(m. p. 139–140°) was shown to be identical with an authentic sample.

β-6-Tetralylpropionic Acid and Methyl Ester.—A mixture of 6-propionyltetralin (20 g.), dioxane (80 ml.), sulfur (10 g.), and concentrated ammonia solution saturated with hydrogen sulfide (100 ml.) was heated in a closed steel tube at 165° for twenty-four hours. The solvents were removed by evaporation on the steam-bath and the residue was hydrolyzed by heating with potassium hydroxide solution (150 ml., 25%) until the odor of ammonia was no longer apparent. The alkaline solution was treated with Norite, filtered and acidified. The crude acid was esterified by refluxing for four hours with methanol (200 ml.), and sulfuric acid (3 ml.). The reaction mixture was poured into water (800 ml.) and extracted with ether; the ether extract was washed with sodium bicarbonate solution, and water, and the ether was removed by distillation. Distillation of the residue gave 15.5 g. (71.5%) of the methyl ester, which boiled at 165–168° (12 mm.). The aforementioned crude acid after recrystallization melted at 81.5–82.5°.[5]

β-2-Naphthylpropionic Acid.—Sulfur (1 g.) and methyl β-6-tetralylpropionate (3.1 g.) were heated for two hours at 235–250°. The crude reaction mixture was saponified by refluxing for two hours with potassium hydroxide (5 g.) dissolved in methanol (25 ml.) and water (50 ml.). The solution was acidified (congo red) with hydrochloric acid. Recrystallization of the crude acid from benzene and petroleum ether (b. p. 60–68°) gave a product which melted at 134–135°.[9]

Summary

1. A study of the chloromethylation of tetralin has been made and it has been demonstrated that at least 30 per cent. of 5-chloromethyltetralin is present in the product.

2. A convenient synthesis of β-5-tetralylpropionic acid is described.

MINNEAPOLIS, MINNESOTA RECEIVED SEPTEMBER 7, 1943

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF KENTUCKY]

Polarographic Investigation of Hydrogen Bonding II. Some Nitrocresols[1]

BY MELVIN J. ASTLE AND WENDELL P. CROPPER[2]

In the first paper in this series[3] the polarographic technique was used to study hydrogen bonding in *o*- and *p*-nitrophenols. It was found that *o*-nitrophenol which contains an intramolecular hydrogen bond was only reduced to the hydroxylamine while the *p*-nitrophenol was reduced completely to the amine. The presence of the hydrogen bond in *o*-nitrophenol caused the nitro group to be more easily reduced than the nitro group in *p*-nitrophenol where no such bond is possible.

It was the purpose of this investigation to study the reduction of several nitrocresols at the dropping mercury cathode in order to determine the effect on the reduction of a nitro group of an OH group in positions which are ortho, meta and para to it when a methyl group is also present on the benzene ring.

Discussion of Results.—For convenience the nitro cresols investigated will be divided into three classes. Class I will consist of those compounds in which the OH group is para to the nitro group and includes 5-nitro-*o*-cresol and 6-nitro-*m*-cresol. Class II consists of those compounds in which the OH group is ortho to the nitro group and includes 3-nitro-*p*-cresol, 3-nitro-*o*-cresol and 4-nitro-*m*-cresol. Class III consists of those compounds in which the OH group is meta to the nitro group and includes 2-nitro-*p*-cresol and 4-nitro-*o*-cresol.

A typical compound of class I in which the nitro and hydroxyl groups are para to each other is illustrated with 6-nitro-*m*-cresol. Current–voltage curves for the reduction of this compound from carefully buffered solutions at 25° were obtained (Fig. 1). The waves were of approximately the same height over the entire *p*H range studied and averaged about 10 microamperes.

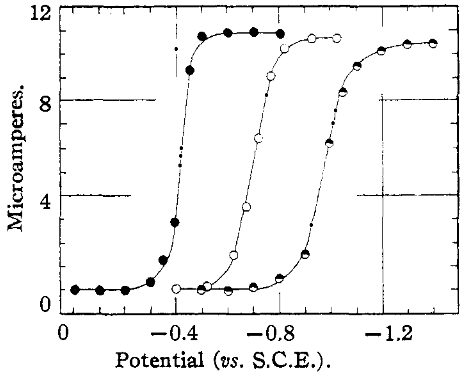

Fig. 1.—Current-voltage curves for 6-nitro-*m*-cresol (0.001 *M*): ●, *p*H 3.6; ○, *p*H 8.0; ◐, *p*H 10.0; $m^{2/3}t^{1/6}$ = 0.94 mg.$^{2/3}$ sec.$^{-1/2}$.

