Cupric (di) glycinate was prepared from glycine and a small excess of freshly precipitated and washed basic cupric carbonate. It was purified by repeated crystallization from water and obtained as the monohydrate. The solutions were analyzed on a Beckman spectrophotometer. The composition of the crystals was determined by iodometric titration for copper. At 25° the solubility was 0.0364 M and the molar extinction coefficient at 6300 Å. was 46. The molar conductivity was 2.8 × 10^{-6} mho cm.$^{-1}$ indicating very slight dissociation into ions.

Values of D obtained at 0.00917 M and 0.0274 M were not significantly different and the pooled results gave a normal cumulative probability distribution. The mean value of D at 25.0 was 0.723 ± 0.004 × 10^{-5} cm.^{2} sec.$^{-1}$. The indicated error is the 95% confidence range for the mean.[5] The molar volume was found from density measurements to be 100.4 cm.^{3} and independent of concentration. D calculated from the Einstein–Sutherland equation assuming a sphere is 0.717 × 10^{-5}. If approximate corrections for departures from a spherical shape are applied D is calculated to be 0.67 × 10^{-7}.[6]

(5) R. B. Dean and W. J. Dixon, *Anal. Chem.*, **23**, 636 (1951).
(6) F. Perrin, *J. phys. radium*, [7] **7**, 1 (1936).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OREGON
EUGENE, OREGON

The Distribution of the Subgroup VII Elements between Pyridine and 4 N NaOH[1]

BY W. GOISHI[2] AND W. F. LIBBY

In the course of studies directed toward the development of a new method for isolating technetium activities from meson irradiated silver samples, extraction from basic media with pyridine was attempted. It appeared reasonable to try this in view of the fact that permanganate has been found to be extractable under these conditions.[3] A preliminary experiment with carrier-free NH₄-Tc⁹⁹O₄ indeed showed that pyridine extracted pertechnetate almost quantitatively from 4 N NaOH. The following is a report of the results of the distribution measurements which were made. The distribution of +7 rhenium and of +7 manganese between the same liquids was also studied.

Experimental

Perrhenate.—Measured volumes of 4 N NaOH containing known amounts of NH₄ReO₄ were equilibrated with measured volumes of pyridine saturated with 4 N NaOH. The layers were analyzed by acidifying to about 4 N with HCl, heating almost to boiling, precipitating Re₂S₇ by passing in hydrogen sulfide,[4] dissolving the collected precipitate in a 1:1 mixture of 6 N NaOH and 30% H₂O₂, and gravimetrically determining the amount of rhenium by conversion to the tetraphenylarsonium derivative.[5] In each case

the sulfide precipitation was repeated on the filtrate from the first sulfide precipitation after first diluting with 4 N HCl, until no more sulfide was precipitated.

Technetium.—Carrier-free NH₄Tc⁹⁹O₄ solutions were extracted with pyridine exactly as in the perrhenate extractions. Measured volumes of standardized NH₄ReO₄ solution were added to the separated layers and the sulfide precipitated[6] and determined as the tetraphenylarsonium derivative as before. The tetraphenylarsonium perrhenate precipitates carrying the pertechnetate[7] were measured with a Geiger counter for their Tc⁹⁹ content.

Manganese.—A small measured volume of a freshly prepared dilute solution of KMnO₄ was poured into a centrifuge bottle containing some pyridine. After shaking for a few seconds 4 N NaOH was poured into the bottle, the mixture again shaken for a few seconds and then immediately centrifuged to hasten the separation of the layers. Speed was essential to minimize the decomposition of the permanganate to form the green manganate. The alkaline layer was siphoned off and a measured portion of it was re-extracted with a measured volume of pyridine. A measured volume of the first pyridine extract was diluted with pyridine until a color match was obtained visually between the diluted solution and the second pyridine solution with the two solutions in long test-tubes filled to the same depth.

The results obtained are summarized in Table I.

TABLE I
DISTRIBUTION BETWEEN PYRIDINE AND 4 N NaOH

Element, M	Distribution coefficient, $\frac{[\text{M}]_{Py}}{[\text{M}]_{aq}}$	$[\text{M}]_{Py}$, (mg. of M/ml.)
Re	255	3.8
	195	7.4
	130	12.8
	30	13.5
Tc	778	3.8 × 10^{-5}
Mn	8000	5

It is clear from Table I that all the subgroup VII elements in their heptavalent states are extractable into pyridine from strongly alkaline aqueous solution.

