liquids at their boiling points Trouton's rule holds,[3] $f(kT_{B_1}) = f(KkT_{B_2})$
$= f\left(\dfrac{T_{C_1}}{T_{C_2}} kT_{B_2}\right)$, from which $\dfrac{T_{C_1}}{T_{C_2}} T_{B_2} = T_{B_1}$, or $\dfrac{T_{B_1}}{T_{C_1}} = \dfrac{T_{B_2}}{T_{C_2}}$ that is the ratio
of boiling-point to critical temperature is a constant.

Guldberg[4] was the first to point out that the ratio of the boiling point to the critical temperature is approximately a constant, the mean being about 0.66. Although the values do vary somewhat, they are nevertheless in the vicinity of that value.

Summary

It has been shown that if the heat of vaporization (ΔH) is assumed to be a function of the temperature alone, the same function for all non-associated liquids, but differing in the constants involved, Guldberg's rule showing the relation of boiling point to critical temperature is derived, indicating that the relation $\Delta H = F(T)$ (for all non-associated liquids) may probably be relied on to approximately the limits of the boiling point critical-temperature ratios.

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DEPOLARIZATION OF THE CHLORINE ELECTRODE BY ORGANIC COMPOUNDS[1]

By MERRILL A. YOUTZ
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The literature upon the subject of electrolytic chlorination of organic substances is not large in comparison with that upon electrolytic oxidation and reduction. Although work has been done upon chlorination of various substances,[2] and upon overvoltage[3] of chlorine, no one has attempted to use the decomposition potential method of determining whether organic

[3] At this point Trouton's rule, rather than the more recent modification of Hildebrand is used because of the fact that the temperatures for which the latter rule holds are known for too few substances to be of any value in checking the relation finally obtained. The derivation would be similar, however, if Hildebrand's modification were used.

[4] Guldberg, Z. physik. Chem., 5, 374 (1890).

[1] This is an abstract of a portion of a thesis submitted to the faculty of the Massachusetts Institute of Technology in May, 1922, by Merrill A. Youtz in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Haber and Moser, "Die Elektrolytischen Prozesse der organischen Chemie," Knapp, Halle, 1910, pp. 81–104. Löb, (Lorenz), "The Electrochemistry of Organic Compounds," Wiley and Sons, New York, 1906.

[3] Müller, Z. Elektrochem., 6, 573 (1900); 8, 426 (1902). Sacerdoti, ibid., 17, 473 (1911). Billiter, "Die Elektrochemischen Verfahren der chemischen Gross-industrie," Knapp, Halle, 1909, vol. II, p. 140. Newbery, J. Chem. Soc., 119, 477 (1921). Lewis, THIS JOURNAL, 33, 299 (1911).

substances could be chlorinated. Also, in no cases have attempts been made to apply measured and limited potentials to control chlorination. The work of Haber[4] on the reduction of nitrobenzene to any desired stage by keeping the cathode potential between certain limits, and that of Dony-Hénault[5] on the oxidation of ethyl alcohol to either acetaldehyde or acetic acid, depending on the anode potential, have not been paralleled in chlorination. The attempt has not been made up to the present, although Nernst[6] long ago stated that probably successive stages of chlorination also depended upon definite potentials.

There are at least three ways by which electrolytic chlorination of organic substances might be effected: (1) the chloride ions, upon being discharged, might react directly with the organic substance according to the equations $2Cl^- + 2\oplus = 2Cl; RH + 2Cl = RCl + H^+Cl^-$; (2) the chloride ions, upon discharge, might react with some added substance, such as iodine, and this compound then react with the organic substance; $2Cl^- + 2\oplus = 2Cl; 2Cl + I_2 = 2ICl; RH + 2ICl = RCl + H^+Cl^- + I_2$; (3) the chloride ions, upon discharge, might react with each other to form gaseous chlorine, and a portion of this react later with the organic substance; $2Cl^- + 2\oplus = 2Cl + Cl_2; RH + Cl_2 = RCl + H^+Cl^-$.

