

compounds of class III cannot form a quinoid structure, it seems probable that complete reduction to the amine cannot occur in alkaline solu-

tions except through the quinoid form of the nitrocresols.

LEXINGTON, KENTUCKY

RECEIVED JULY 17, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

Polarographic Investigation of Hydrogen Bonding. III. Nitrodihydroxybenzenes¹

BY MELVIN J. ASTLE AND STANLY P. STEPHENSON²

In the first paper of this series³ it was shown that the polarographic method is very useful in studying hydrogen bonding in *o*- and *p*-nitrophenols. The presence of the hydrogen bond in *o*-nitrophenol was indicated by lower wave heights and decreased half-wave potentials as compared to those obtained with *p*-nitrophenol. The same general situation was also found to exist in the nitrocresols.⁴ It was the purpose of this investigation to study the effect on a hydrogen bond between an OH group and a nitro group ortho to it when a second OH group is present on the benzene ring.

Five nitrodihydroxybenzenes were studied: namely, 2-nitroresorcinol, 4-nitroresorcinol, 3-nitrocatechol, 4-nitrocatechol and 2-nitrohydroquinone.

Discussion of Results

Current-voltage curves for the reduction of 2-nitroresorcinol from carefully buffered solutions consisted of single waves over the pH range of 2.1 to 11.3 (Fig. 1). The wave heights were practically constant over the entire pH range studied and averaged 10.2 microamperes (Table I).

TABLE I

THE EFFECT OF pH ON THE WAVE HEIGHTS OF THE NITRODIHYDROXYBENZENES

$$m^{2/3}/s^{1/6} = 0.94 \text{ mg.}^{2/3} \text{ sec.}^{-1/6}$$

Concentration of solutions 0.001 molar

pH	Wave heights in microamperes				
	2-Nitrohydroquinone	3-Nitrocatechol	4-Nitrocatechol	2-Nitroresorcinol	4-Nitroresorcinol
2.1	9.23	10.36	10.13	10.36	10.75
3.6	9.48	10.13	10.36	10.13	10.58
5.2	9.69	9.90	9.90	10.35	10.58
6.4	9.69	9.90	10.13	10.36	10.78
8.0	9.69	10.13	10.36	10.36	10.58
9.0	9.69	9.90	10.40	10.36	10.36
9.5	9.69	9.90	10.36	9.90	10.36
10.1	9.69	9.90	10.36	10.24	10.36
11.3	9.69	9.60	9.90	9.69	10.36

These wave heights correspond closely to those obtained with *p*-nitrophenol so that the reduction

(1) From the M. S. thesis of Stanly P. Stephenson. Presented before the Organic Chemistry division of the American Chemical Society, Pittsburgh meeting, Sept. 6-10, 1943.

(2) Present address: Standard Oil Co. of Indiana, Whiting, Indiana.

(3) Melvin J. Astle and W. V. McConnell, *THIS JOURNAL*, **65**, 35 (1943).

(4) Melvin J. Astle and W. P. Cropper, *ibid.*, **65**, 2895 (1943).

process should involve six electrons resulting in complete reduction to the amine. The number of electrons involved in the process was calculated with the aid of the Ilkovič equation assuming the nitroresorcinol would have about the same diffusion coefficient as *benzoic acid*, a molecule which is about the same size. The diffusion coefficient of benzoic acid can then be calculated from its equivalent conductance.⁵ This calculation was made and indicated that 5.9 electrons are involved in the reduction of 2-nitroresorcinol.

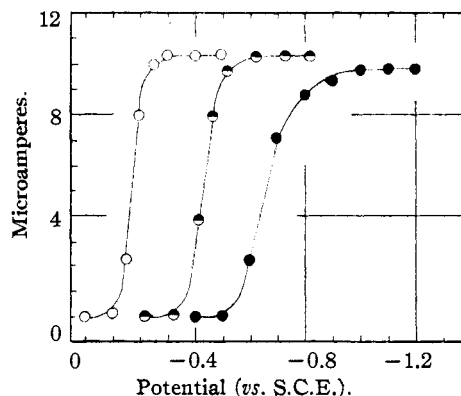


Fig. 1.—Current-voltage curves for 2-nitroresorcinol (0.001 *M*): O, pH 2.1; ◐, pH 8.0; ●, pH 10.1; $m^{2/3}/s^{1/6} = 0.94 \text{ mg.}^{2/3} \text{ sec.}^{-1/6}$.

