A PRELIMINARY POLAROGRAPHIC INVESTIGATION

OF

HYDROGEN BONDING -

THE ORTHO- AND PARA- HYDROXY BENZALDEHYDES

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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry.

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Approved by Spencer C Stanford

February 12, 1944

INTRODUCTION

The hydrogen bond is a bond by hydrogen between two atoms. The hydrogen atom must be loosely held, that is, somewhat acidic; the other atom involved must be basic in the Bronsted sense - ex., nitrogen or oxygen. With only one orbital electron (the 1S orbital), the hydrogen atom can form but one covalent bond. Thus, the hydrogen bond must be largely ionic. The bond is not strong, since its energy, i.e., the energy of the reaction $XH + Y \rightarrow XHY$, is only 5 kcal. per mole. Having small bond energy and small activation energy for its formation or rupture, the hydrogen bond should be of considerable help in the study of reaction mechanism at ordinary temperatures!

At present, one of the better known methods for studying hydrogen bonding is through infrared absorption spectra. In the case of the nitro phenols, the characteristic frequency for the OH vibration is shifted to a lower frequency when hydrogen bonding occurs[1,2].

Semerano[3] has made one of the first studies of hydrogen bonding with the dropping mercury electrode. In the United States, a polarographic method, introduced by Astle[2] and McConnell, has shown marked success with the nitro phenols.

They were able to detect the presence of hydrogen bonds in ortho nitro phenol in carefully buffered water solutions. The half-wave reduction potentials for ortho nitro phenol

were considerably more positive than those for para-nitrophenol in acid solution, but had about the same values in basic solutions. The wave-height for the reduction of ortho-nitrophenol in acid solution was about two-thirds the height for ortho- nitrophenol in basic solution or for para-nitrophenol at any pH. This indicated that the intermediate hydroxylamine formed by reduction of ortho-nitrophenol is sufficiently stabilized by a hydrogen bond so that further reduction to the amine is not possible at the dropping mercury cathode.

Further work with the nitrocresols and nitro dihydroxy benzenes have confirmed the general conclusions[4].

Being less costly than an infrared spectrometer, the polarograph will undoubtedly find wide application in the study of those compounds where hydrogen bonds are associated with groups which can be reduced at the dropping mercury electrode.

The presence of hydrogen bonding in ortho hydroxy benzaldehyde should not permit complete reduction to the hydroxy benzyl alcohol[5]. Instead, the ortho hydroxy benzaldehyde should be partially reduced to only the intermediate compound, a hydroxy hydrobenzoin. The hydrogen bond should prevent the further reduction by stabilization of the intermediate compound.

From spatial considerations, the para isomer (para hydroxy benzaldehyde) should not be able to form hydrogen

bonds. Hence, the para isomer should be completely and more easily reduced. These differences in reduction may be determined from the wave-heights and half-wave potentials of the current-voltage curves for these compounds.

EXPERIMENTAL

Materials: The para hydroxy benzaldehyde was Eastman Kodak bisulfite, purified and melted at 115-117°. The ortho hydroxy benzaldehyde was Eastman Kodak, best grade. Difficulty was experienced in making aqueous solutions of the ortho isomer. Small white particles appeared. They were thought to be oxidation products. The ortho hydroxy benzaldehyde was then purified by distillation in an inert nitrogen atmosphere, under reduced pressure. Main fraction boiled at 89°, 20 mm. Hg pressure. After this distillation, no difficulty was experienced in making solutions.

4×10^{-3} molar water solutions of each compound were prepared. Portions of these stock solutions were diluted to desired concentration, with appropriate buffers. McIlvaine's buffer solutions were used. Solutions were made up so that when three parts of buffer were mixed with one part of 0.004 molar solutions of the reducible materials, the resulting solution was of the desired concentration for the given pH; the resulting strength was then 0.001 molar. Buffers were not made up quantitatively, but the pH values of these solutions were determined on a Beckman glass electrode pH meter. The

high salt content of the buffers made the addition of a supporting electrolyte unnecessary. It was found that 6 ml. of a 0.04% solution of bromcresol green and 12 ml. of a 0.01% alcoholic solution of methyl red added to 2.5 liters of buffer made an excellent maximum suppressor. Incidentally, the use of such dyes was found to be the best method of preventing the formation of mold in the buffers.

Mercury used was vacuum distilled.