Since each electrode process requires a distinctive process at the anode for given conditions, if Process 1 or 2 occurs, the potential should be different than for Process 3 which, as far as the potential is concerned, is the same as though the organic substance were not present. If this latter potential be observed, it may be assumed that true electrolytic chlorination is not occurring; if a lower potential, then another process, perhaps electrolytic chlorination of the substance, is occurring.

The work herein described was an attempt to determine whether or not the anode potentials in chloride solutions containing organic compounds could be used as criteria of the susceptibility of those substances to electrolytic chlorination.

Two methods were used. (1) The anode decomposition potentials of potassium chloride and hydrochloric acid solutions were determined with and without the presence of organic compounds expected to act as depolarizers. (2) After an electrode had been evolving chlorine for some hours, and the potential had risen to a nearly constant value, a supposed depolarizer was added, and the effect upon the potential noted. Method 1 was used principally. The decomposition potentials were found graphically by plotting current values as ordinates and anode potentials as abscissas, and extrapolating the straight parts of the curves after the break, back to the zero current line.

[4] Haber, Z. Elektrochem., 4, 506 (1898).
[5] Dony-Hénault, ibid., 6, 533 (1900).
[6] Nernst, "Theoretical Chemistry," 1916, p. 812.

For measurement of potentials a potentiometer reading to 0.0005 volt, a Weston standard cell, rheostat, and normal calomel electrodes were used. An intermediate vessel containing N potassium chloride solution was used between the calomel electrode and the electrode being measured. For controlling the e.m.f. applied to the cell, a storage battery of 6 cells, a slide-wire rheostat, and a voltmeter were used. A milliammeter was used to measure the current.

. The electrolytic cells were all of the same type but of various sizes, depending upon the anode and upon whether a stirrer was employed. In order that the current density might be perfectly uniform, the cathode was a hollow cylinder of carbon, and the anode also cylindrical and within the cylindrical cathode. A porous cup of appropriate size contained the anode and anode solution. Four anode materials were used, carbon, graphite, platinum, and Duriron. A cylindrical piece of Duriron was not available, and the electrodes were therefore small bars, 8 × 2 × 0.6 cm.

The e.m.f. was applied to the cell in steps of 0.100 volt, increased by that amount every three minutes, and maintained until the next increase. The current and potentiometer readings were taken two minutes after the e.m.f. had been increased. In plotting, the value taken for the calomel electrode referred to the hydrogen electrode as zero was —0.283 volts.[7] Liquid potentials were ignored as they would probably nearly cancel, since only the *difference* between two decomposition potentials was sought. The experiments were carried out at "room temperature," since the effect of small temperature variations was less than the accuracy of the measurements and the graphical extrapolation.

Results

The results are presented in the form of anode potential-current curves for some of the various experiments. (Figs. 1–5.)

Typical results with potassium chloride solution and carbon anodes, using maleic acid, oleic acid, 10% acetic acid, and ethylene, are shown in Fig. 1, Curves A and B and Fig. 2, Curve B. There is apparently a slight depolarization. But the curves for the solutions with a depolarizer do not rise smoothly as does that for potassium chloride alone. It was supposed that perhaps the depolarizer immediately at the anode surface became used up or too much depleted, and that at some small current value, the rate of diffusion through the surface film to the electrode reached a maximum. Then further increase of e.m.f. caused no larger current to flow until the decomposition potential of the chloride ion was reached, and the curve became the curve for chlorine evolution. Such a situation is entirely possible and was realized in the case of ferrous chloride solutions

[7] Beattie, THIS JOURNAL, **42**, 1128 (1920), gives —0.2826 volts.

(Fig. 1, Curve C).[8]   But the evidence of these curves alone did not seem sufficient.   The curves for hydrochloric acid solutions were not like these. Also, curves where limited diffusion causes the shifting over, have been found to be smooth curves, and the height of the horizontal portion to be changed (raised) by stirring, whereas stirring did not affect the maleic acid curve.

