tion with crystals, a faint precipitate barely was discernible even after several hours. The precipitate was much more evident upon cooling to 18.5° and disappeared entirely upon warming to 19.5°. On this basis it is evident that no more than 5.0 g. of lauryl alcohol may be added to 100 g. of lauraldehyde (4.76% solution of the alcohol) without causing precipitation of the hemiacetal at temperatures below 19.0°. The experiment was repeated using 0.36 g. of lauryl alcohol in 5.0 g. of lauraldehyde, and it was found that precipitation of the hemiacetal occurs if more than 7.2 g. of lauryl alcohol is added to 100 g. of lauraldehyde (6.71% solution of the alcohol) at temperatures below 24°.

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Polarographic Behavior of 2,2,2-Trichloroethanol. Acidic Nature of Trichloroethanol

BY PHILIP J. ELVING AND C. EUGENE BENNETT

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As part of a systematic investigation of the effect of various functional groups upon the electrochemical fission of carbon–halogen bonds, the polarographic behavior of the chloroethanols was investigated in order to extend the available data. Only 2,2,2-trichloroethanol of the three 2-chloroethanols gave a polarographic wave in the potential range of 0 to −2.0 v.

One cathodic wave was obtained for trichloroethanol in buffered solution over the *p*H range of 6.0 to 12.4 (Fig. 1); no wave was observed at lower *p*H due to prior hydrogen discharge. No chloroethanol (ethylene chlorohydrin) reduction was observed over the same range. The absence of a second wave of trichloroethanol indicates that dichloroethanol also is not reducible under the conditions studied.

Values of α (calculated from the relation $E_{1/4} - E_{3/4} = 0.056/\alpha$ at 25° and $0.051/\alpha$ at 0°) varied from 0.2 to 0.3 at 60-cm. head and 0.3 to 0.4 at 90-cm. head; values of n evaluated on the basis of the Ilkovic equation were 2.0 ± 0.2.

The $I(i_d/Cm^{2/3}t^{1/6})$ *vs.* *p*H relation (Fig. 1) shows that the current varies considerably in different buffers even at the same *p*H. However, I is essentially constant in a given buffer up to *p*H 11; the decrease at higher *p*H may be due to the smaller diffusion coefficient resulting from anion formation. Hydrolysis is not involved since no measurable decrease in current was observed in any solution upon standing for an hour. The largest I values are found in NH_3 buffers and KCl–NaOH solutions, slightly smaller values in borate, and the smallest in phosphate-containing buffers. The latter decrease may be due to formation of a phosphate compound, as has been noted with chloroethanol.[1]

Polarographic Determination of Trichloroethanol.—The linear relationship between current and concentration (0.1 to 1.0 m*M*) in ammonia buffer at *p*H 8.4 indicates that trichloroethanol can be determined polarographically; under ideal conditions, analytical results accurate to ±2% can be obtained.

Nature of the Reduction Process.—The variations of current with temperature and with drop-time (height of mercury) indicate the current-producing process to be diffusion controlled.

