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

Experimental.—The general technique used has been described.[1,2,6] The buffers used and their *p*H 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.

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

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

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A plot of half-wave potential, $E_{1/2}$ *vs.* *p*H for the α-halogenated acids yields an S-shaped curve,[1] of which only the low *p*H 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 *p*H 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 $E_{1/2}$ 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 *p*H 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 *p*H 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 *p*H-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 *p*H 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 *p*H 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-

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[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**).

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[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.

ingly, the kinetics of hydrolysis of the ester could be studied polarographically.

In order to compare the reduction of undissociated acid and ester, a check run was made with dibromoacetic acid under the same experimental conditions used with the esters. $E_{1/2}$ for the two waves at *p*H 1.0 and 0° are -0.16 and -0.62.

Discussion

Waves for carbon–chlorine bond fission in chloro- and dichloroacetic acids cannot be obtained in the *p*H region where these acids are undissociated, due to hydrogen wave interference. This is not the case with bromo- and dibromoacetic acids or with the most positive wave of trichloroacetic acid. The esters of the latter acids are uniformly more easily reduced than the corresponding acid, the differences ranging from 0.08 to 0.23 v.

On the basis of this behavior, it is possible to predict from a knowledge of $E_{1/2}$ for the esters of chloro- and dichloroacetic acids the $E_{1/2}$ values for the corresponding waves in the undissociated acids (Table I). The average $\Delta E_{1/2}$ (0.15 v.) between the ester and undissociated acid forms for the species for which data are available has been added to the experimental value of $E_{1/2}$ for the ester to obtain a probable $E_{1/2}$ value for the acid. The error given for the latter value is the average deviation of the $\Delta E_{1/2}$ values. Although the error may seem large compared to the $\Delta E_{1/2}$ value, the magnitude of the latter plus the error is small compared to the range of potential in which the acid $E_{1/2}$ may fall.

TABLE I

COMPARISON OF $E_{1/2}$ VALUES FOR ESTER, UNDISSOCIATED ACID AND ANION FORMS OF THE BROMO- AND CHLOROACETIC ACIDS[a]

	Ethyl ester	Acid[b]	Anion[b]
Bromoacetic	−0.48	−0.62	−1.22
Dibromoacetic	−0.08	−0.16	−1.41
Tribromoacetic	Merges with Hg oxidation	At *p*H 3.7, *E* is −0.08 v.	−0.32
Chloroacetic	−1.49[c]	1.64 ± 0.07[e]	
Dichloroacetic	−0.86[c]	1.01 ± 0.07[e]	−1.60[c]
Trichloroacetic	−0.22[c]	−0.45[d]	−1.00[c]

[a] All data at 0° except for the anion values of the bromoacetic acids which are at 25° (reference 1c). [b] The acid value is taken from the *p*H-independent branch of the $E_{1/2}$ *vs.* *p*H plot, that occurs in the low *p*H region. This region varies with the acid but occurs generally between *p*H 0.0 and 2.0. The anion values are taken similarly from the high *p*H branch of the $E_{1/2}$–*p*H plot that starts at about *p*H 6.0 to 8.0, *i.e.*, all anion values are taken with NH_4Cl–NH_3 buffers at *p*H 8.2 except that of tribromoacetic acid, which is taken with a MacIlvaine buffer at *p*H 7.7. [c] These values are from reference 1b. [d] This value is the result of an extrapolation of data in reference 1b to the *p*H-independent acid value. Due to the strongly acidic nature of trichloroacetic acid, the $E_{1/2}$–*p*H curve in the acid region is not truly *p*H-independent at the lowest *p*H values, *ca.* 1.0, for which measurements were taken. However, sufficient data exist to permit extrapolation to the *p*H-independent region which appears to start at about *p*H 0.0. [e] Postulated values; see text.

The importance of this type of relationship in $E_{1/2}$ for acid, anion and ester is exemplified when the polarographic behavior of chloroacetic acid is analyzed. The wave for the latter could not be obtained in buffered solution in the usual *p*H range although different buffers, ionic strengths and temperatures were used. In the acid region, its $E_{1/2}$ of -1.64 (calculated from the ester value) is beyond the hydrogen discharge wave; in the higher *p*H region, $E_{1/2}$ shifts so that it is beyond the discharge potentials of the common cations. For similar reasons, the wave for its ester cannot be obtained in the acid region. However, since $E_{1/2}$ for the ester wave is *p*H-independent, its value can be determined at any *p*H, *e.g.*, in the alkaline region where the available potential span before background electrolyte decomposition is much greater than in the acid region. In general, if the wave for a particular acid cannot be obtained in buffered solution, the possibility exists of studying its ester in buffered or unbuffered solution to obtain a value characteristic of the undissociated acid.

In studying the effect of alkyl substituents on $E_{1/2}$ of bromoacetic acid,[2b] it was found that replacement of a hydrogen by a methyl group, *i.e.*, insertion of a methylene group, caused a shift of about +0.20 v. Successive insertions of methylene groups, *i.e.*, 2-bromo-*n*-butyric acid to 2-bromo-*n*-octanoic acid, caused a smaller (+0.04 v.) but steady decrease in $E_{1/2}$. Since the inductive effect would vanish after at least the ethyl group, the cause for the continuing decrease was thought to be due to an increase in the free energy of adsorption as the alkyl fragment of the molecule increased. Support for this concept is found in the adsorption of alcohols from the vapor phase on mercury,[4] where the increase in the free energy of adsorption is constant in going from butyl to hexyl alcohol. The data for the esters of chloroacetic acid fall in line with the explanation given for the behavior of the α-bromo acids, since there is a similar steady shift of about +0.04 v. in $E_{1/2}$ per methylene group. (It was assumed that the shift from ethyl to propyl would be one-half of that from ethyl to butyl.) The inductive effects on the carbon–halogen bond of replacing the hydroxyl hydrogen of the carboxyl group by a methyl group should be less than the corresponding case where the methyl group replaced a hydrogen on the α-carbon, since in the former case the substituent is further removed from the bond being broken.

An attempt to evaluate the effect of the substitute on the basis of Shikata's rule,[5] would lead to the prediction of an opposite shift, since any influence that increasing the size of the alkoxy group might have, would be in the direction of increasing the electron density on the α-carbon. Such behavior, according to Shikata, should cause polarographic reduction to become more difficult. The contrary nature of the experimental data indicates the caution necessary in attempting to predict polarographic behavior from Shikata's rule.

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