There appeared to be no appreciable overvoltage at these low current densities.   If the substances really were depolarizers and were being chlorinated, the depolarizer curve should remain in the same place while the chlorine curve would be shifted to the right, if the electrode could be given an overvoltage.   No electrode material so far investigated shows a
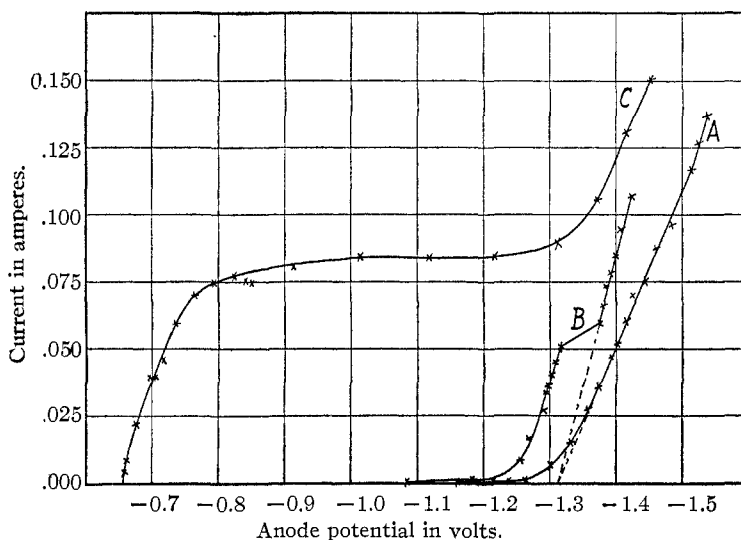

Fig. 1.—Curve A: N KCl; carbon anode; no depolarizer.   Curve B: N KCl; carbon anode; maleic acid (0.25 M); stirring.   Curve C: N HCl; carbon anode; FeCl$_2$ (0.12 N); FeCl$_3$ (0.125 N); no stirring.

chlorine overvoltage immediately, especially at such low current densities. But although it has been found that[9] the presence of fluoride ions materially raises oxygen overvoltage, they did not affect the chlorine overvoltage.

Phenol (Fig. 2, Curve A) gave a large depolarization and a curve exactly as had been expected.   The solution became deep orange in color and it was possible to establish the presence of phenoquinone, an oxidation product of phenol, and the absence of chlorine.

[8] A complete account of this interesting result and its application in calculating the thickness of the surface film surrounding a solid immersed in a liquid has been published.   *Ind. Eng. Chem.*, **15**, 603 (1923).

[9] Skirrow, *Z. anorg. Chem.*, **33**, 25 (1903).

A platinum anode in potassium chloride solution gave a sharper curve than carbon, but no evidence of depolarization with acetic acid.

It was supposed that a Duriron anode might possibly have an over-voltage, and if so might reveal depolarization of substances in case their chlorination potentials were above 1.31 volts. With potassium chloride alone the decomposition potential was about 1.8 volts. But the results with acetic acid, maleic acid, phenol, and ethyl alcohol gave no evidence of depolarization. It is not known to what cause the very high decomposition potential can be ascribed. It did not represent oxygen evolution, as chiefly chlorine was evolved.

In the remainder of the experiments hydrochloric acid was used instead of potassium chloride. The acid solutions were made by diluting 100 cc.
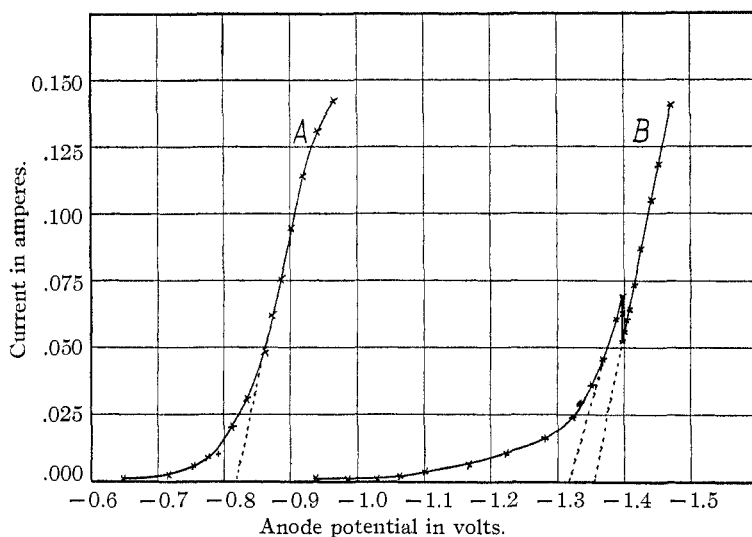

