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

Polarographic Investigations of Hydrogen Bonding. I. ortho- and para-Nitrophenols[1]

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Hydrogen bonds have been postulated to explain the differences in properties between such compounds as ortho- and para-nitrophenols. Thus the low melting point and the greater steam volatility of the *o*-nitrophenol as compared with the *p*-nitrophenol has been attributed to the presence of strong intramolecular hydrogen bonds in the ortho compound. The *p*-nitrophenol which cannot form intramolecular hydrogen bonds because of spatial considerations may form intermolecular bonds which must be broken before the compound can melt. Similarly *p*-nitrophenol forms strong hydrogen bonds with solvents such as water and these must be broken before the compound can be steam distilled.[3]

The most widely used method for studying hydrogen bonding in the nitrophenols has employed the infrared absorption spectra,[4] in which the characteristic frequency for the OH vibration is shifted from its normal position when hydrogen bonding occurs.

It was believed that the polarographic method might prove to be useful in studying hydrogen bonding in cases where such bonds are associated with the groups undergoing reduction at the dropping mercury cathode. In the case of the nitrophenols for example, the presence of the hydrogen bond in the ortho compound might sufficiently modify the nitro group so that the ease of reduction might not be the same as in the para compound where no such hydrogen bonding is possible. This effect is shown by the work of Shikata and Watanabe,[5] who measured the reduction potentials of ortho- and para-nitrophenols in buffered solutions but did not attempt to make an explanation for the observed differences.

The presence of a hydrogen bond in the nitrophenols might determine the degree to which the compound may be reduced. That is, the *p*-nitrophenol might be reduced completely to the amine while the hydrogen bond present in the ortho-nitrophenol might sufficiently stabilize the intermediate nitroso- or hydroxylamine compound so that the reduction might stop with one of these intermediate forms. This should manifest itself by a difference in wave heights on the current-voltage curves obtained.

The polarographic method should be particularly useful in the investigation of hydrogen bonding in water solutions.

Discussion of Results

Current–voltage curves obtained when *p*-nitrophenol was reduced at the dropping mercury cathode from solutions carefully buffered and whose *p*H values ranged from 2.2 to 7, consisted of single waves. Above a *p*H of 7 the curves broke up into two waves, the second of which occurred at potentials close to that at which sodium ion began to be reduced so that there was not a complete leveling off at the top of the wave (Fig. 1). The wave heights over the entire *p*H range of 2.2 to 12 were practically constant although there was a slight increase in the wave heights in solution having *p*H values above 9.5 (Fig. 3). Where the curve broke up into two waves, the current representing the total reduction process (the sum of the two waves) was considered.

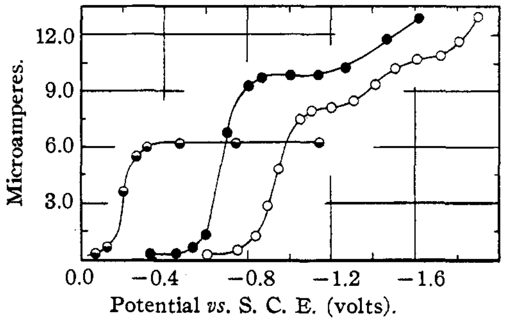

Fig. 1.—Current–potential curve for 10^{-3} *M* *p*-nitrophenol and 10^{-3} *M* *p*-nitrosophenol at 25°, $m^{2/3}t^{1/6} = 1.00$ mg.$^{2/3}$sec.$^{-1/2}$: ◒, *p*-nitrosophenol (*p*H 4); ●, *p*-nitrophenol (*p*H 4); ○, *p*-nitrophenol (*p*H 8).

The half-wave potentials showed a gradual shift toward more negative potentials with in-

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[1] From the M. S. Thesis of Wayne V. McConnell. Presented before the Organic Division of the American Chemical Society, Meeting at Buffalo, September 7–12, 1942.

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[3] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 310.

[4] N. V. Sidgwick and E. N. Allot, *J. Chem. Soc.*, **123**, 2819 (1923).