(6) C. Perrier and E. Segrè, *J. Chem. Phys.*, **5**, 712 (1937).
(7) C. D. Coryell and N. Sugarman, "Radiochemical Studies: The Fission Products," Book 3, Part VI, Paper 259 by L. E. Glendenin, National Nuclear Energy Series, McGraw–Hill Book Co., Inc., New York, N. Y., 1951.

INSTITUTE FOR NUCLEAR STUDIES AND
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO
CHICAGO 37, ILLINOIS

Polarographic Behavior of Organic Compounds. XIII. Chloroacetic Acids and their Ethyl Esters. pH-Independence of Carbon–Halogen Bond Fission. Wave Splitting Due to Buffer Interaction

BY PHILIP J. ELVING* AND CHING-SIANG TANG

In view of the S-shaped relation between pH and $E_{1/2}$ for the polarographic reduction of acids of various types[1,2] including those involving carbon-halogen bond fission, the related system of acid-

* University of Michigan, Ann Arbor, Mich.
(1) P. J. Elving, I. Rosenthal and M. K. Kramer, THIS JOURNAL, **73**, 1717 (1951). This paper includes a bibliography on the polarographic reduction of carbon–halogen bonds, to which the following studies in unbuffered solution should be added: (a) L. Riccoboni, *Gazz. chim. ital.*, **72**, 47 (1942); (b) G. K. Simpson and D. Traill, *Biochem. J.*, **40**, 116 (1946); (c) A. C. Stromberg and L. M. Resinus, *J. Gen. Chem. (U.S.S.R.)*, **16**, 1431 (1946); in buffered solution, P. J. Elving and C. L. Hilton, THIS JOURNAL, **74**, 3368 (1952).
(2) P. J. Elving, J. C. Komyathy, R. E. Van Atta, C. S. Tang and I. Rosenthal, *Anal. Chem.*, **23**, 1218 (1951).

(1) This research was supported in part by the Office of Scientific Research of the Air Research and Development Command of the U. S. Air Force.
(2) A.E.C. Predoctoral Fellow.
(3) H. C. Hornig, G. L. Zimmerman and W. F. Libby, THIS JOURNAL, **72**, 3808 (1950).
(4) W. Geilman and F. Weibke, *Z. anorg. Chem.*, **195**, 289 (1931).
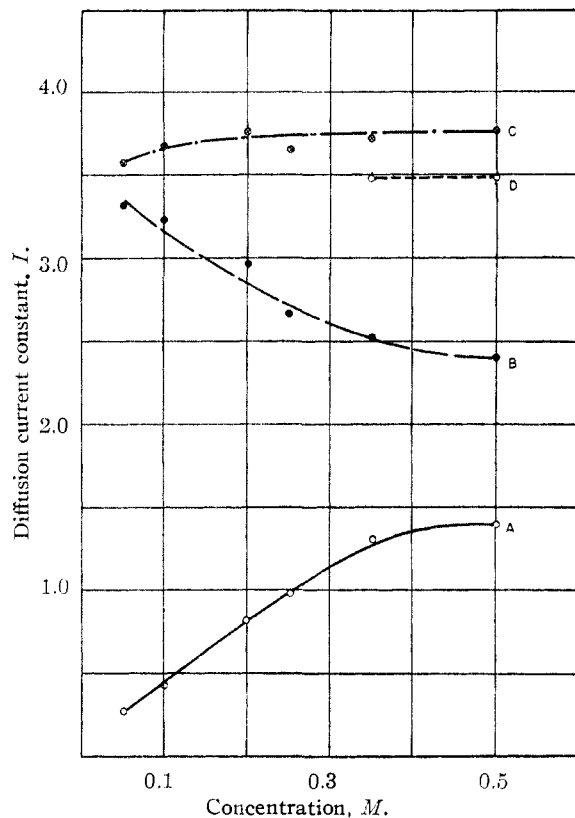(5) H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 305 (1939).