Electrolysis Cell - Our cell consisted of a standard saturated calomel electrode which dipped into a saturated potassium chloride salt bridge solution. An agar bridge saturated with potassium chloride led to a vessel containing the mercury-dropping cathode and solution to be studied. The obvious advantage of such a cell is that all measurements are made with reference to a standard electrode. The fairly rapid deterioration of the agar bridge is a disadvantage. However, work should be done with more than one junction to avoid difficulties due to diffusion; the resistance of the cell is measured every time a new junction is used.

Since difficulties were encountered in making agar bridges according to laboratory manual instruction, the method we used is described here in detail: Take enough agar to make a 3% solution and soak overnight in 200 to 300 ml. of water. Next day, drain off water and add to the agar 100 to 200 ml. of saturated potassium chloride. Heat to boiling; agar will dissolve. This is important. Most instructions do not

recommend this step. However, we found this to be the only way to get the gel to set. Agar bridges when not in use should be kept in distilled water to prevent their drying out.

Capillary - Much trouble was experienced with the mercury-dropping capillary until a satisfactory method of cleaning and care was worked out. Procedures given in the literature are conflicting. The best method is to keep the capillary immersed in distilled water, with a head of mercury sufficient to keep capillary full but not enough to cause Hg to drop. Never should the capillary be removed from solution without first stopping the flow of mercury.

If the capillary becomes plugged, immerse the capillary end completely in boiling aqua regia for four to five hours. Aqua regia is removed by washing with distilled water and alcohol. Capillary is then dried in oven. Progress in cleaning can be noted by observing the capillary under a microscope. For this method, we are indebted to Professor Hurd.

If a number of capillaries are to be kept, fill them with mercury and cover each end with rubber tips ("policemen"). The rubber tips must be boiled in caustic to remove any free sulfur left from vulcanization, otherwise the capillary will become contaminated with HgS.

Thermostat - Temperature was maintained at $25 \pm 0.2°$, with a water bath, bimetallic regulator, and an electric heater. At first a small stirrer was used, but vibrations

from its motor were thought to interfere with the drop rate. However, it is suggested that a small vibrationless stirrer be used to maintain a more constant temperature.

Cell Resistance - References in the literature to measurements of cell resistance are scarce. The only articles we know are those of D. Ilkovic[6] and O. Muller[7].

Whether Ilkovic meant to make a static measurement or not is hard to determine. The fact that he used a resistance in shunt with the electrolysis cell would seem to indicate that he was making a measurement with a D.C. voltage applied to the cell. The shunt would effectively keep the D.C. component off the bridge. But the A.C. bridge would then measure the A.C. resistance of the battery, not the resistance of the cell. For, since battery and electrolysis cell are in parallel, and since the cell's resistance is at least thirty times that of the battery, the cell would appear as an open circuit to the measuring bridge. This was pointed out to us by Mr. H.C. Yovits, of the Physics Department.

Such a measurement, superficially at least, would appear correct, since we usually like to know the characteristics of an instrument under operating conditions. However, to make such a measurement and not get the battery resistance is very difficult.

Hence, we then proceeded to make a static measurement of the cell resistance with the conductance bridge. Here the bridge posts are simply connected directly to the terminals

no voltage is applied, and a balance is obtained. Cell resistance so determined was 2900 ohms, which is a reasonable value for the cell of our design.

Knowing R, the resistance of the circuit; V, the applied voltage; I, the corresponding current; Er, the potential of the non-polarizing reference electrode which is in series with the small polarizable electrode; the potential E, of the polarized small electrode, is obtained from

