \quad (1)$$

No study was made of the effect of pH on the reduction potential; the relation between wave-height and correct limiting current in the solution mentioned and in borate buffers of pH 8 to 13 was apparently linear.

In attempting to formulate a mechanism for the reactions which occur in the polarographic reduction of the polychloroacetate ions over the pH range 6.8 to 10.4, the following facts must be taken into account: the half-wave potentials are independent of pH; the second wave of trichloroacetate is similar in magnitude (diffusion current) to the first wave and is identical with the one wave of dichloroacetate; each of the three waves is irreversible and apparently involves a two-electron process as the current-controlling step; and the concentration of undissociated acid is negligible.

These facts can be formally accounted for by equations 2 and 3

$$Cl_3CCOO^- + H_2O + 2e = Cl_2HCCOO^- + OH^- + Cl^- \quad (2)$$

$$Cl_2HCCOO^- + H_2O + 2e = ClH_2CCOO^- + OH^- + Cl^- \quad (3)$$

if the postulate be made that the influence of the changing hydroxyl ion concentration on the apparently irreversible reactions involved is slight in well-buffered solutions over the pH range specified. A more reasonable formulation which indicates the independence of the current-controlling process from hydrogen ion concentration, can be made on the basis that the current-determining step in the polarographic reduction of the polychloroacetate ions must involve the removal of a halogen atom from the anion

$$ClR^- + 2e = R^= + Cl^- \quad (4)$$

or some equivalent reaction. The subsequent rapid reaction involves the interaction of the carbanion with the solvent to generate the normal ion of one less halogen atom.

The large change in $E_{0.5}$ for the first wave of trichloroacetic acid with changing buffer concentration is surprising. No explanation beyond the possible one of the effect of ionic strength upon the diffusion coefficient can be suggested at present.

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Summary

Acetic and chloroacetic acids give no polarographic waves in pH range 6.8 to 8.8 and potential range +0.4 to −2.0 v. In pH range 6.8 to 10.4 trichloroacetic acid gives two waves while dichloroacetic acid gives one wave which is identical in characteristics with the more negative wave of trichloroacetic acid. The diffusion currents of each of the two waves of trichloroacetic acid and of the one wave of dichloroacetic acid are identical.

The reductions of trichloroacetic acid and dichloroacetic acid are irreversible while a two-electron transfer is indicated for the reaction resulting in each polarographic wave. The process of reduction is believed to consist of the loss of chlorine; trichloroacetate ion is converted to dichloroacetate which at a more negative potential is converted to chloroacetate.

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