Fig. 1.—Variation of diffusion current constant, I, of trichloroacetic acid with concentration of buffer component: (A) Cl-3 wave (interaction with buffer component); (B) Cl-3 wave (non-interaction with buffer component); (C) total Cl-3 wave; (D) Cl-2 wave.

anion–ester was investigated in order to (1) elucidate further the connection between the S-shaped curve and the nature of the electroactive species and (2) determine the relative effect of the functional entities of carboxyl, carboxylate anion and carboxylate ester on carbon–halogen bond fission. The three chloroacetic acids were studied over pH range 0.7 to 11 at an ionic strength of 0.5 M; for comparison, runs were made at other ionic strength levels. In order to decrease the extent of hydrolysis observed at 25°, their ethyl esters were also studied at 0°. In addition, various substituted acetic acids were examined.

Chloroacetic Acids in Buffered Solution.—The data[3] were extended to cover the pH range at different ionic strength levels (Figs. 1 and 2). The waves, as indicated by the temperature coefficient of i_d, were diffusion-controlled; n, based on the Ilkovic equation, was 2 for all normal waves.

Within the potential range available, no wave was observed for chloroacetic acid. Dichloroacetic acid gave one wave (Cl-2 wave[1]) between pH 6.85 and 11.3, whose $E_{1/2}$ was pH-independent. Due to hydrogen ion discharge, no wave was obtained below pH 6.85.

Up to pH 3.1, trichloroacetic acid gave one wave, whose $E_{1/2}$ varied slightly from pH 0.7 to 2.2 and rapidly from pH 2.2 to 3.1. The diffusion current constant, I, and α values diminished with increasing

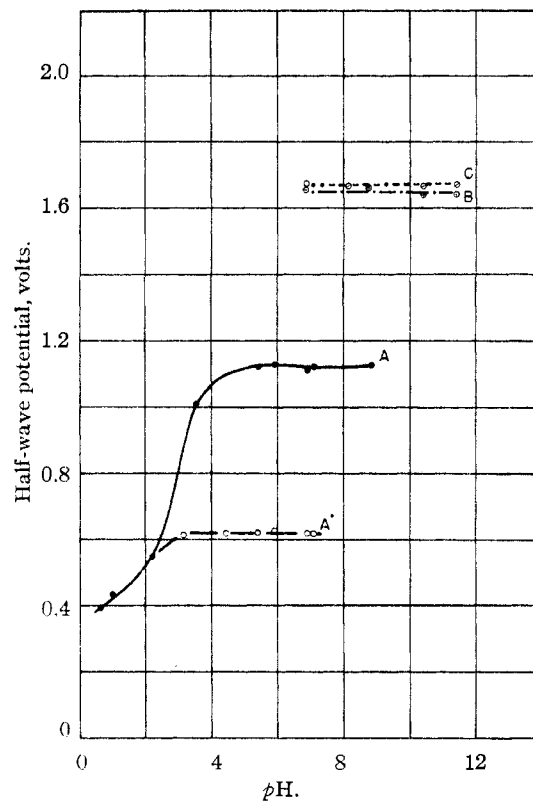(3) P. J. Elving and C. S. Tang, This Journal, **72**, 3244 (1950).

Fig. 2.—Variation of half-wave potential, $E_{1/2}$, with pH: (A) first wave of Cl-3; (A') second wave of Cl-3; (B) Cl-2 wave of trichloroacetic acid; (C) Cl-2 wave of dichloroacetic acid.

pH. From pH 7.7 to 11.3 two waves were obtained; the characteristics of the second wave are those of the Cl-2 wave. $E_{1/2}$ of the first wave (Cl-3 wave) was also pH-independent; I values of both waves were equal. Two waves of pH-independent $E_{1/2}$ were obtained in the intermediate pH region of 4.4 to 5.9; the sum of their I values was equal to I of the Cl-3 wave. Three waves were obtained at pH 6.9, 7.1 and 8.8; the third wave is a Cl-2 wave. Since the sum of the I values of these first two waves is equal to I for the Cl-3 wave, the result of the processes giving rise to the first two waves at pH 4.4 to 8.8 is equivalent to the Cl-3 wave.

The Split Anion Wave.—The characteristics of these first two waves are as follows for varying experimental conditions. (1) pH: From pH 4.4 to 7.1 $E_{1/2}$ and I values are independent of the pH at constant buffer component concentration and ionic strength.

