together with previously unreported values for the N–H, C–N, C=N, C–O (in ethers) and C–S bonds, which are derived from the present work and additional data from the literature. The last column of Table II gives the corresponding increments for molar refraction, as determined by Denbigh[11] and Warrick.[12]

The values for molar sound velocity and molar refraction calculated from these bond increments are compared in Table I with the values from the observed physical properties of the liquids. It is notable that five-membered rings show the larger deviations, especially in the molar velocity. The molar refractions show an average deviation of 1.6% between observed and calculated values, while the molar sound velocities show an average deviation of only 1.2%. In the present case, therefore, the molar sound velocity appears to be more useful than the molar refraction for structure investigations, by being less subject to such anomalies as are due to ring structure and conjugation of double bonds. This conclusion is to be employed with caution, particularly in view of the relatively small number of compounds studied here.

Acknowledgment.—The author is grateful to Dr. G. R. Ringo for stimulating discussions, and to the du Pont Company for samples of the furans and pyrans.

Summary

Through the use of a three-megacycle ultrasonic interferometer, the velocity of sound at 30° in twenty-two cyclic compounds has been determined. Densities and refractive indices at 30° are reported also.

Correlations have been found between molecular structure and sound velocity. For example, substituting nitrogen, oxygen or sulfur for a ring carbon causes a decrease in adiabatic compressibility.

For these liquids, the molar sound velocity is more nearly an additive property than the commonly-used molar refraction. It is possible, therefore, to predict the velocity of sound in pure liquids with an average accuracy of a few per cent., simply from the molecular structure and the density.

RECEIVED SEPTEMBER 14, 1948

[11] Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

[12] Warrick, THIS JOURNAL, **68**, 2455 (1946).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF POLAROID CORPORATION]

Polarographic Studies of Some Hindered and Unhindered Aromatic Nitro Compounds

BY MELVIN FIELDS,[1] CLAUDE VALLE, JR., AND MARSHALL KANE

Steric inhibition of resonance results in marked alterations of physical and chemical properties of organic molecules. Familiar examples of this phenomenon are the reduction of the dipole moments of nitromesitylene and nitrodurene from the values characteristic of aromatic nitro derivatives to approximately those of the aliphatic nitro compounds,[2] the striking alterations in the ultraviolet absorption of diphenyl derivatives[3] and of aromatic amines bearing bulky ortho substituents,[4] and the anomalous acid and base strengths of certain phenols, hydrocarbons and aromatic amines.[5] That the rates of chemical reactions may also be modified by the steric inhibition of resonance in a reacting molecule is illustrated by the numerous examples cited by Wheland.[6]

In this communication we wish to report on the results of a study of the effects of the steric inhibition of resonance on the polarographic characteristics of certain aromatic nitro compounds. Although the polarograph has been employed in the investigation of such varied phenomena as hydrogen bonding in nitrophenols[7] and in amidines,[8] semiquinone formation[9] and keto–enol tautomerism,[10] this instrument does not appear to have been utilized for the study of the effects of damped resonance on the properties of organic molecules. Suppression of the normal resonance of a reducible group with an aromatic nucleus might be expected to affect not only the ease of reduction but also the nature of the products of the reaction. In terms of the polarographic characteristics of a substance there might be observed a shift in the half-wave potential of a given stage of reduction, a change in the total number of electrons involved per molecule of electrode reaction or perhaps an alteration in the number of polarographic waves or distinct steps in which the over-all reaction occurs.

The substances which we studied were nitro-

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[2] Birtles and Hampson, *J. Chem. Soc.*, 10 (1937); Ingham and Hampson, *ibid.*, 981 (1939).

[3] Pickett, Walter and France, THIS JOURNAL, **58**, 2296 (1936); O'Shaughnessy and Rodebush, *ibid.*, **62**, 2906 (1940); and Williamson and Rodebush, *ibid.*, **63**, 3018 (1941).

[4] Remington, *ibid.*, **67**, 1838 (1945).

[5] Wheland, "The Theory of Resonance and its Application to Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 185.

[6] Reference 5, p. 272.