[5] M. Shikata and M. Watanabe, *J. Agr. Chem. Soc. Japan*, **4**, 1934 (1928).

creasing *p*H up to a *p*H of 11 (Table I). Beyond this point there was a gradual decrease in reduction potential. Similar results were obtained by Shikata and Watanabe.[5]

TABLE I

*p*H	Wave ht., microamps.[a] o-Nitrophenol	*p*-Nitrophenol	Half-wave pot., volts[b] o-Nitrophenol	*p*-Nitrophenol
2.2	6.84	9.59	−0.34	−0.54
3.0	6.86	9.43	− .44	− .60
4.0	7.02	9.59	− .52	− .68
5.0	7.00	9.48	− .62	− .76
6.0	6.82	9.60	− .65	− .80
7.0	7.88	9.38	− .73	− .86
8.0	9.01	9.71	− .80	− .96
9.5	9.69	9.85	− .92	−1.08
11.0	9.80	9.95	− .97	−1.02
12.0	9.90	9.98	− .98	−0.97

[a] Concentration of nitrophenols 0.001 molar, temperature 25°, $m^{2/3}t^{1/6} = 1.0$ mg.$^{2/3}$ sec.$^{-1/2}$. [b] Against saturated calomel electrode.

The wave heights for the reduction of the *o*-nitrophenol were almost constant in the *p*H range 2.2 to 6 (Fig. 2). This height was about two-thirds of that noted for the *p*-nitrophenol. Above a *p*H of 6 the wave heights increased rapidly until a *p*H of 9.5 was reached at which point they again reached a constant height. Above a *p*H of 9.5 these wave heights were almost equal to those obtained with the para compound.

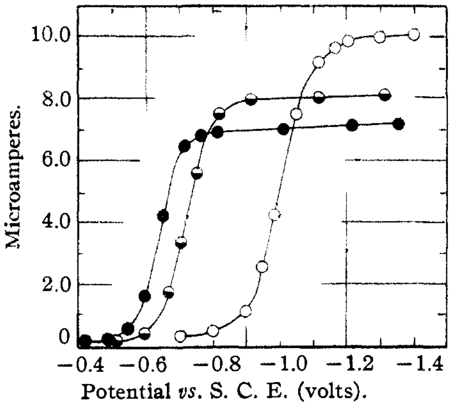
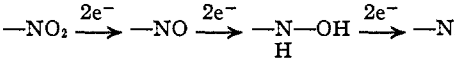


Fig. 2.—Current–potential curves for 10^{-3} *M* *o*-nitrophenol at 25°, $m^{2/3}t^{1/6} = 1.00$ mg.$^{2/3}$sec.$^{-1/2}$: ●, *p*H 5; ◒, *p*H 7; ○, *p*H 12.

The half-wave potentials of *o*-nitrophenol were considerably lower than those obtained for the *p*-nitrophenol at low *p*H and they became progressively more negative with increasing *p*H values, finally approaching the half-wave potential observed for the *p*-nitrophenol at *p*H values of 11 and 12.

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. Two electrons are involved in each step.



$$—NO_2 \xrightarrow{2e^-} —NO \xrightarrow{2e^-} —\underset{\textstyle H}{N}—OH \xrightarrow{2e^-} —NH_2$$

In the case of a normal nitro group the reduction has been postulated to go to completion with the formation of the amine. This should involve six electrons. The number involved in the cases here studied may be calculated by means of the Ilkovic equation

$$I_d = 605nD^{1/2}CM^{2/3}t^{1/6}, \text{ or}$$
$$n = I_d/(605D^{1/2}CM^{2/3}t^{1/6})$$

The only difficulty here is in obtaining the correct value for the diffusion coefficient *D*. This may be calculated by assuming that Stokes' law will hold under these conditions.[6] Determining the diffusion coefficient in this way the number of electrons involved in the reduction of *o*-nitrophenol in basic solution is calculated to be 5.4. The number of electrons involved should be either 4 or 6 and since Stokes' law is only an approximation in this case because of the relatively small size of the nitrophenol molecule, the number of electrons indicated for the reduction of *o*-nitrophenol in basic solution seems to be 6. The diffusion coefficient for *o*-nitrophenol may also be calculated by assuming that the molecule is approximately the same size as benzoate ion and therefore should diffuse at about the same rate. The diffusion coefficient for the benzoate ion may be determined from its equivalent conductance at infinite dilution.[7] Making the calculation for the diffusion coefficient of *o*-nitrophenol based upon this assumption gives a value of 8.86 × 10^{-6} cm.^{2} sec.$^{-1}$ at 25° and substituting this value into the Ilkovic equation and solving for the number of electrons involved gives a value of 5.5, again indicating that 6 electrons are involved in the reduction of *o*-nitrophenol in basic solution. Since the wave heights obtained with *p*-nitrophenol are almost equal to those of the ortho compound in basic solution, apparently six electrons are involved in this reduction also.

p-Nitrosophenol should have approximately the same diffusion coefficient as *p*-nitrophenol and if both compounds are reduced to the amine the wave height for the nitroso compound should be two-thirds as high as that obtained from *p*-nitro-

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

(7) Kolthoff and Lingane, *ibid.*, p. 51

phenol or from *o*-nitrophenol in basic solution. Accordingly the wave heights for *p*-nitrosophenol were determined. With a 0.001 molar solution the ratio of the wave heights for the *p*-nitrosophenol to that for the *p*-nitrophenol was found to be 0.622 at a *p*H of 4 and 0.688 at a *p*H of 8 (Fig. 1). These data further substantiate the idea that the normal nitro group is reduced completely to the amine at *p*H values between 2.2 and 12.