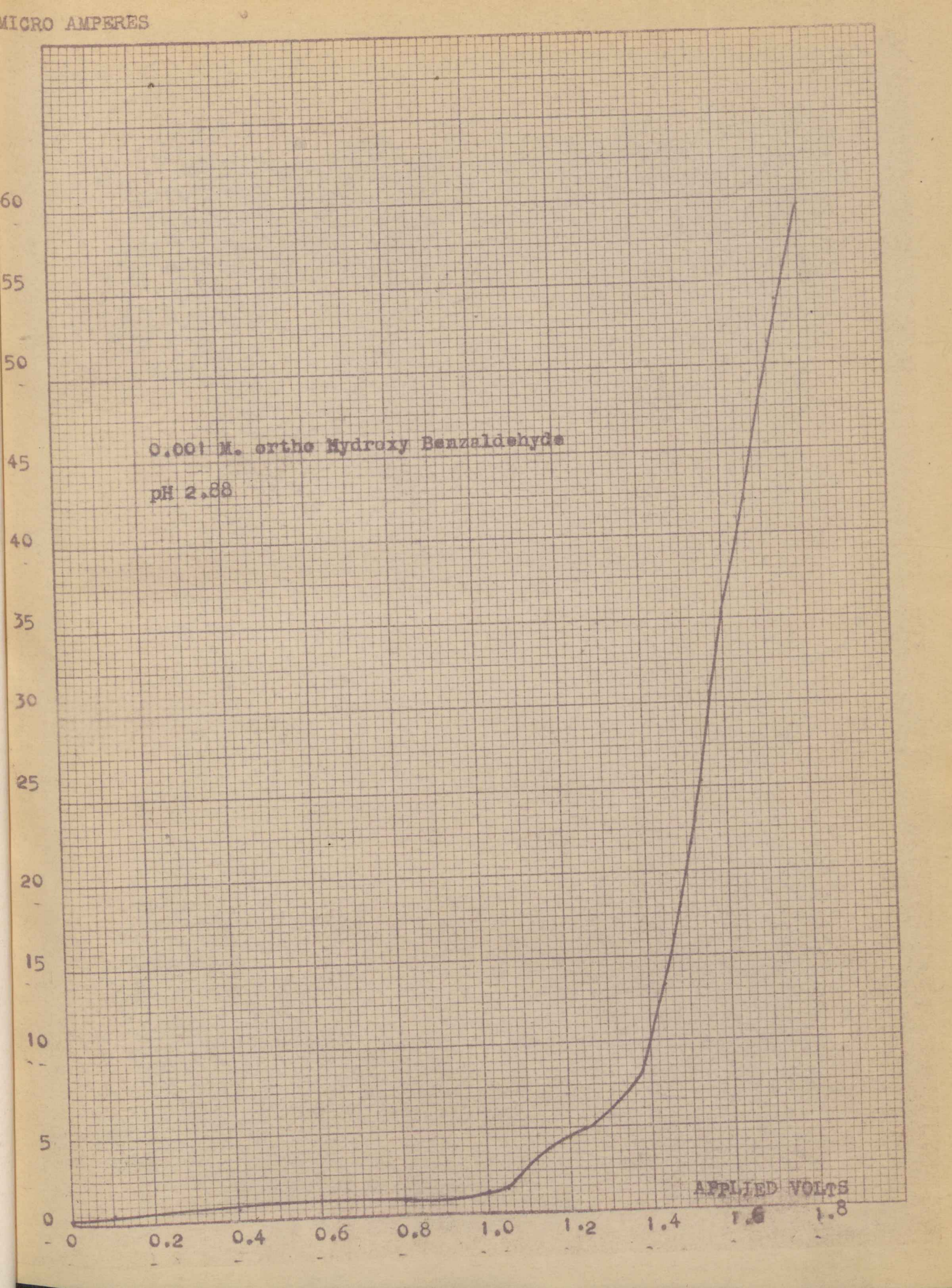
$$E = Er + V - IR.$$

Whether Müller's[7] method is equivalent to the above method should make an interesting experiment.

Instrument - The instrument was a Fisher "Elecdropode", manually operated. Capillaries having a dropping rate of about 3.8 seconds at a mercury height of 69 cm. were used. The $m^{2/3}t^{1/16}$ value for the capillary was 2.84 mg.$^{2/3}$ sec.$^{-1/2}$, as determined by a method of Kolthoff[8].

Galvonometer sensitivity was 1.90×10^{-2} micro amperes per scale division as determined by a method of Kolthoff[9].

In order to remove oxygen from the solutions, commercial tank nitrogen was passed through the electrolysis cell. Nitrogen was found to be satisfactory without a Jones reductor. Nitrogen was first passed through a sample of the cell solution so that the gas would not remove the compound to be reduced from the solution by a process analogous to steam distillation.