[7] Astle and McConnell, THIS JOURNAL, **65**, 35 (1943); Astle and Cooper, *ibid.*, **65**, 2395 (1943); Astle and Stephenson, *ibid.*, **65**, 2399 (1943).

[8] Runner, Kilpatrick and Wagner, *ibid.*, **69**, 1406 (1947).

[9] Müller, *Ann. N. Y. Acad. Sci.*, **40**, 91 (1940).

[10] Semerano and Chisini, *Gazz. chim. ital.*, **66**, 504 (1936); Müller and Baumberger, THIS JOURNAL, **61**, 590 (1939); Zambatti and Ferrante, *Arch. Sci. biol.* (*Italy*), **26**, 51 (1940).

benzene, *o*-, *m*- and *p*-nitrotoluene, 2-nitro-1,4-dimethylbenzene, 3-nitro-1,2-dimethylbenzene, nitromesitylene and nitrodurene. Of these compounds only nitromesitylene and nitrodurene would be expected to exhibit the effects of inhibition of the resonance of a nitro group with a benzene ring. The other members of the group were investigated in order to determine how the polarographic behavior of the unhindered aromatic nitro compounds is affected by the introduction of one and of two methyl groups into the nucleus and to provide reliable data obtained under identical conditions for comparison of the characteristics of the hindered and unhindered compounds. Although nitrobenzene and other aromatic nitro compounds were studied polarographically by Shikata and co-workers,[11] the nitrotoluenes and nitroxylenes were not included in these investigations. Furthermore, since much of Shikata's work appeared before significance of the half-wave potential was understood, much of his data on "reduction potentials" are now of qualitative value only.

Experimental

Preparation and Purification of Materials.—The samples of nitrobenzene, *o*-, *m*- and *p*-nitrotoluene, 2-nitro-1,4-dimethylbenzene, 3-nitro-1,2-dimethylbenzene and nitromesitylene used were Eastman Kodak Co. white label grade chemicals. The liquids were purified by distillation at reduced pressure through a 30″ Podbielniak column. The sample of *p*-nitrotoluene used melted at 52–53° after several crystallizations from methanol. Nitromesitylene, crystallized several times from methanol, melted sharply at 43–44°. The physical properties of the liquid nitro compounds used are listed in Table I.

TABLE I

PHYSICAL CONSTANTS OF LIQUIDS

Compound	B. p., °C.	Mm.	$n^{20}D$
Nitrobenzene	72.8	10.0	1.5522
o-Nitrotoluene	95.0	10.0	1.5468
m-Nitrotoluene	95.4	10.5	1.5460
2-Nitro-1,4-dimethylbenzene	105.8	10.5	1.5415
3-Nitro-1,2-dimethylbenzene	110.0	10.0	1.5432

Nitrodurene was prepared by nitric acid oxidation of acetoxymercuridurene according to the procedure of Smith and Taylor[12]; the sample used melted at 113–114°.

Instruments and Cells.—Polarographic measurements were made using a manual apparatus similar to the one described by Lingane and Kolthoff.[13] The usual H-type polarographic cell with a saturated calomel reference electrode was employed. At a pressure of 60 cm. of mercury the capillary had a drop time of 4.6 seconds and an *m*-value of 1.530 mg. of mercury per second measured on open circuit in 80% aqueous dioxane solution 0.30 *M* in sodium hydroxide.

Supporting Electrolytes.—The polarograms of the nitro compounds were run in buffered 80% aqueous dioxane solutions in which the concentration of supporting electrolyte in the final solutions was 0.38 *M* for the *p*H 1.0 and *p*H 7.2 solutions and 0.30 *M* for the *p*H 12.0 solutions. The dioxane was purified by prolonged refluxing over sodium. Elimination of maxima was achieved by the addition of 0.01% gelatin.