The reduction of the nitro group might well be considered to go first to the nitroso group, then to the hydroxylamine and finally to the amine.

$$-NO_2 \xrightarrow{2e^-} -NO \xrightarrow{2e^-} -NHOH \xrightarrow{2e^-} -NH_2$$

Each step requires two electrons. The reduction of the normal nitro group has been postulated to go to completion with the formation of the amine. This should require six electrons. If we assume that this nitrocresol has about the same diffusion coefficient as a molecule of benzoic acid which is about the same size we get a value of 8.86 × 10^{-6}

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[1] From the M.S. thesis of Wendell P. Cropper. Presented before the Organic Division of the American Chemical Society, Pittsburgh meeting, September 6 to 10, 1943.

[2] Present Address, Standard Oil Co. of Indiana, Whiting, Indiana.

[3] Astle and McConnell, THIS JOURNAL, 65, 35 (1943).

TABLE I

THE EFFECT OF *p*H ON THE WAVE HEIGHTS FOR 0.001 MOLAR SOLUTIONS OF NITROCRESOLS, $m^{2/3}t^{1/6} = 0.94$ mg.$^{2/3}$sec.$^{-1/2}$

		Wave height in microamperes							
Compound	Class	*p*H 2.2	3.6	5.4	6.4	8.0	9.0	10.1	11.3
6-Nitro-*m*-cresol	I	11.0	11.0	10.3	10.3	10.7	10.3	10.1	10.1
5-Nitro-*o*-cresol	I	11.0	10.6	10.7	10.3	10.6	10.6	10.2	10.1
4-Nitro-*m*-cresol	II	6.2	6.2	6.2	6.2	7.9	8.6	8.9	9.1
3-Nitro-*o*-cresol	II	6.6	6.6	6.8	6.6	8.2	8.0	9.2	9.3
3-Nitro-*p*-cresol	II	7.5	7.5	7.1	7.1	8.6	9.4	10.1	10.6
2-Nitro-*p*-cresol	III	10.7	10.6	7.7	7.7	7.7	7.5	7.7	7.3
4-Nitro-*o*-cresol	III	10.6	10.6	7.5	7.7	7.5	7.5	7.2	7.1

TABLE II

THE EFFECT OF *p*H ON THE HALF-WAVE REDUCTION OF NITROCRESOLS (AGAINST A SATURATED CALOMEL ELECTRODE)

		Half wave potential (against S. C. E.)							
Compound	Class	*p*H 2.2	3.6	5.4	6.4	8.0	9.0	10.1	11.3
6-Nitro-*m*-cresol	I	−0.35	−0.42	−0.54	−0.58	−0.68	−0.81	−0.92	−0.93
5-Nitro-*o*-cresol	I	.30	.35	.45	.52	.61	.72	.82	.78
4-Nitro-*m*-cresol	II	.20	.24	.37	.42	.52	.65	.71	.68
3-Nitro-*o*-cresol	II	.20	.22	.31	.37	.51	.58	.69	.71
3-Nitro-*p*-cresol	II	.21	.27	.36	.42	.51	.63	.69	.67
2-Nitro-*p*-cresol	III	.28	.32	.44	.50	.57	.66	.75	.76
4-Nitro-*o*-cresol	III	.23	.30	.42	.48	.56	.65	.73	.74

sq. cm. sec.$^{-1}$, calculated from its equivalent conductance. It is then possible to calculate the number of electrons involved in the reduction process.[4] That is according to the Ilkovič equation $n = I_d/605D^{1/2}Cm^{2/3}t^{1/6}$. where n is the number of electrons involved in the process, D is the diffusion coefficient, C is the concentration of the reducible substance in millimoles per liter, m is the mg. of mercury falling from the capillary per second and t is the time of formation of the mercury drop in seconds. This calculation gives a value of 6.1 for the number of electrons involved in the reduction of this nitrocresol indicating that 6-nitro-*m*-cresol is reduced completely to the corresponding amine over the entire *p*H range studied.