The half-wave reduction potentials for 2-nitroresorcinol become more negative with increasing pH (Table II).

This relationship is linear from a pH of 2.1 to 8, but at pH values greater than 8 the effect of pH on the reduction increases more rapidly.

The current-voltage curves for the other compounds studied were very similar to those obtained for the reduction of 2-nitroresorcinol except that the curves for the reduction of 4-nitrocatechol in basic solution broke up into two waves (Fig. 2). The wave heights were essentially the same indicating that there was complete reduction of the nitro group to the amine in every case over the entire pH range studied (Table I).

The fact that the current-voltage curves for 4-nitrocatechol broke up into two waves in basic solution indicates that the reduction proceeds in

(5) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers Inc., New York, N. Y., 1941, p. 48.

TABLE II
THE EFFECT OF pH ON THE REDUCTION POTENTIALS OF THE
NITRODIHYDROXYBENZENES

pH	Half-wave potential (S.C.E.)				
	2-Nitrohydroquinone	3-Nitrocatechol	4-Nitrocatechol	2-Nitroresorcinol	4-Nitroresorcinol
2.1	-0.20	-0.16	-0.34	-0.17	-0.26
3.6	.25	-.24	-.45	-.25	-.36
5.2	-.32	-.33	-.52	-.32	-.47
6.4	-.38	-.37	-.57	-.36	-.54
8.0	-.42	-.49	-.65	-.44	-.68
9.0	-.51	-.74	-.82 ^a	-.49	-.80
9.5	-.55	-.72	-1.32 ^a	-.57	-.85
10.1	-.63	-.73	-1.32 ^a	-.66	-.97
11.3	-.78	-.73	-0.93 ^a	-.93	-1.27
			-1.37 ^a		

^a Two waves.

two steps. The first wave is just one-third of the total wave height corresponding to the reduction of the 4-nitrocatechol to the nitroso compound while the second wave corresponds to the reduction of the nitroso compound to the amine. This is the first observed case in which the reduction of the nitroso compound requires a higher potential than the reduction of the corresponding nitro compound.

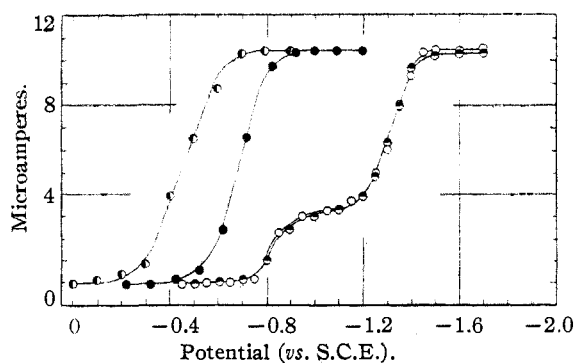


Fig. 2.—Current-voltage curves for 4-nitrocatechol (0.001 M): \odot , pH 3.6; \bullet , pH 8.0; \circ , pH 9.0; \ominus , pH 10.1; $m^{2/3}t^{1/6} = 0.94 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$.

The half-wave reduction potentials of these compounds showed some significant similarities and some significant differences (Table II). Between a pH of 2.1 and 8.0 the half-wave reduction potentials for 2-nitroresorcinol, 3-nitrocatechol and 2-nitrohydroquinone were essentially the same (Fig. 3). Over the same pH range 4-nitrocatechol had half-wave reduction potentials which were consistently higher than those for the above three compounds, while those for 4-nitroresorcinol were intermediate between these extremes and showed greater increase with increasing pH than was the case with any of the other compounds (Fig. 3).

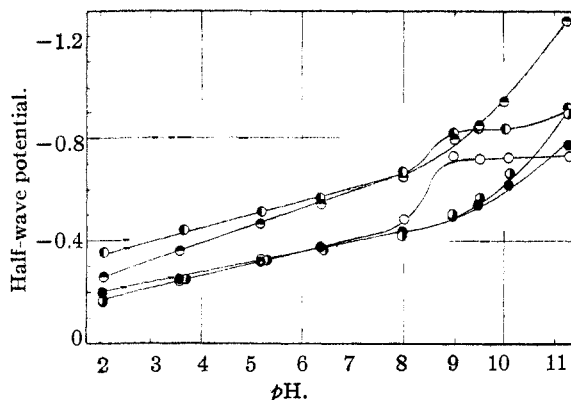


Fig. 3.—The effect of pH on the half-wave reduction potential: \odot , 4-nitrocatechol, \ominus , 4-nitroresorcinol; \circ , 3-nitrocatechol; \bullet , 2-nitroresorcinol; \bullet , 2-nitrohydroquinone; $m^{2/3}t^{1/6} = 0.94 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$.