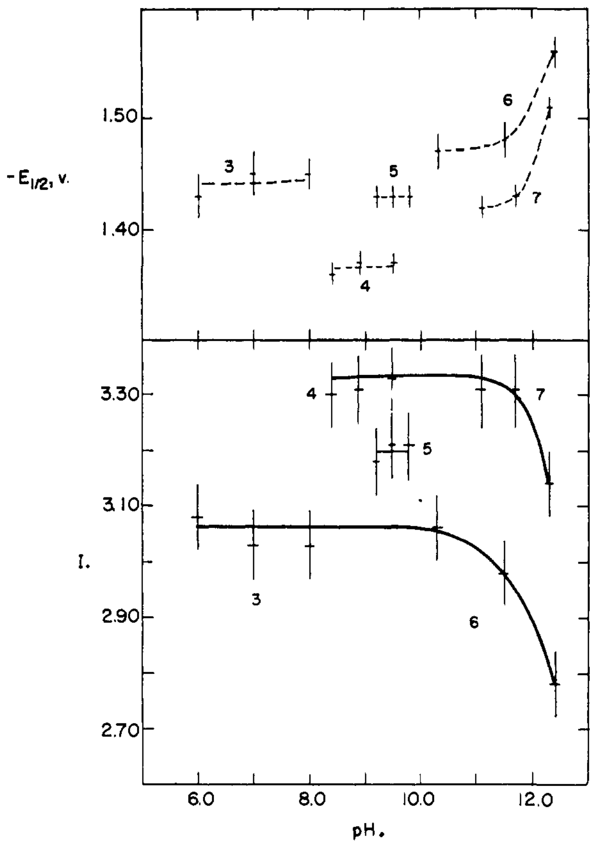

Fig. 1.—Variation of $E_{1/2}$ and I (diffusion current constant) with *p*H for trichloroethanol at 25° and 60 cm. Concentration of the alcohol was 0.5 m*M*. The numbers refer to the buffers listed in Table I. The size of each point indicates the possible uncertainty.

Application of the Ilkovic equation (diffusion coefficient calculated by Stokes–Einstein equation) and coulometric runs (ammonia buffer at *p*H 8.4) indicate the reduction process to involve two electrons per molecule. The two-electron wave of trichloroethanol could conceivably be due to carbon–chlorine or carbon–hydroxyl bond fission with the formation of 2,2-dichloroethanol or 1,1,1-trichloroethane. The fission of the carbon–hydroxyl bond is rather unlikely in this case since the weaker bond (the bond becomes weaker as the acidity decreases) of chloroethanol and ethanol is non-reducible under similar conditions. Polyhalogenated organic compounds generally show a stepwise reduction of carbon–halogen bonds,[2] *e.g.*, with a compound such as ethyl trichloroacetate the first chlorine comes off more readily than the second one, which in turn comes off more readily than the third. Of the three waves, the more negative ones correspond to the two waves of ethyl dichloroacetate, and the most negative wave corresponds to the one wave of ethyl chloroacetate. Therefore, the following over-all electrode reaction probably accounts for the observed behavior

$$Cl_3C—CH_2OH + 2e^- + H^+ \longrightarrow Cl_2CH—CH_2OH + Cl^- \quad (1)$$

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[1] R. H. A. Plimmer and W. J. N. Burch, *J. Chem. Soc.*, 286 (1929).

[2] P. J. Elving, *Record Chem. Progr.* (*Kresge-Hooker Sci. Lib.*), **14**, 99 (1953).

Additional evidence for reaction 1 is that the $E_{1/2}$ corresponds closely to those of chloral hydrate[3a] and trichloroacetaldehyde diethyl acetal[3b] which are similar in structure to trichloroethanol. Runs in 0.1 M tetra-*n*-butylammonium iodide in 67% methanol–water showed only one wave of $E_{1/2}$ of −1.67 v. over the potential range of 0 to −2.5 v. *vs.* S.C.E. Dichloro- and chloroethanol are probably reduced at more negative potentials.

Acidic Nature of Trichloroethanol.—Ethanol in aqueous solutions behaves as an extremely weak acid; trichloroethanol, by analogy with the chloroacetic acids, would be expected to be a much stronger acid. The $E_{1/2}$ values (Fig. 1) seem to be independent of pH in a given buffer system up to pH 10 or 11; at higher pH, $E_{1/2}$ shifts to more negative potentials. Accurate $E_{1/2}$ values could not be determined at pH higher than 12.4 due to interference from background discharge. Presumably, if values in the higher pH region were known, an S-type $E_{1/2}$ *vs.* pH curve would be obtained.