The current–voltage curves for 5-nitro-*o*-cresol were very similar to those for 6-nitro-*m*-cresol. The wave heights indicated complete reduction to the amine over the entire *p*H range studied. The half-wave reduction potentials for these two compounds are appreciably more negative than those for either of the other two classes of compounds (Table II).

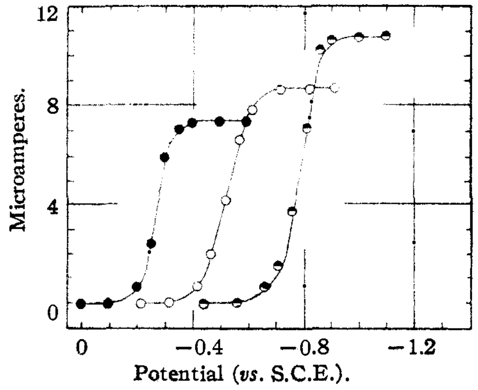

Fig. 2.—Current–voltage curves for 3-nitro-*p*-cresol (0.001 *M*): ●. *p*H 3.6: ○. *p*H 8.0; ◐, *p*H 11.3: $m^{2/3}t^{1/6} = 0.94$ mg.$^{2/3}$ sec.$^{-1/2}$.

Current–voltage curves for the reduction of a compound in which the nitro group is ortho to the OH group (Class II) are illustrated with 3-nitro-*p*-cresol (Fig. 2). These curves were of about the same height in acid solution but were only two-thirds the height of those obtained for class I compounds (Table I). Between a *p*H of 7 and 9.5 there is an increase in the wave height and at a *p*H of 9.5 this height again becomes constant and equal to the height of the waves for class I compounds.

The current–voltage curves for the reduction of 3-nitro-*o*-cresol and 4-nitro-*m*-cresol were very similar to those obtained with 3-nitro-*p*-cresol except that the wave heights were a little lower. These lower wave heights are probably the result of the great difficulty encountered in getting these compounds dissolved in water. The concentrations of these solutions are, therefore, somewhat less than 0.001 molar. The interesting observation is that as with 3-nitro-*p*-cresol, the curves in acid solution are just two-thirds the height of the curves obtained with these compounds in alkaline solution.

The lower wave heights obtained with these compounds of class II in acid solutions would indicate that the reduction involves only 4 electrons rather than 6 as was the case with class I cresols, and that the reduction therefore stopped with the formation of the hydroxylamine. Beyond a *p*H of 9.5 the wave heights indicate that 6 electrons are required and the reduction is therefore complete to the amine. The smaller wave heights for compounds of class II can be explained by postulating the existence of a hydrogen bond be-

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[4] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers Inc., New York, N. Y., 1941, p. 48.

tween the nitro group and the hydroxyl group ortho to it which stabilizes the hydroxylamine intermediate sufficiently so that further reduction is prevented.

In alkaline solution the nitrocresate ion is formed so that a hydrogen bond is impossible and the hydroxylamine intermediate can be further reduced to the amine. The curves in Fig. 3 would indicate that between a *p*H of 7 and 9.5 an equilibrium exists between chelated molecules and nitrocresate ions. This observation follows from a consideration of the wave heights intermediate between those obtained in acid and in alkaline solutions. These intermediate wave heights would result from the reduction of the chelated nitrocresol molecules to the hydroxylamine and the nitrocresate ions which are in equilibrium with them to the amine.

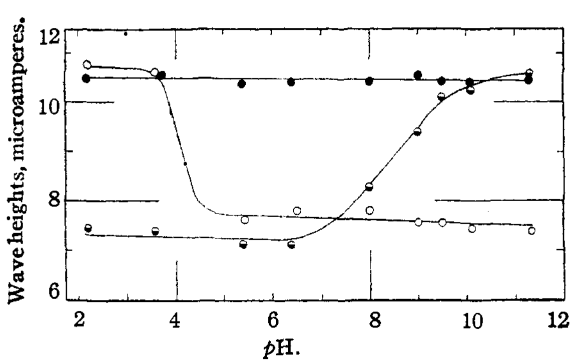


Fig. 3.—The effect of *p*H on the wave heights of 0.001 molar solutions of nitrocresols: ◓, 3-nitro-*p*-cresol; ○, 2-nitro-*p*-cresol; ●, 6-nitro-*m*-cresol; $m^{2/3}t^{1/6}$ = 0.94 mg.$^{2/3}$ sec.$^{-1/2}$.