Fig. 2.—Curve A: N KCl; carbon anode; phenol (5%). Curve B: N KCl; carbon anode; acetic acid (10%).

of concd. acid (d., 1.19), to one liter. Typical results with a carbon anode are shown in Figs. 3 and 4. Fig. 3, Curve B, with 70% acetic acid, indicated depolarization in the manner expected, and consequently an electrolysis of a similar solution was conducted with a carbon anode for four hours at 4 amps. although at a much higher current density. The anolyte was fractionally distilled and found to contain about 6 g. of chloro-acetic acid. An experiment with ordinary chlorine, under exactly similar conditions, gave no trace of chloro-acetic acid.

We do not believe, however, that acetic acid is a depolarizer at the low current densities involved in the determination of the decomposition potential, in spite of the curve of Fig. 3, Curve B. The reason will be

indicated under the discussion of experiments with platinum and hydrochloric acid.

In order to study toluene and other insoluble hydrocarbons, they were dissolved in a mixture of 70–80% acetic acid and hydrochloric acid. In the four cases studied (Fig. 3, Curve C), toluene, *m*-xylene, mesitylene and amylene, the depolarization intercept was about the same as for acetic acid alone, 1.25–1.26 volts, indicating no result for the hydrocarbons themselves. Yet toluene, though at a higher current density, can be very efficiently chlorinated under these conditions.[10]

Crotonic acid (Fig. 4, Curve A) appears to depolarize to a slight extent. Ether apparently does not. Aniline (Fig. 4, Curve B) gives a large de-
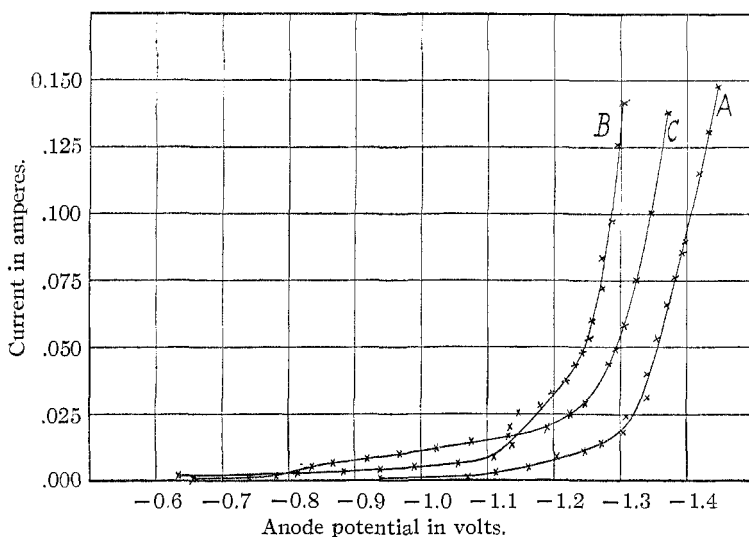
Fig. 3.—Curve A: 1.2 *N* HCl; carbon anode; no depolarizer. Curve B: 1.2 *N* HCl; carbon anode; acetic acid (700 cc. per liter); Curve C: 1.2 *N* HCl; carbon anode; acetic acid (700 cc. per liter); toluene (100 cc. per liter).

polarization and an intercept at 0.83 volt, but this corresponds to oxidation and the formation of aniline black.[11]

In the case of acetone, no depolarization is evident for a 10% solution; but for a 20% solution (Fig. 4, Curve C) and for 50% and 75% solutions, there apparently is depolarization. Acetone can be readily chlorinated in hydrochloric acid solution.[12] In this case also, as for acetic acid, we believe that another effect accounts for the apparent depolarization.