At pH values greater than 8 the relationship between pH and half-wave potential is no longer linear. The reduction potentials for both nitroresorcinols increase much more rapidly with increasing pH but the curves remain parallel with 4-nitroresorcinol being more difficultly reducible.

Beginning at a pH of 8 the reduction potentials for both nitrocatechols increase very abruptly but at a pH of 9 there is a complete leveling off of the curve and between a pH of 9 and 11 the reduction potentials no longer increase with increasing pH (Fig. 3). The curves for both nitrocatechols are similar but have different characteristics from the curves for the nitroresorcinols.

The curve for 2-nitrohydroquinone differs from both the nitroresorcinol and nitrocatechol curves in basic solutions but more closely resembles those obtained with the nitroresorcinols.

Of the compounds studied, only 4-nitrocatechol is incapable, for steric reasons, of forming intramolecular hydrogen bonds and the fact that a higher potential is required to reduce it seems significant. Of the other compounds studied, 2-nitroresorcinol, 3-nitrocatechol, and 2-nitrohydroquinone show almost identical reduction potentials over the pH range for 2.1 to 8. This behavior would suggest that the nitro group in 4-nitrocatechol is different for some reason, from the nitro group in the other three compounds.

The presence of an intramolecular hydrogen bond in 2-nitroresorcinol, 3-nitrocatechol, and 2-nitrohydroquinone may be used to explain the greater ease of reduction of these compounds. It has been shown by Astle and McConnell⁶ that a similar situation exists in the case of the nitrophenols. *o*-Nitrophenol, which contains intramolecular hydrogen bonds, is reduced at a lower potential than is *p*-nitrophenol, which contains no such hydrogen bonds.

This lowering of the reduction potential in compounds which form intramolecular hydrogen

(6) Melvin J. Astle and W. V. McConnell, *THIS JOURNAL*, **65**, 35 (1943).

bonds involving a nitro group can be attributed to interference with the normal resonance of the nitro group. Formation of a hydrogen bond involving only one of the oxygen atoms of the nitro group would cause these oxygen atoms to be no longer equivalent as they are in the normal resonance structure. Therefore, the oxygen atom not involved in the formation of the hydrogen bond would be more easily reduced.

In 2-nitroresorcinol there is the possibility that both oxygen atoms of the nitro group could be involved in the formation of intramolecular hydrogen bonds. It seems significant, however, that the curve for the half-wave potential plotted against the pH of the solution for 2-nitroresorcinol agrees with similar curves for 3-nitrocatechol and 2-nitrohydroquinone (Fig. 3). This agreement indicates the presence of the same type of nitro group in all three cases and since only one hydrogen bond is possible in 3-nitrocatechol and 2-nitrohydroquinone it would appear that water solutions of 2-nitroresorcinol contain only a single intramolecular hydrogen bond, even though two are sterically possible. If both of the oxygen atoms on the nitro group of 2-nitroresorcinol are hydrogen bonded with the hydroxyl groups ortho to them, there should be no groups available for forming hydrogen bonds with the solvent. This situation should make 2-nitroresorcinol as volatile in steam or in a stream of gas as is *o*-nitrophenol. This, however, is not the case. Extended degassing of solutions of *o*-nitrophenol resulted in an appreciable decrease in the wave heights of the current-voltage curves resulting from the loss of *o*-nitrophenol from solution through volatilization.⁷ Natural gas was bubbled through a solution of 2-nitroresorcinol at a pH of 2.1 for four hours without appreciably decreasing the wave height of the current-voltage curve, indicating that there was no appreciable loss of 2-nitroresorcinol through volatilization. This behavior would seem to substantiate the idea that there are not two intramolecular hydrogen bonds present in the 2-nitroresorcinol molecule.