(2) Buffer component concentration: At pH 8.8, I for the first wave increased as the buffer component concentration was increased while that of the second wave decreased. The sum of the I values was the same at each concentration. I of the first wave is lower in buffer 4 than in buffer 3 at the same concentration of buffer component. The I total of the two waves is identical in both buffers.

(3) Ionic strength: Ionic strength was increased by either increasing the buffer component concentration or adding potassium chloride. Two well-

defined waves were obtained at low ionic strength; these merged gradually at higher ionic strength. As the latter was increased from 0.05 to 0.5 at pH 5.4, $E_{1/2}$ for the first wave became 0.4 v. more negative, while $E_{1/2}$ for the second wave became 0.15 v. more positive. Within experimental error, both of these changes of $E_{1/2}$ with ionic strength appear to be linear. When the concentration of the buffer component was increased at constant ionic strength, $E_{1/2}$ values were not changed; I of the first wave increased and that of the second wave decreased. Increasing KCl concentration at constant ionic strength did not affect I of either wave.

(4) Temperature coefficients of i_d indicate diffusion-controlled processes.

Since the amount of acid present above pH 4.4 is practically nil and the amount formed by the anion recombination during the reduction process is apparently negligible, the reduction processes involved are due to the anion of trichloroacetic acid. The effects observed can be explained on the basis that the anion exists in two reducible forms, one of which is due to interaction with the buffer component. Since I values for the first wave increase with increasing buffer component concentrations, that wave is due to the anion–buffer component complex. Since both waves are diffusion-controlled, the equilibria involving anion and buffer component are slow in rate as compared to the rate of reduction of the more readily reduced species.

$E_{1/2}$ of the complexed wave shifts to a more negative value as the ionic strength is increased, as found for the undissociated form of an acid,[2] while $E_{1/2}$ of the uncomplexed wave shifts to a more positive value in conformity with the expected behavior for an anionic form.[2] Accordingly, the interaction is between the trichloroacetate and $H_2PO_4^-$, HPO_4^- or HOAc to form a more acidic species than the anion itself, since the fission of a carbon–halogen bond is more easily accomplished in the acidic form than in the corresponding anion form.[1,2] In view of the lack of interaction in the more alkaline region, it would seem that $H_2PO_4^-$ is the interacting species in phosphate solution.

Since only one Cl-3 wave was obtained in buffers 5 and 6, it is presumed that they did not interact in the same manner with trichloroacetate.

The $E_{1/2}$–pH relation for trichloroacetate tends toward the S-shape (Fig. 2). No limiting portion is obtained in the acidic region because trichloroacetic acid is a strong acid, and pH 0.7 is not sufficiently acidic for the pH-independent portion of the relation to be revealed.

Acids in Unbuffered Solution.—It is probable that many of the waves reported in the literature for organic acids in unbuffered solution are actually due to hydrogen ion discharge. Acetic, chloroacetic, 2-chloropropionic and phenylacetic acids gave no polarographic wave, other than base solution decomposition, in buffered solution over pH range 0.7 to 11; each gave one well-defined wave in unbuffered 0.5 M KCl solution. The latter wave is due to hydrogen ion discharge; its $E_{1/2}$ varies with the dissociation constant and concentration of the acid, i.e., with the pH of the solution.

The hydrogen discharge waves of dichloro- and trichloroacetic acids in unbuffered solution were poorly defined because they combined with the Cl-2 wave; i_d of the hydrogen wave can be estimated by deducting i_d of the Cl-2 wave from the observed i_d. The Cl-3 wave of trichloroacetic acid was clear; its $E_{1/2}$ and i_d are identical to those of the wave in the alkaline region. Therefore, trichloroacetic acid behaves in 0.5 M KCl solution (pH 3.5) as a mixture of hydrogen ion and trichloroacetate anion; the first wave is the Cl-3 anion wave and the second wave is composed of the Cl-2 and hydrogen waves. The hydrogen discharge wave for the chloroacetic acids has been reported by Korshunov, et al.,[4] who did not observe any wave due to carbon–halogen bond fission and therefore did not differentiate the discharge and fission waves.

