form calcium chloride with all the calcium, and the heats of solution approach those in solutions of phosphoric acid.

Substitution of the heats of formation, $Ca(H_2PO_4)_2 \cdot H_2O(c)$, −816,820; $Ca^{++}(aq)$,[4] −129,770; $H_2PO_4^-(aq)$,[5] −311,320; and $H_2O(liq)$,[4] −68,317 cal. mole$^{-1}$ in the equation

$$Ca(H_2PO_4)_2 \cdot H_2O(c) + (aq) = Ca(H_2PO_4)_2 \cdot H_2O(aq) = Ca^{++}(aq) + 2H_2PO_4^-(aq) + H_2O(liq)$$

yields a value of −3910 cal. mole$^{-1}$ for the heat of solution of $Ca(H_2PO_4)_2 \cdot H_2O(c)$ at infinite dilution. This value represents the difference between large numbers; also, one of the values used in its derivation—the heat of formation of $H_2PO_4^-(aq)$—is uncertain. With the uncertainty involved in the extrapolation of the observed heats of solution to infinite dilution, the hypothetical heat of solution of $Ca(H_2PO_4)_2 \cdot H_2O(c)$ at infinite dilution can be fixed no closer than within the range −3 to −4 kcal. mole$^{-1}$.

WILSON DAM, ALA.

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[4] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

[5] Derived from the heat of formation of $H_3PO_4$ (aq), −309,440 cal. mole$^{-1}$, and the heat of the first ionization of $H_3PO_4$, −1880 cal. mole$^{-1}$, as reported by T. D. Farr, Tennessee Valley Authority, *Chem. Eng. Rept.* No. 8 (1950).

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

# Electrochemical Behavior of Aromatic N-Nitrosohydroxylamines

BY PHILIP J. ELVING AND EDWARD C. OLSON

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The electrochemical behavior of three aromatic N-nitrosohydroxylamines was studied: N-nitrosophenylhydroxylamine N-nitroso-α-naphthylhydroxylamine and N-nitroso-*p*-xenylhydroxylamine, whose ammonium salts are known as cupferron, neocupferron and *p*-phenylcupferron, respectively; the last is a new compound. Three well-defined polarographic waves can occur in the *p*H region from −0.4 to 12. The first wave split (change from wave I to II) results from a tautomeric equilibrium between the nitroso hydroxy and amine oxide forms; the second wave split (change from wave II to III) is due to a typical acid–anion equilibrium. Coulometric studies, and isolation and identification of major reduction products by macroscale electrolysis at controlled potential indicate that the reduction in acidic solution (waves I and II) proceeds by a process, or processes, involving a total of 6 electrons to the aromatic hydrazine. In alkaline solution (wave III) only 4 electrons are involved with the final product being the aromatic hydrocarbon; the mechanism proposed has been substantiated by following the change in *p*H of the solution with electrolysis of the nitrosohydroxylamine. The apparent discrepancies in previous work have been elucidated.

A systematic study of the polarographic and coulometric behavior of N-nitrosophenylhydroxylamine,[1] N-nitroso-α-naphthylhydroxylamine (neocupferron) and a new compound, N-nitroso-*p*-xenylhydroxylamine (*p*-phenylcupferron), usually added as the ammonium salts, was undertaken to elucidate the reduction pattern and to resolve apparent differences in the literature.[2,3] Such an investigation also served as background for the development of analytical methods including amperometric titration methods employing cupferron as titrant.

Previous polarographic study[2] of N-nitrosophenylhydroxylamine indicated two waves in the *p*H range from 1.1 to 12.5. A similar study[3] of N-nitroso-α-naphthylhydroxylamine, the abstract of which appeared after the present investigation was underway, described four polarographic waves in the same *p*H region; the apparent differences in behavior between the two closely related structures was not too convincingly explained; even so, the explanations involved selective emphasis. Attempted coulometric studies were unsatisfactory and the results were not given.[3]

## Polarographic Behavior[4]

Figures 1 and 2 and Table I summarize the variations of half-wave potential, $E_{1/2}$, and of limiting

TABLE I

DIFFUSION CURRENT CONSTANTS OF AROMATIC N-NITROSOHYDROXYLAMINES[a]

| | $I = i_d/Cm^{2/3}t^{1/6}$ | | |
|---|---|---|---|
| *p*H | Cupferron | Neocupferron | *p*-Phenylcupferron |
| 10% $H_2SO_4$ | 10.5 | 9.38 | 6.47 |
| 1.02 | 10.8 | 8.84 | 6.71 |
| 1.99 | 10.2 | 9.10 | 6.19 |
| 2.80 | 10.1 | 9.39 | 6.19 |
| 3.78 | 10.1 | 9.56 | 5.66 |

[a] These were measured on oxygen-free solutions, about 10 min. after mixing. The values, although reproducible, may be in slight error due to acid decomposition.