Since toluene was known to be chlorinated at boiling temperatures,[13]

[10] Fichter and Glänzstein, *Ber.*, **49**, 2473 (1917).
[11] *J. Phys. Chem.*, **8**, 539 (1904).
[12] Riche, *Compt. rend.*, **49**, 176 (1859). Richard, *ibid.*, **133**, 878 (1901).
[13] Cohen and others, *J. Chem. Soc.*, **87**, 1034 (1905); **97**, 1623 (1910).

that conditon was tried.   For 6 N hydrochloric acid at a graphite anode at boiling temperature, the intercept was 1.13 volts.   The result for an acetic acid solution of toluene, into which hydrogen chloride had been passed until the concentration was 6 N, was 1.15 volts.   No depolarization is evident.

A few experiments were performed with smooth platinum anodes in hydrochloric acid solutions.   The results do not show depolarization for crotonic acid (which did depolarize at a carbon anode), maleic acid, or 20% acetone.   With 50% acetone, and with 80% acetic acid (Fig. 5), apparently there is some depolarization.   But as stated above, we do not believe these cases represent depolarization of the kind sought.   A solution which
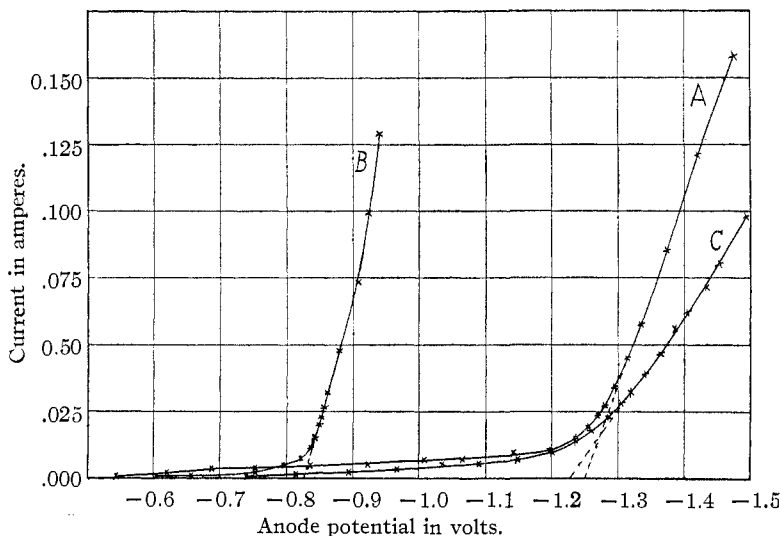

Fig. 4.—Curve A: HCl (1.2 N); carbon anode; crotonic acid (0.5 M).   Curve B: HCl (1.2 N); carbon anode; aniline (0.4 M).   Curve C: HCl (1.2 N); carbon anode; acetone (200 cc. per liter).

is one half or more of acetic acid or acetone must be a far different environment for chloride ions than water is, and it is hardly to be expected that the free energies (and consequently the decomposition potentials) will be the same in the two cases.   In the case of acetic acid, an attempt was made to show this in another way.   Consider the double cell

Pt + H$_2$(1 atm.),HCl(C$_1$ M),AgCl + AgAg + AgCl,HCl(C$_2$ M),Pt + H$_2$(1 atm.) (1)
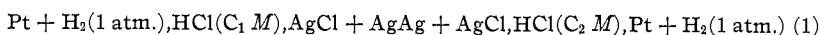
The net effect of passing one faraday through it from left to right is to transfer one mole of hydrogen chloride from the concentration C_2 to the concentration C_1, and the e.m.f. of the cell is a measure of the difference of the free energies of the hydrogen chloride at the two concentrations. In the cell