It is to be noticed (Table II) that the reduction potentials for these nitrocresols of class II are in substantial agreement over the entire *p*H range studied and are considerably more positive than the reduction potentials of class I compounds.

Current–voltage curves for compounds in which the nitro group is meta to the OH group (class III) are illustrated for 2-nitro-*p*-cresol (Fig. 4). In acid solutions these curves consist of two waves, the first wave being two-thirds the total wave height which was the same as for class I compounds. These waves indicate reduction to the amine in two steps, first to the hydroxylamine and then to the amine. With increasing *p*H the hydroxylamine becomes more difficultly reducible until at a *p*H of 5 this intermediate is not reduced at a potential below that for the reduction of sodium ion which was used as the supporting cation. At a *p*H of 5 the curve becomes two-thirds the height of the curve in acid solution and complete reduction to the amine is not accomplished (Table I). The same type of curve was obtained with 4-nitro-*o*-cresol. The half-wave reduction potentials for nitrocresols of class III are intermediate between those for Class I and Class II compounds.

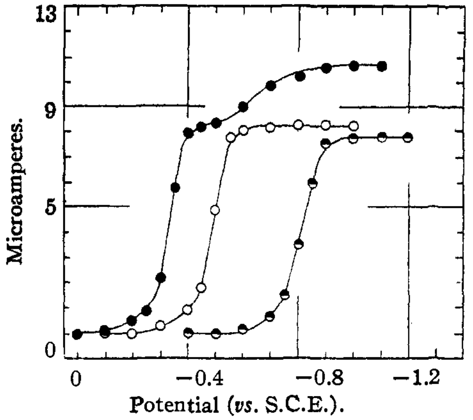
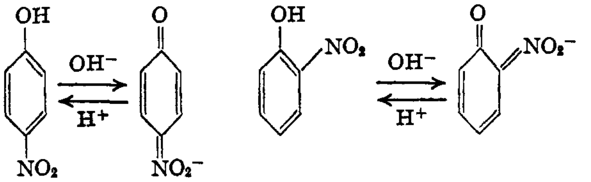


Fig. 4.—Current–voltage curves for 2-nitro-*p*-cresol (0.001 *M*): ●. *p*H 3.6; ○. *p*H 6.4; ◓. *p*H 10.0; $m^{2/3}t^{1/6}$ = 0.94 mg.$^{2/3}$ sec.$^{-1/2}$.

When *o*- and *p*-nitrophenols are introduced into alkaline solutions they are known to go over into quinoid forms.



Since *m*-nitrophenol cannot form such a quinoid structure and since nitrocresols of class III, which fall into this category, are reduced only to the hydroxylamine at high *p*H values it seems probable that complete reduction to the amine is dependent upon the ease of formation of a quinoid structure. It is also suggested that it is the quinoid rather than the normal phenolic form of Class I and II nitrocresols which are reduced at higher *p*H values. Confirmation of these ideas is suggested by the work of Elb[5] and co-workers, who found that contrary to other aromatic nitro compounds, *o*- and *p*-nitrophenols do not give intermediate compounds on electrolytic reduction. With these compounds the reduction goes directly to the corresponding aminophenol. *m*-Nitrophenol on the other hand behaved normally giving the usual intermediate compounds.

A consideration of the half-wave reduction potentials shows that compounds of class II are more easily reduced than compounds of class I. The lower half-wave potentials of class II compounds might be attributed to an interference with the normal resonance of the nitro group by the OH group in the ortho position to it through the formation of a hydrogen bond. This hydrogen bond which involves only one oxygen atom of the nitro group makes these two oxygen atoms no longer equivalent as they are in the normal resonance structure. Therefore, while one oxygen is stabilized through hydrogen bond formation, the

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(5) Elb, *Z. Elektrochem.*, 7, 133 (1900).

second is more easily reduced than the oxygen of a normal nitro group. The lower half-wave potentials of class II compounds in basic solutions is attributed to the lesser stability of the ortho quinoid as compared to the para quinoid structures.

Compounds of class III have reduction potentials intermediate between those for class I and II. It follows therefore that the nitro group in class III compounds is more easily reduced than the nitro group in class I. This difference might be attributed to the unstabilizing effect of the abnormal orientation of the nitro group with respect to the OH group. This unstabilizing effect however. is not as great as that produced by the hydrogen bond present in nitrocresols of class II.