The following supporting electrolytes were used: *p*H 1.0, sodium acetate–hydrochloric acid; *p*H 7.2, sodium dihydrogen phosphate–disodium hydrogen phosphate; *p*H 12.0, sodium hydroxide. The *p*H values mentioned refer to those determined by measurement with a glass electrode[14] and are uncorrected for the non-aqueous solution error.[15]

Procedure.—In order to decrease the time required for deaeration of the polarographic solutions and thus to reduce the loss of the nitro compound during the deaeration process, the distilled water, the dioxane and the stock buffer solutions were freed from dissolved oxygen by bubbling purified nitrogen through the refluxing liquids for a period of about one to two hours. The oxygen-free solutions were then stored under nitrogen. The volumetric flasks were flushed with nitrogen before use, and the polarographic solutions were made up and mixed so as to minimize contact with air. When prepared by this technique, the solutions in the polarographic cell required only ten minutes sweeping prior to measurement. The nitrogen used was purified by passage through a tube filled with freshly-reduced copper filings maintained at 400 to 450°. Most of the measurements were made at a concentration of nitro compound of about 1.0×10^{-4} *M;* where it was desired to check the effect of concentration of reducible material on the half-wave potential and on the wave height, measurements were also made at a concentration of 5.0×10^{-4} *M*. All potentials were measured against a saturated calomel reference electrode (S. C. E.); the half-wave potentials referred to in this paper have been corrected for the *iR* drops of the solutions. Diffusion currents were corrected for the residual current of the supporting electrolyte. All measurements were made at 25 ± 0.5°.

Results and Discussion

The marked differences in the polarographic behavior of nitrobenzene and several other aromatic nitro compounds with an unhindered nitro group and that of nitromesitylene and nitrodurene are illustrated by the representative current–voltage curves shown in Figs. 1–6 for some of these compounds. Substances of the first group all yield two fairly well defined waves in buffered 80% aqueous dioxane solution at *p*H 1.0 and only a single distinct wave at *p*H 12.0. In alkaline solution the derivatives with a methyl substituent ortho to the nitro group reveal a tendency for the polarographic wave to break up near the diffusion current region into two separate steps. The polarogram of *p*-nitrotoluene also shows a barely perceptible indication of separating into two waves, but in this case the inflection occurs in the first third of the wave. Complete separation of the two waves is not achieved for any of the unhindered compounds under these conditions. On the other hand, nitromesitylene and nitrodurene each produce a single wave in strongly acid solution and two distinct waves in sodium hydroxide solution. At *p*H 7.2 a single wave is observed for compounds of both classes although with nitrodurene there is a slight indication of a second wave following the main one. In buffered 80% aqueous dioxane solution of *p*H 7.2 the half-wave potentials are

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[11] Shikata, *Trans. Faraday Soc.*, **21**, 42 (1925); Shikata and co-workers, *J. Agr. Chem. Soc. Japan*, **1**, 533 (1925); **4**, 924 (1928).

[12] Smith and Taylor, THIS JOURNAL, **57**, 2460 (1935).

[13] Lingane and Kolthoff, *ibid.*, **61**, 825 (1939).

[14] Coleman Electric Company, Model 3A *p*H Electrometer.

[15] Dole, "Principles of Experimental and Theoretical Electrochemistry," McGraw-Hill Book Co., New York, N. Y., 1935, p. 240.

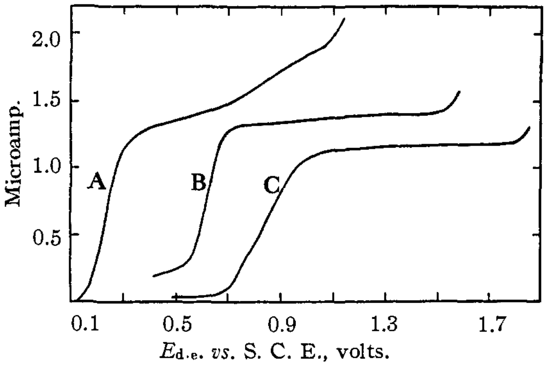

Fig. 1.—Polarograms of nitrobenzene in buffered 80% aqueous dioxane solutions: A, *p*H 1.0, concn., 1.06 × 10^{-4} *M;* B, *p*H 7.2, 1.06 × 10^{-4} *M;* C, *p*H 12, 1.01 × 10^{-4} *M.*