In acid solutions the wave heights for the reduction of *o*-nitrophenol are two-thirds the height obtained from *o*-nitrophenol in basic solutions. This would indicate that the reduction involves only four electrons under these conditions and therefore the reduction process must stop with the formation of the hydroxylamine. This can readily be explained by postulating the existence of a hydrogen bond which stabilizes the hydroxylamine sufficiently so that further reduction is prevented.

In basic solution the phenate ion is formed so that a hydrogen bond is impossible and the hydroxylamine can thus be further reduced to the amine. The curves in Fig. 3 would indicate that between *p*H's of 6 and 9.5 an equilibrium exists between chelated molecules and ions containing the normal nitro group. Part of the molecules would then be reduced to the hydroxylamine and part to the amine as indicated by the curve heights intermediate between those obtained in acid and in basic solutions.

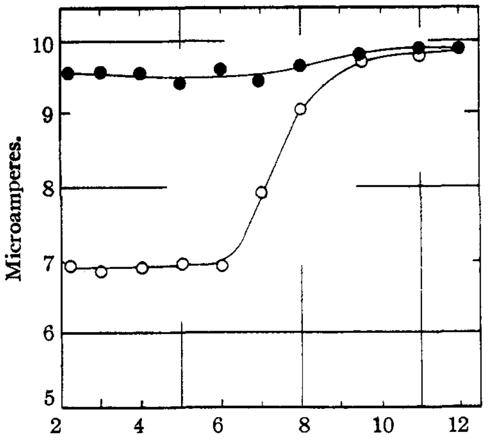

Fig. 3.—Effect of *p*H on wave height for 0.001 molar *o*-nitrophenol and *p*-nitrophenol solutions: ●, *p*-nitrophenol; ○, *o*-nitrophenol.

By substituting *o*-nitroanisole for *o*-nitrophenol in order to prevent the occurrence of hydrogen bonds, the current–voltage curves obtained did not show the abrupt increase in wave height between *p*H's of 6 and 9.5 as was observed with the *o*-nitrophenol. Instead there was a gradual decrease in wave height with increasing *p*H. Calculations such as were made with the *o*-nitrophenol indicated that 5.6 electrons were involved in the reduction at a *p*H of 4. Within the accuracy of the calculation of the diffusion coefficient the reduction to the amine is indicated.

When the solutions were subjected to extended degassing, considerable difficulty was encountered in getting consistent values for the wave heights for the *o*-nitrophenol in acid solution. No such difficulty was encountered in basic solution of this compound or with the *p*-nitrophenol or *o*-nitroanisole at any *p*H.

Since *o*-nitrophenol is steam volatile, this difficulty was probably due to removal of this compound from solution by the degassing process. Experiments on the effect of extended degassing proved this to be the case and offered confirmatory evidence for the validity of the polarographic method for the detection of hydrogen bonds in the nitrophenols. Nitrogen was bubbled through solutions of the *o*-nitrophenol at *p*H's of 4 and 5 and wave heights of the curves obtained were plotted against the volume of nitrogen passed through the solution (Fig. 4). The wave heights varied inversely with the volume of nitrogen used and the curves for both *p*H values almost coincided. This apparently indicated that the same degree of volatility exists at both of these *p*H's.

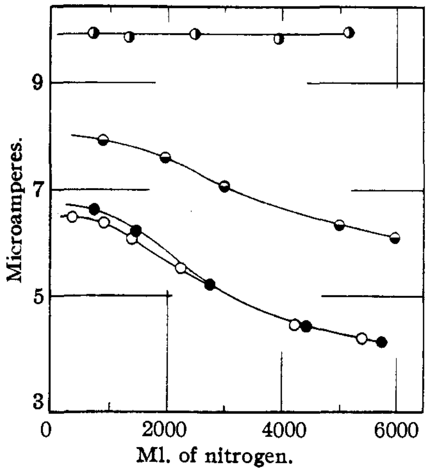

Fig. 4.—Effect of extended degassing on wave height for the reduction of *o*-nitrophenol: ◑, *p*H 11; ◒, *p*H 7; ●, *p*H 5; ○, *p*H 4.