TABLE II

COMPOSITION OF MACILVAINE BUFFERS, IONIC STRENGTH = 1

| $Na_2HPO_4 \cdot 12H_2O$, g./l. | $H_3Cit \cdot H_2O$, g./l. | KCl, g./l. | *p*H |
|---|---|---|---|
| 1.4 | 20.6 | 74.5 | 1.99 |
| 14.7 | 16.7 | 68.7 | 2.80 |
| 27.6 | 12.9 | 62.8 | 3.78 |
| 36.9 | 10.2 | 55.5 | 4.72 |
| 45.2 | 7.7 | 48.9 | 5.69 |
| 58.9 | 3.7 | 40.4 | 6.76 |
| 69.6 | 0.6 | 32.9 | 7.58 |

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[1] The ammonium salt which is the form in which the compound is usually used, is called cupferron; for convenience, this name will henceforth be used to designate both the compound and its ammonium salt. The names, neocupferron and *p*-phenylcupferron, apply and will be used in the same sense.

[2] I. M. Kolthoff and A. Liberti, THIS JOURNAL, **70**, 1885 (1948).

[3] C. Calzolari and A. Donda, *Ann. Chim. (Rome)*, **43**, 753 (1953).

[4] Detailed tables of experimental data can be secured from the authors.

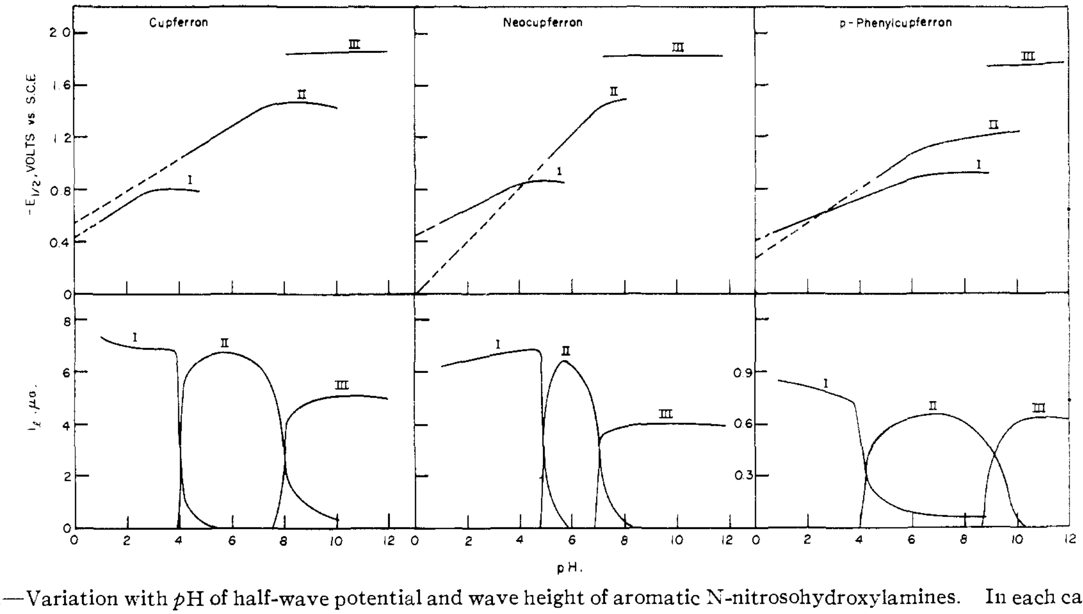

Fig. 1.—Variation with $p$H of half-wave potential and wave height of aromatic N-nitrosohydroxylamines. In each case curve I refers to wave I, II to wave II and III to Wave III. The concentrations are cupferron, 0.33 m$M$; neocupferron 0.32 m$M$; and phenylcupferron, 0.0062 m$M$.