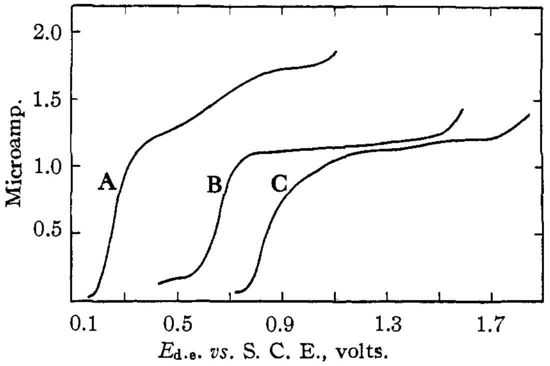

Fig. 2.—Polarograms of *o*-nitrotoluene in buffered 80% aqueous dioxane solutions: A, *p*H 1.0, concn., 0.99 × 10^{-4} *M;* B, *p*H 7.2, 0.99 × 10^{-4} *M;* C, *p*H 12, 0.99 × 10^{-4} *M.*

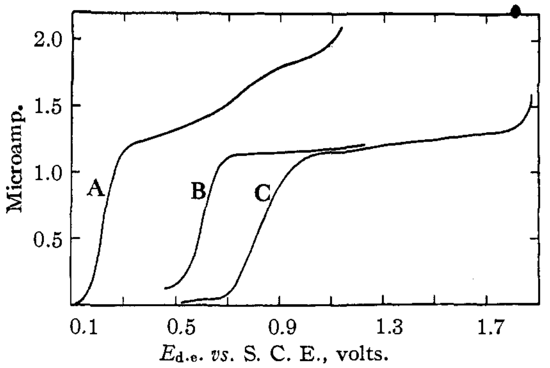

Fig. 3.—Polarograms of *m*-nitrotoluene in buffered 80% aqueous dioxane solutions: A, *p*H 1.0, concn., 0.99 × 10^{-4} *M;* B, *p*H 7.2, 0.99 × 10^{-4} *M;* C, *p*H 12, 0.99 × 10^{-4} *M.*

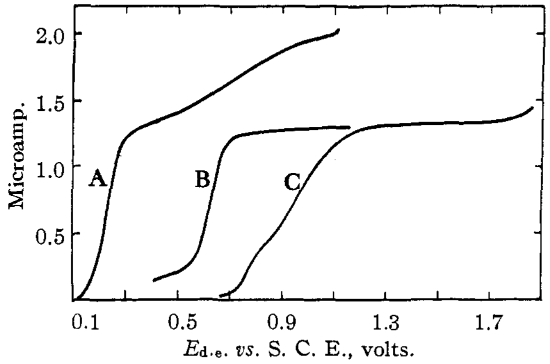

Fig. 4.—Polarograms of *p*-nitrotoluene in buffered 80% aqueous dioxane solutions: A, *p*H 1.0, concn., 1.14 × 10^{-4} *M;* B, *p*H 7.2, 1.02 × 10^{-4} *M;* C, *p*H 12, 1.14 × 10^{-4} *M.*

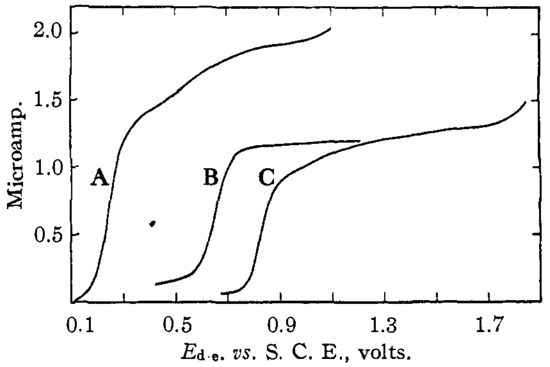

Fig. 5.—Polarograms of 3-nitro-1,2-dimethylbenzene in buffered 80% aqueous dioxane solutions: A, *p*H 1.0, concn., 1.02 × 10^{-4} *M;* B, *p*H 7.2, 1.02 × 10^{-4} *M;* C, *p*H 12, 1.02 × 10^{-4} *M.*