Esters.—Ethyl chloroacetate gave one pH-independent wave in buffered and unbuffered solution ($E_{1/2} = -1.43$ at 25°). Below pH 6.8, hydrogen ion discharged before or with the reduction of the ester. Above pH 9.0, the ester was hydrolyzed. At 0°, $E_{1/2} = -1.50$ from pH 6.8 to 10.4 where the ester wave was obtainable. In buffered and unbuffered solution where hydrogen ion discharge or hydrolysis did not interfere, ethyl dichloroacetate gave two waves of $E_{1/2}$ -0.70 and -1.43 at 25°, and -0.86 and 1.50 at 0°. Under similar conditions, ethyl trichloroacetate gave three waves only at 0° of $E_{1/2}$ -0.22, -0.86 and -1.51.

The I values for the different waves, e.g., Cl-1 wave, was smallest for ethyl trichloroacetate, intermediate for dichloroacetate and largest for chloroacetate in conformity with the size and expected diffusion coefficients of the esters. Each wave is diffusion-controlled and irreversible; α varied from 0.3 to 0.4 for the Cl-1 and Cl-2 waves, and from 0.7 to 0.8 for the Cl-3 wave; n was two for each wave.

Relative Effect of the Functional Group.—Reduction of the polychloroacetic acids and their esters involves the successive removal of halogen atoms, i.e., trichloroacetate to dichloroacetate to chloroacetate to acetate.[1,3] $E_{1/2}$ values of the esters are pH-independent. $E_{1/2}$ values of the acids are independent of pH in the region where the acid exists practically entirely as either the undissociated acid or the anion; in the intermediate pH region, $E_{1/2}$ becomes more negative as pH increases.

The effect of the polychloromethyl group on the fission of a carbon–chlorine bond in that group may be considered to be the same for all species derived from the same acid. The principal factor in the $E_{1/2}$ values obtained, therefore, must be the presence of the undissociated carboxyl group, the dissociated carboxyl group or the carboalkoxyl group. In determining the mechanism of carbon–halogen bond fission at an electrode, it would be helpful to know the effect of these groups on the chemical bond fission; this information is not available.

The electrochemical reduction of the carbon–halogen bond is accomplished most easily in the

(4) I. A. Korshunov, Z. B. Kuznetsova and M. K. Shchennikova, Zhur. Fiz. Khim., **23**, 1292 (1949); C. A., **44**, 2873 (1950).

ester, followed in turn by the acid and then the anion. Comparison of the behavior of acid, anion and ester must be made in light of the equilibrium effects[1,2] involved in the reduction of the anion. Study of the effect of the alkoxyl group in halo esters[5] indicates that as the electron-releasing power of the ester group increases, the ease of fission increases. Similar evidence is found for the effect of chain length on the ease of carbon–halogen bond fission in the 2-bromo-n-alkanoic acids.[6]

Role of pH.—The behavior of the esters, in conjunction with the nature of the S-shaped curve for the pH-dependence of reduction in the acids, definitely establishes the fission of the carbon–halogen bond at the mercury electrode as a pH-independent process.

Experimental.—The general technique used has been described.[1,2,6] The buffers used and their pH range were: (1) KCl + HCl, 0.7 to 2.2; (2) NaOAc + HOAc, 4.5 to 5.5; (3) Na_2HPO_4 + citric acid, 3.1 to 7.3; (4) Na_2HPO_4, 8.6 to 8.9; (5) NH_4Cl + NH_3, 7.7 to 8.8; (6) Na_2HPO_4 + NaOH, 10.4 to 11.3.

Acknowledgment.—The authors wish to thank the Atomic Energy Commission and the Research Corporation for grants-in-aid.

(5) I. Rosenthal, C. S. Tang and P. J. Elving, THIS JOURNAL, **74**, 6112 (1952).

(6) I. Rosenthal, C. H. Albright and P. J. Elving, *J. Electrochem. Soc.*, **99**, 227 (1952).

SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

Polarographic Behavior of Organic Compounds. XIV. Carbon–Halogen Bond Fission in System Acid–Anion–Ester; Estimation of Acid Half-wave Potentials

BY ISADORE ROSENTHAL, CHING-SIANG TANG AND PHILIP J. ELVING*

RECEIVED MAY 8, 1952

A plot of half-wave potential, $E_{1/2}$ vs. pH for the α-halogenated acids yields an S-shaped curve,[1] of which only the low pH branch appears to be free of the influence of kinetic factors involving dissociation of the acid.[2] It is in this region, therefore, that comparison of $E_{1/2}$ values should have the clearest relation to the strength of the bonds cleaved at the dropping mercury electrode. Often, $E_{1/2}$ values for acids cannot be obtained in this low pH region due to prior appearance of a hydrogen discharge wave.[1b] The present study shows how these values may be obtained with reasonable accuracy from the $E_{1/2}$ values of the corresponding esters and sets forth the possibility that the relationship between acid and ester forms found with the halogenated acids may be used to good advantage in studying other difficultly reducible acids.