MICRO AMPERES
60
55
50
45
40
35
30
25
20
15
10
5
0
0.001 M. ortho Hydroxy Benzaldehyde
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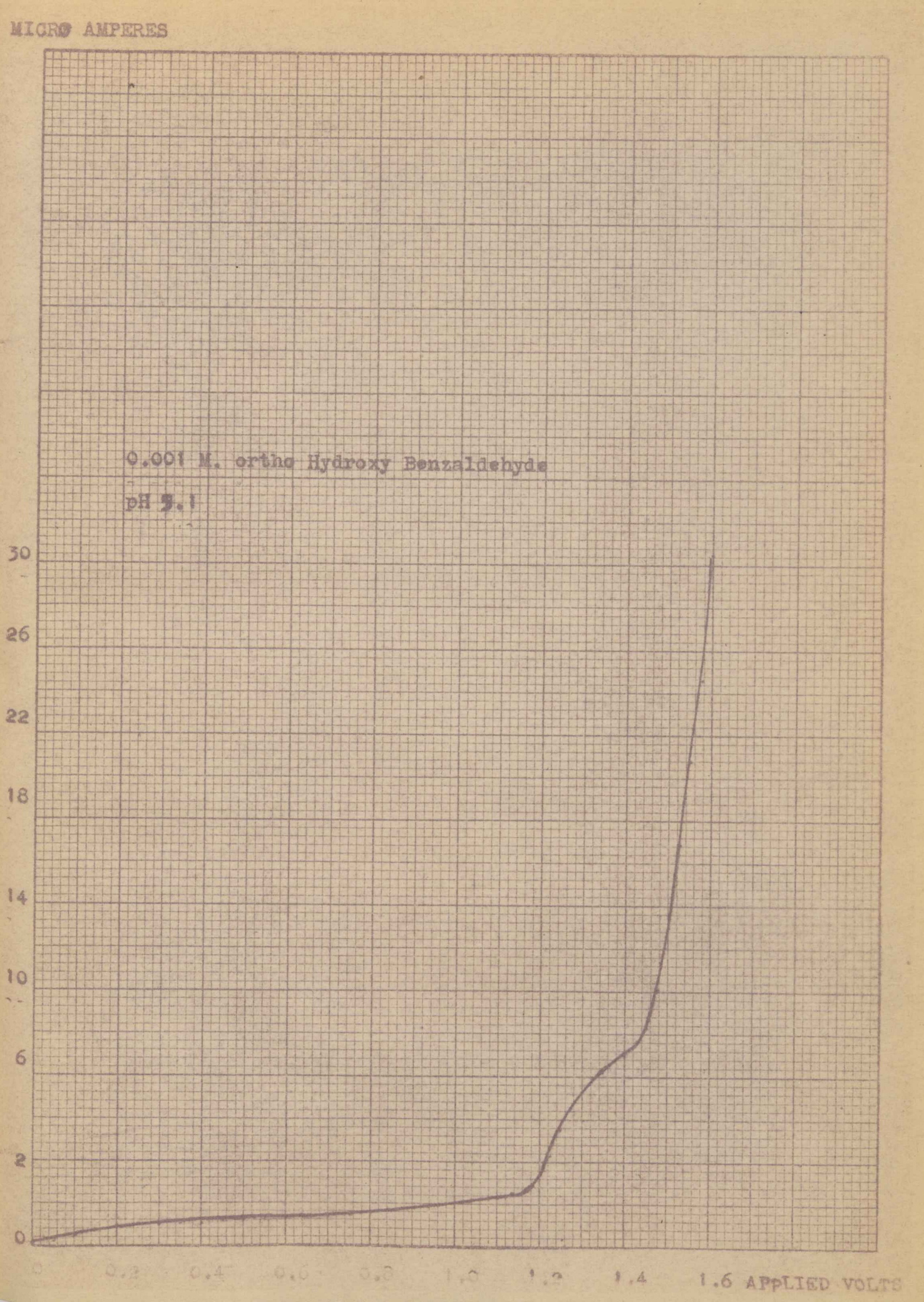
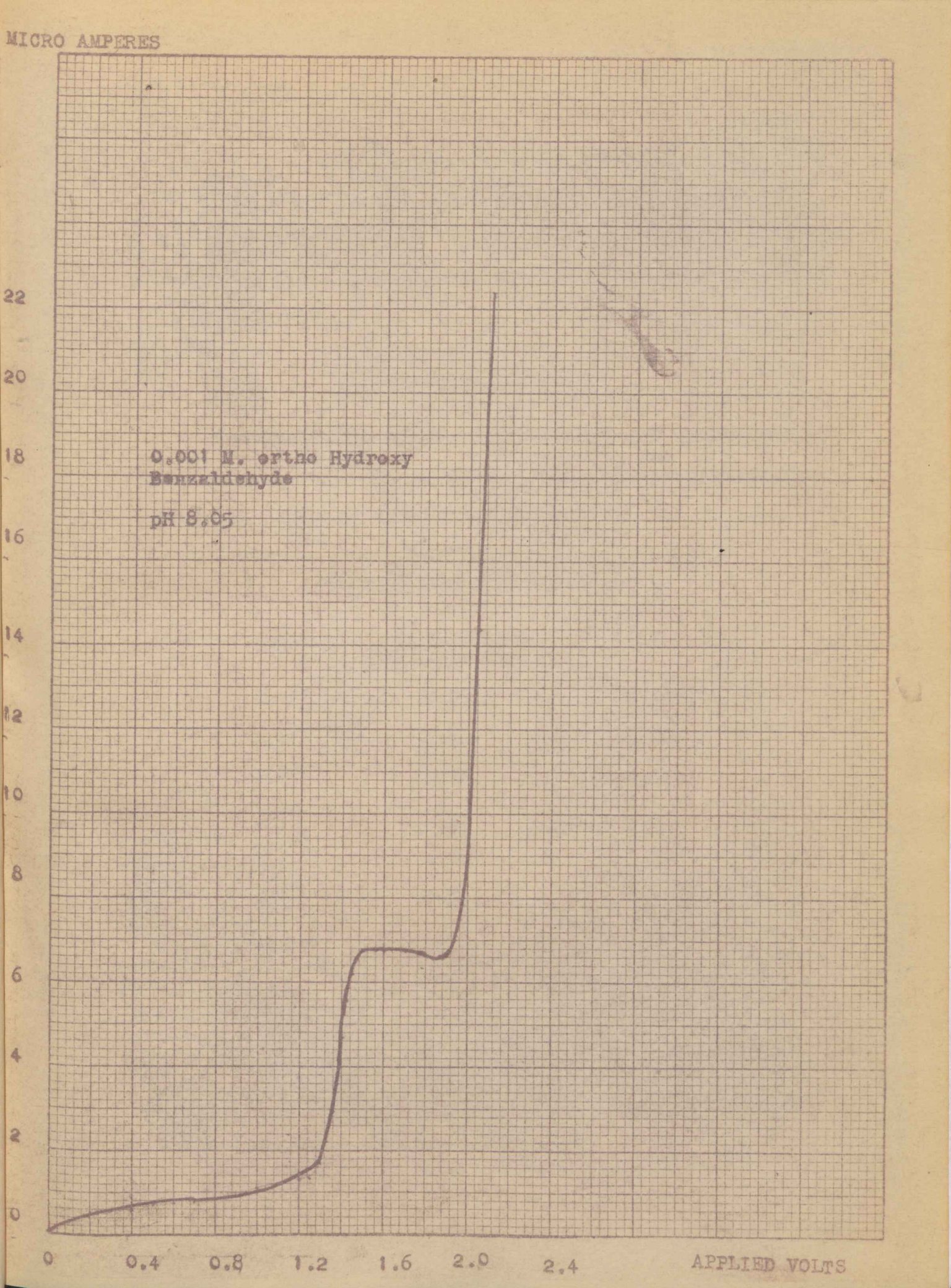
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.8
APPLIED VOLTS