Experimental

Preparation of Materials: 3-Nitro-*o*-cresol.[6]—Ten grams of *o*-toluidine was mixed with 20 ml. of concentrated sulfuric acid and 80 ml. of water and cooled below 15°. A solution of 30 g. of sodium nitrite in 100 ml. of water was added slowly. After the diazotization was complete. the flask was placed in a boiling water-bath and at once a 50% solution of sulfuric acid was added as long as active evolution of nitrogen occurred. The mixture was steam distilled; the 3-nitro-*o*-cresol obtained from the distillate was crystallized several times from dilute alcohol and melted at 70°.

4-Nitro-*o*-cresol.[7]—Ten grams of *o*-toluidine was dissolved in 100 g. of concentrated sulfuric acid and the mixture cooled to 5°. Ten grams of finely powdered potassium nitrate was then gradually added so that the temperature rose to 10° and remained at about that point. In order to complete the reaction a few ml. of fuming nitric acid were added, the end-point of the reaction being that point at which the temperature of the mixture suddenly begins to fall. The solution was poured at once onto a block of ice. whence the crystalline sulfate separated and was drained from excess acid. The sulfate was dissolved in water and decomposed with sodium carbonate and the 4-nitro-*o*-toluidine obtained was recrystallized from alcohol.

Ten grams of the 4-nitro-*o*-toluidine were dissolved in 150 ml. of 10% sulfuric acid and cooled to 0° whereupon a part of the sulfate precipitated. Diazotization was accomplished by adding a solution of 5 g. of sodium nitrite in 20 ml. of water. The clear diazonium salt solution was placed on a hot water-bath and a mixture of 100 ml. of sulfuric acid and 200 ml. of water was added in small portions until no more nitrogen was evolved. The 4-nitro-*o*-cresol separated out on cooling and after several recrystallizations from a benzene–ligroin mixture melted at 118°.

2-Nitro-*p*-cresol.—2-Nitro-*p*-cresol was prepared by means of the same procedure as for the preparation of 4-nitro-*o*-cresol except that *p*-toluidine was substituted for *o*-toluidine. The 2-nitro-*p*-cresol was recrystallized from water and had a melting point of 79°.

3-Nitro-*p*-cresol.[8]—Ten grams of *p*-toluidine was diazotized with sodium nitrite and sulfuric acid in the presence of 18 g. of potassium nitrite. The diazonium salt solution was then decomposed by heating it to 60°. The 3-nitro-*p*-cresol was purified by steam distillation followed by recrystallization several times from alcohol. The compound melted at 36°.

5-Nitro-*o*-cresol.—Ten grams of *o*-cresol. 4 g. of sodium hydroxide and 8 g. of sodium nitrite were dissolved in 200 ml. of water and the temperature of the mixture held below 5° for about two hours with occasional shaking. At the end of this period the crude nitroso cresol was filtered out and added to 100 ml. of concentrated nitric acid and the temperature again held below 5° for about one-half hour. The crude 5-nitro-*o*-cresol obtained in small yields was then filtered out and recrystallized from ligroin giving a compound which melted at 96°.

4-Nitro-*m*-cresol and 6-Nitro-*m*-cresol.[9]—Fourteen grams of *m*-toluidine was mixed with 25 g. of concentrated sulfuric acid in 250 ml. of water and the whole cooled to 15°. To this mixture was added slowly a solution of 9 g. of sodium nitrite in 25 ml. of water. The diazonium salt was decomposed with nitric acid (sp. gr. 1.33) by refluxing until there was no further evolution of nitrogen. The isomers were then separated by steam distillation. The 4-nitro-*m*-cresol separated from the distillate and after recrystallization from ligroin melted at 56°. The 6-nitro-*m*-cresol remained in the flask. This isomer was separated by an ether extraction and recrystallized from dilute alcohol. It melted at 129°.

Stock solutions of each of the nitrocresols (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 *p*H values in the acid range McIlvaine's standard buffer solutions were prepared and alkaline buffers were made from sodium borate–sodium hydroxide mixtures.[10]

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

Apparatus.—In an electrolysis cell kept at a constant temperature of 25° was placed the 0.001 molar nitrocresol solution. Current-voltage curves were obtained with these solutions over the *p*H range of 2.1 to 11.3 with the aid of a Fisher "Elecdropode." This instrument was manually operated and used a capillary made from a drawn out thermometer and had a dropping rate of between 3 and 4 seconds per drop. The calibration of the capillary gave $m^{2/3} t^{1/6} = 0.94$ mg.$^{2/3}$ 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 several nitrocresols from carefully buffered solutions at the dropping mercury cathode has been investigated.