Such S-shaped relations between pH and $E_{1/2}$ have been observed for a variety of acidic compounds, *e.g.*, unsaturated acids,[4] 2-haloalkanoic acids,[2,5] iodobenzoic acids,[6] iodophenols[6] and nitrophenol.[7] Tachi[8] determined the pK_a of neutral red and benzoylacetone from such a relation. The interpretation of this relationship is discussed by Saito,[5a] Tanford and Wawzonek,[9] and Elving and Rosenthal.[4b]

Experimental

Chemicals.—Stock alcoholic solutions (10.0 millimolar) were prepared from a redistilled research sample of 2,2,2-trichloroethanol (Westvaco Chemical Division of the Food Machinery Corp.), b.p. 55° at 15 mm., n^{25}D 1.4852 (lit. b.p. 58–60° at 16 mm.), and Eastman Kodak Co. white label grade ethylene chlorohydrin. Nitrogen used for deoxygenating was purified and equilibrated by bubbling through sulfuric acid an alkaline pyrogallol solution, water and a portion of the test solution. Buffer solutions (Table I) were prepared from C.P. chemicals.

Apparatus.—A Leeds and Northrup Type E Electro-Chemograph was used for all polarographic and potential measurements. A Beckman model G pH meter was used for pH measurement. All measuring apparatus was calibrated. A thermostated H-cell[10] employing a saturated calomel reference electrode was used. The dropping mercury electrode, prepared from Corning marine barometer tubing, had m and t values (open circuit, distilled water, 25°, 60 cm. head) of 0.916 mg./sec. and 5.6 sec. Coulometric runs were made in a modified Lingane apparatus[11] maintained at 25 ± 0.1°.

TABLE I

BUFFER SOLUTIONS

Buffer	pH	Composition
1	2.2	0.5 M KCl with added HCl
2	4.9	0.5 M NaOAc with added HOAc
3	6.0	0.126 M $Na_2HPO_4 \cdot 12\ H_2O$, 0.0368 M citric acid monohydrate and 0.156 M KCl
	7.0	0.164 M $Na_2HPO_4 \cdot 12\ H_2O$, 0.0176 M citric acid monohydrate, and 0.073 M KCl
	8.0	0.194 M $Na_2HPO_4 \cdot 12\ H_2O$, 0.0028 M citric acid monohydrate
4	8.3–9.6	0.5 M NH_4Cl with added NH_3
5	9.2	0.082 M $Na_2B_4O_7 \cdot 10\ H_2O$ and 0.320 M KCl
	9.5	0.082 M $Na_2B_4O_7 \cdot 10\ H_2O$, 0.302 M KCl, with added NaOH
	9.8	0.082 M $Na_2B_4O_7 \cdot 10\ H_2O$, 0.285 M KCl, with added NaOH
6	10.3	0.163 M $Na_2HPO_4 \cdot 12\ H_2O$ with added NaOH
	11.5	0.145 M $Na_2HPO_4 \cdot 12\ H_2O$ with added NaOH
	12.4	0.105 M $Na_2HPO_4 \cdot 12\ H_2O$ with added NaOH
7	11.1–12.3	0.5 M KCl with added NaOH

Procedure.—The test solutions (ionic strength of 0.45), prepared by mixing measured volumes of stock and buffer solutions, had essentially the same pH as the buffer used. The test solution was deoxygenated and then electrolyzed; the nitrogen atmosphere was maintained throughout the electrolysis.

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By-product from the Osmium Tetroxide Hydroxylation of 20-Cyano-17-pregnene-21-ol-3,11-dione 21-Acetate

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Hydrolytic cleavage of the osmium tetroxide complex (II), obtained as an intermediate in the hydroxylation of 20-cyano-17-pregnene-21-ol-3,11-dione 21-acetate (I)[1] yields predominantly IIIa together with varying amounts of a by-product. This by-product was found to be a nitrogen-containing substance giving a strong test for cyanide and possessing two acetate functions as measured by acetyl group determination. The by-product rapidly reduced Tollens reagent, gave a positive Porter–Silber test,[2] and otherwise exhibited normal characteristics for the 17-hydroxy cortical side-chain. This substance, however, failed to give a dinitrophenylhydrazone derivative at room temperature under conditions whereby IIIa rapidly derivatized; pregnane-3α,17α,21-triol-11,20-dione 3,21-diacetate also did not derivatize under similar

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