The curve of pH against half-wave potential for 4-nitroresorcinol is of interest. The half-wave potentials for this compound lie intermediate between those of 4-nitrocatechol and the other compounds studied from a pH of 2.1 to 6, and the slope of the curve in this region is steeper than those for the other compounds (Fig. 3). From a pH of about 6 to 8 the curves for 4-nitroresorcinol and 4-nitrocatechol agree reasonably well. Reduction potentials are very sensitive to slight differences in structure and it has already been shown that the formation of a hydrogen bond between an OH group and a nitro group ortho to it results in the lowering of the half-wave potential for the reduction of the normal nitro group. Since the reduction potentials for 4-nitrocatechol and 4-nitroresorcinol are in substantial agreement over the

pH range of 6 to 8 it seems logical to assume that the nitro groups are the same in both compounds. For steric reasons 4-nitrocatechol cannot form an intramolecular hydrogen bond. Therefore, between a pH of 6 and 8 there should be no hydrogen bond in 4-nitroresorcinol. At pH values less than 6, molecules of 4-nitroresorcinol appear to possess weak, intramolecular hydrogen bonds. This follows from the observation that although the reduction potentials in the region are less negative than those for 4-nitrocatechol, they are still more negative than those for 2-nitroresorcinol, 2-nitrohydroquinone and 3-nitrocatechol. These intermediate reduction potentials can be explained if we assume that the hydrogen bond has sufficient effect on the normal resonance of the nitro group to render easier its reduction. The fact that the half-wave potentials are not as low as those of the three compounds in which we have postulated the presence of hydrogen bonds is indicative that the nitro group is not as completely affected, and that the hydrogen bond is weaker. Also it should be noted that the slope of the curve indicates a much greater effect of pH on the strength of the hydrogen bond than is the case in the other bonded compounds.

All the hydrogen bonded compounds studied in this paper possess weaker bonds than are found in *o*-nitrophenol. The hydrogen bond is sufficiently strong in *o*-nitrophenol to prevent the reduction of the intermediate hydroxylamine compound formed, while in all compounds studied in this investigation, reduction is complete to the amine.

The data reported here have indicated that the introduction of a second hydroxyl group onto the benzene ring, particularly in the meta position, decreases the strength of any possible intramolecular hydrogen bond in the molecule.

Since the hydrogen bond is ionic in character, it is suggested that the hydroxyl group bonded to the nitro group in the dihydroxybenzenes is less ionic than is the hydroxyl group in the nitrophenols. It follows, then, that almost all the ionization of these compounds involves the hydroxyl group which is not bonded to the nitro group. This effect is particularly noticeable when the hydroxyl groups are meta to each other as in the nitroresorcinols.

In basic solutions, since ionization of the hydroxyl groups should be almost complete, there can be no hydrogen bonding. It would appear that the positions of the hydroxyl groups with respect to each other exert a marked effect on the ease of reduction of the nitro group (Fig. 3). This statement seems evident from the similar characteristics of the two curves for the nitro resorcinols and the two curves for the nitrocatechols. The same arrangement of the hydroxyl groups results in curves of the same shape regardless of the position of the nitro group.

(7) Melvin J. Astle and W. V. McConnell, *THIS JOURNAL*, **65**, 35 (1943).

Experimental

Preparation and Purification of Materials.—The method of Kauffman and Kugel⁸ was used to prepare 4-nitroresorcinol. Sodium carbonate (21.2 g.) was added to 11 g. of resorcinol dissolved in 310 ml. of water; 15.4 g. of benzoyl chloride was added and the mixture stirred vigorously. The monobenzoate was obtained as small, hard pellets. After recrystallization from benzene the monobenzoate was dissolved in acetic acid and nitrated with one part of nitric acid (d. 1.2). The nitromonobenzoate was hydrolyzed in 10% sodium hydroxide to obtain 4-nitroresorcinol, which after several recrystallizations from carbon tetrachloride melted at 120–121°.

The preparation of 3- and 4-nitrocatechol was carried out according to the method of Weselsky and Benedikt as modified by Foglesong and Newell.⁹ A solution of 10 g. of catechol in 500 ml. of ether was treated with 4 ml. of fuming nitric acid, and the resulting solution was allowed to stand for twenty-four hours. This solution was then shaken with three successive 300-ml. portions of water, after which the ether layer was evaporated to dryness. The dry residue was then extracted with petroleum ether which removed the 3-nitrocatechol. The 3-nitrocatechol was obtained after recrystallization from petroleum ether as yellow needles melting at 86°.