Whenever the OH group is ortho to a nitro group (Class II) the reduction of the nitro group occurs at more positive potentials than when the OH group is in the para (Class I) or meta (Class III) positions.

Compounds of class II are reduced to the hydroxylamine in acid solutions and completely to the amine in alkaline solutions, while compounds of class I are reduced completely to the amine at all *p*H values. This indicates stabilization of the hydroxylamine in class II compounds through intramolecular hydrogen bonding.

Compounds of class III are reduced in acid solutions in two steps; first to the hydroxylamine, then to the amine. In basic solutions the reduction stops at the hydroxylamine stage. Since

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(6) A. Deninger, *J. prakt. Chem.*, [2] **40**. 299 (1889).

(7) F. Ullmann and R. Fitzenkamm. *Ber.*, **38**, 3790 (1906).

(8) O. Neunhoeffer and H. Kolbel, *ibid.*, **68**. 260 (1935).

(9) E. Khotinsky and W. Jacopson-Jacopmann. *ibid.*, **42**. 2097 (1909).

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

compounds of class III cannot form a quinoid structure, it seems probable that complete reduction to the amine cannot occur in alkaline solutions 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. Nitrodihydroxybenzenes[1]

BY MELVIN J. ASTLE AND STANLY P. STEPHENSON[2]

In the first paper of this series[3] 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 *p*H range of 2.1 to 11.3 (Fig. 1). The wave heights were practically constant over the entire *p*H range studied and averaged 10.2 microamperes (Table I).

TABLE I

THE EFFECT OF *p*H ON THE WAVE HEIGHTS OF THE NITRODIHYDROXYBENZENES

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

Concentration of solutions 0.001 molar

*p*H	2-Nitro-hydro-quinone	3-Nitro-catechol	4-Nitro-catechol	2-Nitro-resorcinol	4-Nitro-resorcinol
	Wave heights in microamperes				
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 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 benzoil 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.

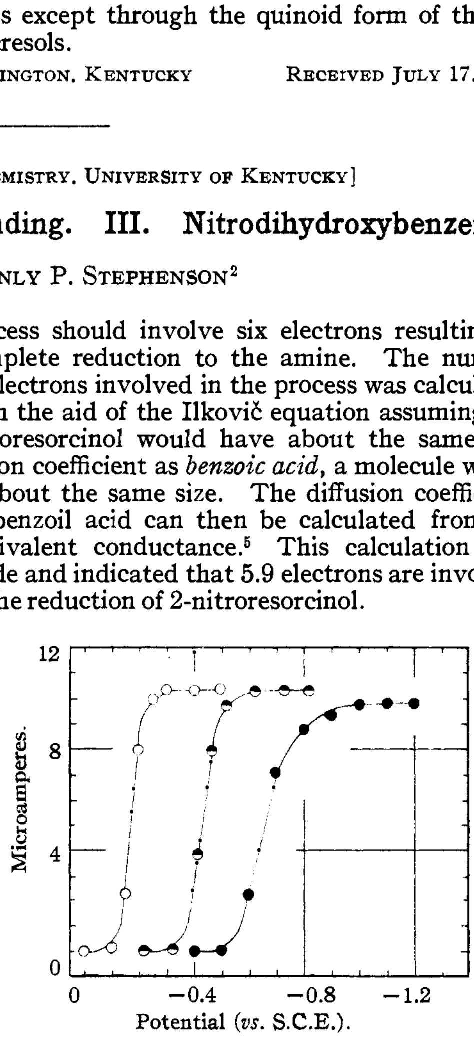

Fig. 1.—Current–voltage curves for 2-nitroresorcinol (0.001 *M*): O, *p*H 2.1: ◐, *p*H 8.0: ●, *p*H 10.1: $m^{2/3}t^{1/6} =$ 0.94 mg.$^{2/3}$ sec.$^{-1/2}$.

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

This relationship is linear from a *p*H of 2.1 to 8, but at *p*H values greater than 8 the effect of *p*H 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 *p*H 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

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[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, 2395 (1943).

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