C + Cl$_2$(1 atm.),HCl(2 N, in H$_2$O),HCl(2 N, in H$_2$O),C + H$_2$(2 atm.)   (2)
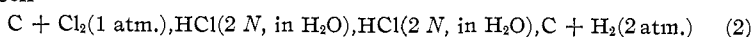
the effect of the passage of one faraday through it from left to right is to decompose 1 mole of hydrogen chloride into $\frac{1}{2}H_2$ and $\frac{1}{2}Cl_2$. Of this approximately 0.8 mole is derived from the anode portion and 0.2 mole from the cathode portion, because of transference. Assuming reversibility, the e.m.f. of the cell is a measure of the free energy of decomposition (or formation) of one mole of hydrogen chloride in 2 N solution in water. In the cell

　　　C + Cl$_2$(1 atm.),HCl(2 N, in 80% HAc),HCl(2 N, in H$_2$O),C + H$_2$(1 atm.)　(3)
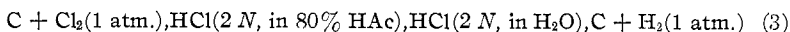
the effect of the passage of one faraday through it from left to right is to decompose one mole of hydrogen chloride into $\frac{1}{2}H_2$ and $\frac{1}{2}Cl_2$. Of this approximately 0.8 mole is derived from the anode portion (in acetic acid),
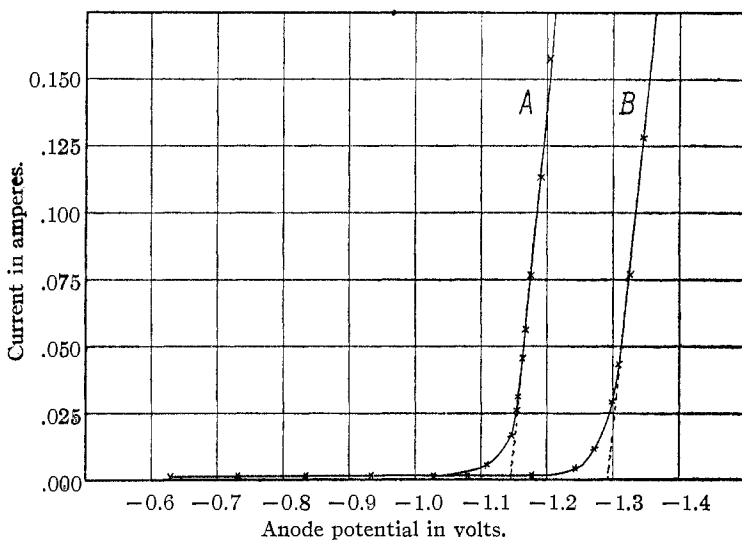

Fig. 5.—Curve A: 2 N HCl, Pt anode; acetic acid (800 cc. per liter). Curve B: 2 N HCl; Pt anode; no depolarizer.

and 0.2 mole from the cathode portion. Assuming reversibility, the e.m.f. of this cell is a measure of the free energy of decomposition (or formation) of 0.8 mole of hydrogen chloride in 2 N solution in 80% acetic acid, plus the free energy of decomposition (or formation) of 0.2 mole of hydrogen chloride in 2 N solution in water. Then the difference of e.m.f. of Cells 2 and 3 above is a measure of the difference of the free energies of decomposition (or formation) of 0.8 mole of hydrogen chloride in 2 N solution in water, and of 0.8 mole of hydrogen chloride in 2 N solution in 80% acetic acid.

The difference in the anode decomposition potentials found (Fig. 5) is about 0.14 volt. Now in Cell 1, if the hydrochloric acid solution in the left cell be replaced by the 80% acetic acid solution of 2 N hydrochloric