A solution of *o*-nitrophenol having a *p*H of 7 was treated similarly in order to test its degree of volatility. When plotted against the volume of nitrogen passed through the solution, the wave heights did not decrease as rapidly as they did when the solutions of lower *p*H were used (Fig. 2). This is an indication of less volatility and consequently of less hydrogen bond formation at the *p*H of 7 than was noted at *p*H's of 4 and 5. This result is in agreement with previous statements that complete chelation does not occur in *o*-nitrophenol at a *p*H of 7. At a *p*H of 11 there was no appreciable decrease of wave height on extended degassing.

As previously mentioned, in acid solutions *o*-nitrophenol is reduced at lower potentials than *p*-nitrophenol and *o*-nitroanisole also indicating that *o*-nitrophenol possesses some peculiarity which is not present in the other two compounds. The fact that the reduction of *o*-nitrophenol is accomplished more easily (at lower potential) may be attributed to an interference with the normal resonance of the nitro group. The hydrogen bond involving only one of the oxygen atoms 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 second is more easily reduced than the oxygen in a normal nitro group.

From *p*H's 9.5 to 12 there were no indications of hydrogen bond formation in *o*-nitrophenol. This is based on three observations: (1) the wave height is almost equal to that of *p*-nitrophenol, (2) the compound is not volatile, and (3) the reduction potential approaches that of *p*-nitrophenol at a *p*H of 12.

Experimental

Preparation and Purification of Materials.—*o*-Nitrophenol and *p*-nitrophenol were purified by recrystallizing four times from a water–ethyl alcohol mixture. The resulting compounds melted at 44–45° and 113–114°, respectively.

The *o*-nitroanisole was Eastman Kodak Co. best purity and had a refractive index of n^{20}_{D} 1.5614.

The *p*-nitrosophenol was prepared by the method of Bridge.[8]

Stock solutions of each of these substances (4×10^{-3} molar) in water or in alcohol–water mixtures were prepared. Portions of these stock solutions were diluted to the proper concentrations with the appropriate buffer, placed in an electrolysis cell and allowed to come to equilibrium in a constant temperature bath maintained at 25° before the current–voltage curves were obtained.

McIlvaine's standard buffer solutions were prepared for the *p*H range from 2.2 to 8. Mixtures of sodium borate and sodium hydroxide solutions were used for the *p*H range of 9.5 to 12.[9]

These solutions were made up to a concentration such that when three parts of the buffer were mixed with one part of the 0.004 molar solutions of the reducible materials the resulting solution consisted of the desired concentration for the given *p*H; the resulting strength of the nitro compounds was then 0.001 molar. The *p*H values of these solutions were checked on a Leeds and Northrup *p*H meter.

Apparatus.—In an electrolysis cell kept at a constant temperature of 25 ± 0.1° were placed the 0.001 molar nitrophenol or nitroanisole in carefully buffered solutions. Current-voltage curves were obtained with these solutions over the *p*H range of 2.2 to 12 with the aid of a Fisher "Elecdropode." This instrument was manually operated. Capillaries having a dropping rate of about 4 seconds per drop at a mercury height of 50 cm. were used. These were made by drawing out thermometer tubing.

More than one capillary was used throughout the work. Therefore in order to compare results obtained, all wave heights were referred to a capillary whose $m^{2/3}t^{1/6}$ values were 1.0 mg.$^{2/3}$ sec.$^{-1/2}$.

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

Summary

The polarographic method has been used to detect the presence of hydrogen bonds in *o*-nitrophenol in carefully buffered water solutions. The half-wave reduction potentials for *o*-nitrophenol are considerably more positive than those for *p*-nitrophenol or *o*-nitroanisole in acid solution but have about the same values in basic solutions. The wave height for the reduction of *o*-nitrophenol in acid solution is about two-thirds the height for *o*-nitrophenol in basic solution or for *p*-nitrophenol at any *p*H. This indicates that the intermediate hydroxylamine formed by the reduction of *o*-nitrophenol is sufficiently stabilized by the presence of a hydrogen bond so that further reduction to the amine is not possible at the dropping mercury cathode. In solutions whose *p*H values range from 6 to 9.5 the *o*-nitrophenol seems to be a mixture of chelated and unchelated molecules. At *p*H values greater than 9.5, *o*-nitrophenol does not show the presence of any hydrogen bonds.

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(8) J. Bridge, *Ann.*, **277**, 85 (1893).

(9) W. M. Clark, "The Determinations of Hydrogen Ions," II ed. Williams and Wilkins Co., Baltimore, Md., 1927, pp. 112–216.