Study of the effect of n-alkyl substituents on $E_{1/2}$

* University of Michigan, Ann Arbor, Mich.

(1) (a) P. J. Elving and C. S. Tang, THIS JOURNAL, **72**, 3244 (1950); (b) *ibid.*, **74**, 6109 (1952); (c) P. J. Elving, I. Rosenthal and M. K. Kramer, *ibid.*, **73**, 1717 (1951).

(2) (a) P. J. Elving, A. J. Martin, C. S. Tang and I. Rosenthal, *Anal. Chem.*, accepted for publication; (b) I. Rosenthal, C. H. Albright and P. J. Elving, *J. Electrochem. Soc.*, **99**, 227 (1952).

of bromoacetic acid[2b] indicated that the ease of reduction increased with the size of the alkyl group. The present paper contains a similar study on the size of the alkoxyl group in chloroacetic ester; shifts in ease of reduction are interpreted in terms of structure.

Experimental

The experimental procedure has been described.[1b] The buffer solutions used (ionic strength of 0.5) and their pH were: (1) 0.5 M KCl with added HCl, 0.81, 1.20, 1.80; (2) 0.5 M NaOAc with added HOAc, 4.51, 5.51; (3) 0.5 M NH_4Cl (unbuffered), 4.9; (4) 0.5 M KCl (unbuffered), 5.5; (5) 0.5 M NH_4Cl with added NH_3, 8.20, 8.80.

Fresh stock solutions of the esters were prepared in aqueous 40% purified 1,4-dioxane as needed; the final test solution had a dioxane concentration of 2% which did not measurably affect the pH or polarographic behavior.

Results and Conclusions

Diffusion-controlled, irreversible waves[3] were obtained, whose n values (Ilkovic equation) indicated each wave to be due to a two-electron process as found for other carbon–halogen bond fission processes.[1,2]

Ethyl bromoacetate and the three chloroesters each give one well-defined wave of pH-independent $E_{1/2}$ in both unbuffered and buffered solution; this wave represents conversion to ethyl acetate (Br-1 and Cl-1 waves[1b,c]). Ethyl dibromoacetate and tribromoacetate each give two waves. The more negative wave is, in each case, identical in behavior with that of ethyl bromoacetate. The more positive wave is due to the conversion of dibromoacetate ester to bromoacetate ester; the expected Br-3 wave representing the reduction of the ethyl tribromoacetate to dibromoacetate cannot be observed due to mercury oxidation.

The diffusion current constants, I, for the bromoacetate wave of each bromo ester are constant over the pH range, but are different among the three esters with ethyl bromoacetate having the largest I (2.7), followed in decreasing order by the dibromoacetate (2.2) and the tribromoacetate (1.6). This decrease in I is connected with the nature of the step-wise reduction process. With ethyl tribromoacetate, e.g., the only monobromoacetate present is that formed by the reduction of the tribromoacetate and so the rate of supply of the monobromoacetate to the electrode is controlled by the rate of diffusion of the tribromoacetate. This explains why I values vary inversely with the size of the parent molecule even though the carbon–halogen bond fission in each case occurs in the same molecule.

Similarly, the slightly different I values (Me 2.2, Et 1.8, Bu 1.7) among the chloroesters are expected since the methyl ester being the smallest molecule of the three esters would be expected to have the largest diffusion coefficient and hence the largest i_d.

At 25° and pH 8.8, ethyl bromoacetate gave two well-defined waves ($E_{1/2}$ −0.43 and −1.24). The more positive wave was due to ester reduction, while the other wave was that of bromoacetic acid, indicating partial hydrolysis of the ester. Accord-

(3) $E_{1/2}$ values in volts at 0°. Ethyl esters: bromoacetate −0.47 (−0.43 at 25°); dibromoacetate −0.08 and −0.48; tribromoacetate −0.08 and −0.48. Chloroacetate esters: methyl −1.54, ethyl −1.50, n-butyl −1.41.