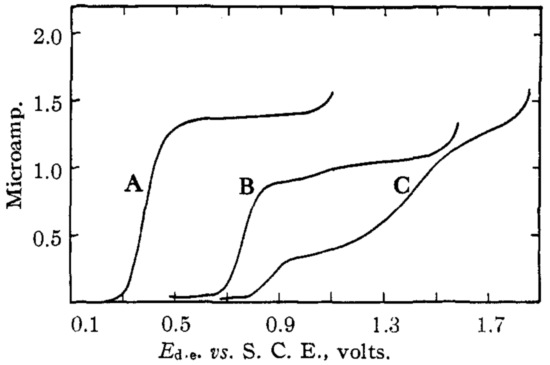

Fig. 6.—Polarograms of nitrodurene in buffered 80% aqueous dioxane solutions: A, *p*H 1.0, concn., 0.98 × 10^{-4} *M;* B, *p*H 7.2, 0.98 × 10^{-4} *M;* C, *p*H 12, 0.99 × 10^{-4} *M.*

independent of and the wave heights proportional to concentration over the range of 1 × 10^{-4} to 5 × 10^{-4} *M* for all the compounds except nitrodurene whose low solubility prohibited extension of the measurements beyond 2 × 10^{-4} *M*. Nitrobenzene showed similar behavior at *p*H 1.0 and 12.0. The data in Table II indicate that the presence of one methyl group and, in the cases of the two nitroxylenes studied, of two methyl substituents has only a small effect on the half-wave potential of the first polarographic wave, $(E_{1/2})_1$. For these substances and for nitrobenzene itself the values of $(E_{1/2})_1$ fall within the narrow ranges of −0.22 to −0.26 v. at *p*H

1.0, − 0.60 to −0.66 v. at *p*H 7.2 and −0.82 to −0.84 v. at *p*H 12.0. The polarogram of *p*-nitrotoluene which at *p*H 12 shows a slight indication of separating into two waves has a half-wave potential, calculated from the total wave height, of −0.91 v. *vs.* S.C.E. The replacement of hydrogen by methyl groups, however, has a much more striking effect on $(E_{1/2})_2$, the half-wave potential of the second wave observed at *p*H 1.0. Although in some cases this step is poorly defined, estimates of $(E_{1/2})_2$ are sufficiently accurate to show that the effect of the methyl substituents is to shift toward more positive values the potential at which this stage of reduction occurs.

TABLE II

HALF-WAVE POTENTIALS VOLTS *vs.* S.C.E.

Compound	*p*H 1.0 $(E_{1/2})_1$	*p*H 1.0 $(E_{1/2})_2$	*p*H 7.2 $(E_{1/2})_1$	*p*H 12.0 $(E_{1/2})_1$
Nitrobenzene	−0.24	−0.84	−0.62	−0.83
o-Nitrotoluene	− .26	− .64	− .66	− .84
m-Nitrotoluene	− .22	− .71	− .60	− .82
p-Nitrotoluene	− .24	− .71	− .62	− .91[a]
2-Nitro-1,4-dimethylbenzene	− .25	− .58	− .64	− .82
3-Nitro-1,2-dimethylbenzene	− .25	− .59	− .65	− .82
Nitromesitylene	− .38	....	− .75	− .88,[b] − 1.36[c]
Nitrodurene	− .38	....	− .75	− .87,[b] − 1.42[c]

[a] A slight inflection was observed in this case; since the "break" between the two steps is only barely perceptible, the value above refers to the total wave. [b]First wave. [c] Second wave.

One effect of the steric inhibition of resonance of a nitro group with a benzene ring is to render more difficult the reduction of the nitro group. At *p*H 1.0 the $(E_{1/2})_1$ values of nitromesitylene and nitrodurene are −0.38 v. *vs.* S.C.E., approximately 0.12 to 0.16 v. more negative than those for the other compounds studied; at *p*H 7.2 a similar shift in $(E_{1/2})_1$ is observed with the values for the hindered compounds approximately 0.09 to 0.15 v. more negative than those of the unhindered. Values of the half-wave potentials for nitromesitylene and nitrodurene at *p*H 12.0 are respectively −0.88 and −0.87 v. *vs.* S.C.E. for the first stage of reduction and −1.36 and −1.42 v. *vs.* S.C.E. for the second. These values are only approximate because of the poorly defined limiting heights of the waves.