MICRO AMPERES
0.001 M. ortho Hydroxy Benzaldehyde
pH 9.1
30
26
22
18
14
10
6
2
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6 APPLIED VOLTS


MICRO AMPERES
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20
18
16
14
12
10
8
6
4
2
0
0.001 M. ortho Hydroxy
Benzaldehyde
pH 8.05
0
0.4
0.8
1.2
1.6
2.0
2.4
APPLIED VOLTS

At one time it was found difficult to obtain a consistent drop rate. It was suggested that the mercury reservoir might be "creeping" down the rod which supported it. A clamp was placed under the reservoir. This very effectively prevented the "creep", and consistent drop rates were then obtained.

DISCUSSION OF RESULTS

Polarographic waves were obtained for ortho-hydroxy benzaldehyde from a pH of 2.4 to 8.1. The current-voltage curves consisted of single waves.

Ortho-Hydroxy Benzaldehyde

pH	Wave Height (in micro amps.)	n
2.4[a]	2.80	0.54
5.1[a]	5.22	1.02
8.0[a]	6.45	1.26
2.9[b]	2.45	0.48
5.8[b]	5.30	1.03
8.1[b]	5.50	1.07

a - cell resistance 10,000 ohms (probably air bubbles in junction).
b - cell resistance 2900 ohms.

Values of wave heights are low, probably due to extrapolation of residual current. Instead, a "blank" for each pH

should be run, and this value of the residual current subtracted from the height of the wave plateau. See Müller[10] and Kolthoff[11].

As can be seen, the wave height for the reduction of the o-hydroxy benzaldehyde in very acid medium is only about one-half its value in alkaline medium. In alkaline medium where hydrogen bonding becomes impossible for the ortho compound, its reduction should go to the hydroxy benzyl alcohol.[6] However, in strongly acid solutions, hydrogen bonding is present and interferes with complete reduction.

The number of electrons involved in the reduction may be calculated by means of the Ilkovic equation:

$$I_d = 605nD^{1/2}CM^{2/3}t^{1/6} \quad \text{or}$$

$$n = \frac{Id}{605D^{1/2}CM^{2/3}t^{1/6}}$$

where

Id = average current in microamperes during life of a drop,

n = number of electrons required per mole of the electrode reaction,

D = diffusion coefficient of the reducible or oxidizable substance in the units $cm.^2 sec.^{-1}$,

C = its concentration in millimoles per liter,

m = rate of flow of mercury from the dropping electrode capillary expressed in the units $mg. sec.^{-1}$,

t = drop time in seconds.

The difficulty here is obtaining the value for the diffusion coefficient D. It may be calculated by assuming that the molecule is about the same size as the benzoate ion and thus should diffuse at the same rate. The diffusion coefficient for the benzoate ion is determined from its equivalent conductance at infinite dilution[12]. Making the calculation for the diffusion coefficient of ortho-hydroxy benzaldehyde on this basis gives a value of 8.86×10^{-6} cm.^{2} sec.$^{-1}$ at 25°. Substituting into the Ilkovic equation and solving for the number of electrons gives the "n" values tabulated.

The half-wave potential, the voltage point where the curve inflects before going into a wave plateau, is also significant. It will be noted from the graphs that the more acid the solution, the lower the half-wave potential. In other words, reduction in acid solution, since less voltage is required, is easier than reduction in basic solution. The hydrogen bond makes the oxygen of the CHO group of ortho-hydroxy benzaldehyde less negative. Being more positive, the oxygen attracts electrons more readily and hence is more easily reduced.

Thus, in acid solution, reduction is made easier by the presence of hydrogen bonding (as determined from the half-wave potentials); although complete reduction is prevented by hydrogen bonding (as determined from the wave-heights).

These views, however, are not conclusive, since reduction to hydroxy benzyl alcohol involves two electrons, while reduction to the intermediate reaction product involves one electron. Moreover, we were unable to obtain polarographic waves with the para isomer. Thus, we did not have a "control". We had hoped to show that the wave height of the para compound remained constant with any pH, and hence the para compound showed no hydrogen bonding.

It is believed that the reason we did not obtain characteristic current-voltage curves was that the para isomer, not having protective hydrogen bonding, had been oxidized. Hence, the para isomer could not be reduced at the dropping mercury electrode. In future polarographic work with para-hydroxy benzaldehyde, we recommend that the compound, after being prepared or purified, be kept in a sealed glass tube filled with nitrogen until ready for use. Then solutions should be prepared and the polarogram made within the hour.

SUMMARY

The polarographic method should be able to determine the presence of hydrogen bonds in ortho-hydroxy benzaldehyde in carefully buffered water solutions. The wave-height for the reduction of ortho-hydroxy benzaldehyde in acid solution is about one-half the height in basic solution. This would seem to indicate that the intermediate reduction product is formed by the reduction of ortho-hydroxy benzaldehyde in acid medium. This intermediate is stabilized by the presence of a

hydrogen bond, so that further reduction to the hydroxy benzyl alcohol is not possible at the dropping mercury electrode.

Moreover, since the more acid the solution the smaller the voltage required for reduction, hydrogen bonding in ortho-hydroxy benzaldehyde makes reduction easier to take place.

In alkaline solutions, ortho-hydroxy benzaldehyde, when reduced, proceeds to hydroxy benzyl alcohol, as determined from wave-height considerations.

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