The residue from the petroleum ether extraction was steam distilled to remove the last traces of 3-nitrocatechol, after which the residue in the flask was evaporated to dryness and the 4-nitrocatechol obtained by extraction with boiling xylene. After boiling off the xylene and three recrystallizations from water, the 4-nitrocatechol was obtained as sulfur yellow needles melting at 174°. The yield of nitrocatechols is about 80% of the theoretical, about 8% being 3-nitrocatechol.

The 2-nitrohydroquinone was prepared by the method of Elbs.¹⁰ Fifty grams of potassium persulfate and 50 g. of sodium hydroxide were added to a solution of 35 g. of *o*-nitrophenol in two liters of water. The mixture was allowed to stand for two days; it was then acidified with sulfuric acid. The unchanged *o*-nitrophenol was removed by steam distillation, and the residue extracted with ether. The ether was evaporated and the product recrystallized several times from water. The product melted at 132–133° and the yield was about 30%.

The 2-nitroresorcinol was Eastman Kodak Co. best grade and had a melting point of 85°.

Stock solutions of each of the dihydroxybenzenes (0.002 *M*) in water were prepared. To obtain the current-voltage curves the solutions were diluted to the proper concentration with specially prepared buffers, placed in an electrolysis cell, and allowed to reach thermal equilibrium (25°) in a constant temperature bath before the curves were obtained.

For *pH* values in the acid range McIlvaine's standard buffer solutions were prepared and alkaline buffers were made from sodium borate-sodium hydroxide mixtures.¹¹

(8) H. Kauffman and W. Kugel, *Ber.*, **44**, 753 (1911).

(9) J. E. Foglesong and I. L. Newell, *This Journal*, **52**, 386 (1930).

(10) K. Elbs, *J. prakt. Chem.*, **48**, 179 (1893).

(11) W. M. Clark, "The Determination of Hydrogen Ions," 2d ed., The Williams & Wilkins Co., Baltimore, Md., 1927, pp. 112–116.

The following modifications were used: buffers were made up at twice the stated concentration and were made 0.2 *M* with potassium chloride. Equal quantities of each buffer and the desired nitro compound were mixed, giving buffered solutions 0.001 *M* with respect to the nitro compound and 0.1 *M* with respect to potassium chloride. The *pH* values of these solutions were checked with a Leeds and Northrup *pH* meter.

Apparatus.—In an electrolysis cell kept at a constant temperature of 25±0.1° was placed the 0.001 molar nitro-dihydroxybenzene in carefully buffered solution. Current-voltage curves were obtained with these solutions over the *pH* range of 2.1 to 11.3 with the aid of a Fisher "Electropode." This instrument was manually operated and used a capillary which had a dropping rate of between 3 and 4 seconds per drop. The calibration of the capillary gave $m^{1/2}/t^{1/2} = 0.94 \text{ mg.}^{1/2} \text{ sec.}^{-1/2}$.

In order to remove oxygen from solution, degassing was accomplished by passing natural gas through the electrolysis cell. The natural gas was first bubbled through lead acetate solution, then through a Jones reductor and finally through a sample of the cell solution before entering the cell itself.

Summary

The reduction of five nitro-dihydroxybenzenes in carefully buffered solutions at a dropping mercury cathode has been studied and current-voltage curves obtained. These curves show that when intramolecular hydrogen bonds are sterically possible, as in the case of 3-nitrocatechol, 2-nitrohydroquinone and 2-nitroresorcinol, the nitro groups are more easily reduced than the nitro group in 4-nitrocatechol where no such bond is possible.

Even though 2-nitroresorcinol is sterically capable of having both nitro oxygens tied up in hydrogen bonding with the ortho OH groups, the evidence would indicate that only one such bond is present.

Between a *pH* of 5.5 and 8.5 the same type of nitro group seems to be present in both 4-nitroresorcinol and 4-nitrocatechol and therefore no hydrogen bonding seems probable in the case of 4-nitroresorcinol in this *pH* range. A weak hydrogen bond seems probable in 4-nitroresorcinol at lower *pH* values.

The presence of a second OH group on the benzene ring weakens the hydrogen bond between the nitro group and the OH group in the *ortho* position to it.

The ease of reduction of the nitro groups in basic solution seems to be a function of the arrangement of the two OH groups with respect to each other.