TABLE III

DIFFUSION CURRENT CONSTANTS[a]

Compound	*p*H 1.0 $(i_d)_1$ $Cm^{2/3}t^{1/6}$	$(i_d)_t$[b] $Cm^{2/3}t^{1/6}$	*p*H 7.2 i_d $Cm^{2/3}t^{1/6}$	*p*H 12.0 i_d $Cm^{2/3}t^{1/6}$
Nitrobenzene	6.7	9.0	5.7	5.5
o-Nitrotoluene	6.8	9.1	5.2	5.4[c]
m-Nitrotoluene	6.6	9.2	5.4	5.9
p-Nitrotoluene	7.0	9.7	5.5	5.6[d]
2-Nitro-1,4-dimethylbenzene	7.3	9.3	4.9	5.3
3-Nitro-1,2-dimethylbenzene	7.5	9.4	5.1	5.6
Nitromesitylene	...	7.7	4.6	1.2[e]; 2.8[f]
Nitrodurene	...	7.6	5.1	1.9[e]; 5.2[f]

[a] Microamp./millimole/mg.$^{2/3}$sec.$^{1/2}$. [b] Calculated from the total wave height. [c] The single well-defined wave showed a slight tendency to break up into two waves; the diffusion current constant was calculated from the total wave height. [d] A slight inflection was observed in this case; since the "break" between the two steps is barely perceptible, the value above refers to the total wave height. [e] First wave. [f] Second wave.

The diffusion current constants of the nitro compounds listed in Table III were calculated from the Ilkovic equation using drop-times measured at the same potentials as the diffusion currents. For each of the compounds with an unhindered nitro group the ratio of the diffusion current constant of the first wave to that of the total wave at *p*H 1.0 is about 0.75. Since a value only slightly higher than this is obtained for the ratio of the diffusion current constant of the single wave of nitromesitylene or nitrodurene to the average value of the constant for the total wave of the unhindered compounds, the *n*-values of the over-all reactions in acid solution are probably different for the two classes of aromatic nitro compounds. The marked decrease in the values of the diffusion current constants on going from acid to neutral and alkaline solutions suggests a change in the nature of the products of the electrode reactions. At *p*H 7.2 and *p*H 12.0 these constants for a compound with an unhindered nitro group are approximately six-tenths as large as that for the total wave of the compound at *p*H 1.0. Furthermore, the diffusion current constants of nitromesitylene and nitrodurene at *p*H 7.2 are only slightly lower than the average value for the unhindered compounds under these conditions, suggesting that the *n*-values of the electrode reactions may not be too dissimilar. Although at *p*H 12 the polarograms of nitromesitylene and nitrodurene consist of two distinct waves with the second two or three times the height of the first, the poor definition of the total wave heights in these cases makes it difficult to estimate reliable values for the diffusion current constants.

Although it is clear from the data already presented that there are pronounced differences in the polarographic characteristics of normal aromatic nitro compounds and those in which resonance of the nitro group with the benzene ring is inhibited by bulky ortho substituents, it would be interesting to compare the electron requirements of the electrode reactions. Unfortunately the lack of reliable data for the diffusion coefficients of these compounds in the supporting electrolytes used prevents calculation of the *n*-values from the Ilkovic equation, but coulometric measurements[16] should provide an unequivocal answer to the problem.