acid, and that on the right by 2 N hydrochloric acid in water, then the e.m.f. of the cell would measure the difference of the free energies of decomposition (or formation) of one mole of hydrogen chloride in the two solutions. Then 0.8 of this value should give 0.14 volt, the value derived from the decomposition-potential measurements. The two parts of this double cell were set up separately and their potentials measured. The values were: Pt + H_2(1 atm.), HCl(2 N, in H_2O), AgCl + Ag; $E_1 = 0.176$ volt; Pt + H_2(1 atm.), HCl(2 N, in 80% HAc), AgCl + Ag; $E_2 = -0.044$ volt. Combined as in Cell 1 the e.m.f. of the combination is $E_1 - E_2 = 0.220$ volt. Then $0.8 \times 0.22 = 0.176$ volt, which measures the difference of free energies of 0.8 mole of hydrogen chloride in the two solutions. Considering the numerous assumptions, this value checks the value found, 0.14 volt, nearly enough to make it likely that the latter does not represent depolarization by the acetic acid, due to substitution of hydrogen by chlorine.

Hence, also, the depolarizations suspected in strong acetic acid solutions of toluene, xylene, mesitylene and amylene, and the strong acetone solutions are probably due to the same cause.

The work described above is all that has been done by this method, since apparently the method would not reveal any depolarization effect so pronounced as to be unmistakable evidence of chlorination.

Since many organic compounds may be more or less readily chlorinated electrolytically, however, it is probable that an overvoltage, built up by electrolysis, and consequent chlorine evolution for some time, is necessary. If, then, such an overvoltage is once built up, it might be possible to add a supposed depolarizer and observe an immediate drop in potential due to replacement of chlorine evolution by the chlorination reaction. A small amount of work was done to test out this possibility.

350 Cc. of 2 N hydrochloric acid solution, of which 175 cc. was anolyte, contained in a porous cup, was electrolyzed for several hours with carbon cathode and platinum anode at a current density of 5 amps. per sq. dm. The hydrogen chloride lost was replaced by adding the proper amounts of concd. hydrochloric acid at intervals. The anode potential was measured from time to time. After several hours it rose about 0.4 to 0.7 volt above the initial value. But when the depolarizer (acetone, acetic acid, chloro-acetone, or chloro-acetic acid) was added, the expected large decrease did not take place. Only a slight drop occurred, followed by an immediate rise to the original value. Hence the experiments were discontinued, as there seemed no likelihood of detecting depolarizations by these means.

Van Name and Maryott[14] tried a very similar procedure, namely, adding various substances to an electrode evolving chlorine, but without building up an overvoltage, and noting the effect upon the potential. They found no decrease for benzene, carbon tetrachloride, ether, acetone, chlorobenzene, p-dichlorobenzene, and hexachlorobenzene. Phenol produced a slight lowering.

[14] Van Name and Maryott, *Am. J. Sci.*, **35**, 153 (1913).

In conclusion, the writer wishes to express his thanks and appreciation to Professor Robert E. Wilson for valuable suggestions and advice during the course of this work.

Conclusions

1. The anode decomposition potential method is not suitable as a general test of whether or not organic compounds can be chlorinated.

2. Since there is only slight evidence of chlorination below the potential for reversible chlorine evolution, probably a chlorine overvoltage is necessary for efficient chlorination.

3. It has been shown to be possible to chlorinate acetic acid electrolytically in a solution of hydrochloric acid in 70% acetic acid.

4. The development of an overvoltage on a platinum anode by continued electrolysis, and the subsequent addition of acetone, chloro-acetone, acetic acid, or chloro-acetic acid does not reveal depolarization.

Summary

1. Anode decomposition potential experiments have shown that various organic substances give little or no depolarization of the chlorine electrode in such a way as to chlorinate the substance, although the substances may be chlorinated at higher current densities.

2. Chloro-acetic acid has been produced at a carbon anode in a mixture of acetic acid (70%) and hydrochloric acid (1.2 N). Molecular chlorine does not give chloro-acetic acid under these conditions.

3. The depolarization at a platinum anode in a 2 N hydrochloric acid solution in 80% acetic acid has been shown to be due, not to chlorination, but to the differing free energies of hydrochloric acid in that solution and in water solution.

4. The addition of any one of several organic substances to the solution about a platinum anode, which has been evolving chlorine long enough to build up an overvoltage of about 0.5 volt, does not reduce the anode potential.

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