Comparison of the polarographic behavior of the substances studied here with that of aliphatic nitro compounds is of interest because it would be

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[16] Lingane, THIS JOURNAL, 67, 1916 (1945).

anticipated that the characteristics of the hindered aromatic nitro compounds would show certain similarities to those of the aliphatic nitro derivatives. Unfortunately, however, the only data reported for the aliphatic compounds were determined in solutions in which nitromesitylene and nitrodurene are not sufficiently soluble to permit measurements to be made. The straight-chain primary and secondary aliphatic nitro compounds with one to four carbon atoms resemble the hindered aromatic compounds in that they have been reported to yield only a single polarographic wave in acid solution; on the other hand, the aliphatic compounds are apparently non-reducible in 0.1 M aqueous sodium hydroxide or tetramethylammonium hydroxide solution.[17] In 0.05 M aqueous sulfuric acid solutions the aliphatic compounds have half-wave potentials in the range -0.57 to -0.69 v. *vs.* S.C.E. and would appear to be somewhat more difficultly reducible in acid solution than any of the substances investigated in the present work. Although the shift in half-wave potentials toward more negative values on going from the unhindered to the hindered aromatic derivatives is in the direction anticipated from the values reported for the aliphatic nitro compounds, closer comparison of the polarographic behavior of nitromesitylene and nitrodurene with that of aliphatic nitro derivatives must await re-examination of the characteristics of the latter and determination of the *n*-values of the polarographic waves for members of both series.

Summary

The polarographic characteristics of nitrobenzene, *o*-, *m*- and *p*-nitrotoluene, 2-nitro-1,4-dimethylbenzene, 3-nitro-1,2-dimethylbenzene, nitromesitylene and nitrodurene have been examined in buffered 80% aqueous dioxane solutions at *p*H 1.0, 7.2 and 12. The behavior of nitromesitylene and nitrodurene is distinctly different from that of the aromatic nitro compounds examined in which steric inhibition of resonance does not exist.

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RECEIVED[18] OCTOBER 11, 1948

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(17) DeVries and Ivett, *Ind. Eng. Chem., Anal. Ed.*, **13**, 339 (1941).

(18) Original manuscript received June 2, 1948.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Quantitative Interpretation of the Polarographic Hydrolysis Current of Chromic Ion

BY JAMES J. LINGANE AND ROBERT L. PECSOK[1]

Chromic ion undergoes stepwise reduction at the dropping electrode, the first wave corresponding to reduction to chromous ion and the second to complete reduction to the metal.[2,3] Kolthoff and Lingane[4] called attention to the fact that the height of the second wave is significantly larger than twice the height of the first when the supporting electrolyte is unbuffered, and they attributed the discrepancy to the simultaneous discharge of hydrogen ion from the hydrolysis of the chromic ion. This has also been noted by Willis.[5]

In the present study this phenomenon has been investigated systematically, and interpreted quantitatively on the basis of diffusion current theory. Relations have been derived which are of general applicability in polarographic studies of hydrolytic equilibria in metal salt solutions.

Experimental

Polarographic measurements were made in an H-type cell provided with a saturated calomel electrode as previously described.[6] Atmospheric oxygen was removed by purified hydrogen or nitrogen. All measurements were made with the cell in a water thermostat at 25.0 ± 0.1°. The drop time of the capillary varied from three seconds with an open circuit to about two seconds at an applied potential of two volts, and was timed as necessary at each potential. An automatic m-measuring device[7] was employed.

Polarograms were either recorded with a Sargent Model XI Polarograph, or obtained with a manual apparatus based on a circuit previously described.[8]

Residual currents were obtained in all cases and the proper correction applied.

The *p*H of the solutions was measured with a glass electrode.

Chromic Solutions.—Stock solutions of 0.1000 M chromic chloride and chromic sulfate were prepared determinately by reduction of a known quantity of pure potassium dichromate with sulfur dioxide or hydrogen peroxide in the appropriate acid, and the excess reducing agent was removed by boiling. A neutral solution of chromic chloride was made up from the reagent grade hexahydrate and standardized by determination of the chromium content. The stock solutions were diluted to 0.01 M before use in order to increase the accuracy of measurement. The ionic state of the chromium in these solutions was believed to be an equilibrium mixture of the hexaaquo- and the dichlorotetraaquochromic ions.

A stock solution of 0.1 M chromic perchlorate was prepared by reduction of a known quantity of reagent grade sodium chromate with hydrogen peroxide in perchloric acid,

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(6) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

(7) J. J. Lingane, *ibid.*, **16**, 329 (1944).

(8) J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939).