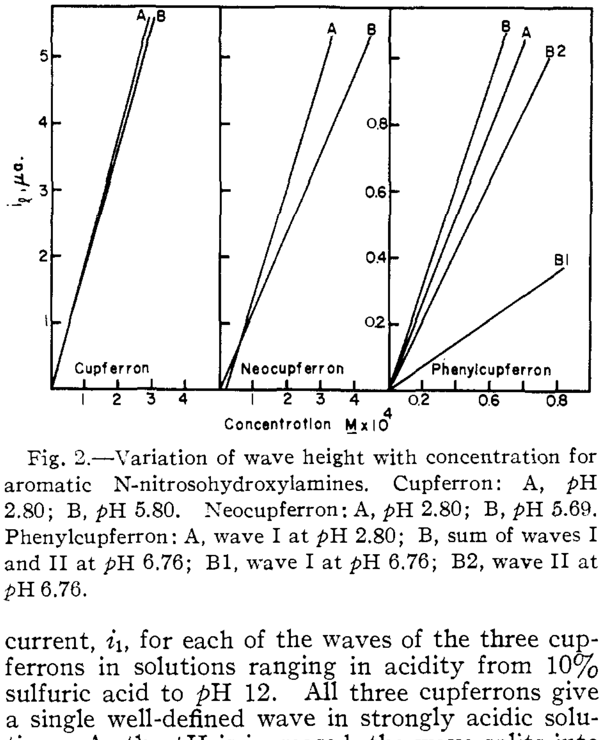

Fig. 2.—Variation of wave height with concentration for aromatic N-nitrosohydroxylamines. Cupferron: A, $p$H 2.80; B, $p$H 5.80. Neocupferron: A, $p$H 2.80; B, $p$H 5.69. Phenylcupferron: A, wave I at $p$H 2.80; B, sum of waves I and II at $p$H 6.76; B1, wave I at $p$H 6.76; B2, wave II at $p$H 6.76.

current, $i_l$, for each of the waves of the three cupferrons in solutions ranging in acidity from 10% sulfuric acid to $p$H 12. All three cupferrons give a single well-defined wave in strongly acidic solution. As the $p$H is increased, the wave splits into two at about $p$H 4 to 5. A second wave split occurs at somewhat higher $p$H. Extrapolation of the straight line portions of the plots of $E_{1/2}$ *vs.* $p$H to $p$H 0.00 for the first two waves of each compound leads to the expressions

Cupferron:

$_{\mathrm{I}}E_{1/2} = -0.42 - 0.132p\mathrm{H}$, $_{\mathrm{II}}E_{1/2} = -0.53 - 0.120p\mathrm{H}$
$_{\mathrm{III}}E_{1/2} = -1.85$

Neocupferron:

$_{\mathrm{I}}E_{1/2} = -0.44 - 0.100p\mathrm{H}$, $_{\mathrm{II}}E_{1/2} = +0.03 - 0.201p\mathrm{H}$
$_{\mathrm{III}}E_{1/2} = -1.82$

Phenylcupferron:

$_{\mathrm{I}}E_{1/2} = -0.40 - 0.081p\mathrm{H}$, $_{\mathrm{II}}E_{1/2} = -0.26 - 0.130p\mathrm{H}$
$_{\mathrm{III}}E_{1/2} = -1.75$

The significance of the coefficient of the $p$H is not clear. A coefficient of about 0.12 indicates that $E_{1/2}$ varies with the square of the hydrogen ion concentration; for a reversible reaction, this might be interpreted to mean that two hydrogen ions are involved per electron transferred. $E_{1/2}$ for the third wave is $p$H-independent in all three cases. Kolthoff and Liberti[2] give for the similar equation for their first cupferron wave, $_{\mathrm{I}}E_{1/2} = -0.58 - 0.128\ p\mathrm{H}$; this would tend to indicate that their first wave and the present second wave are identical.

Wave height is directly proportional to concentration (Fig. 2); $E_{1/2}$ is unaffected by change in concentration. Increasing the ionic strength at $p$H 1.08 from 0.1 to 1.0 shifts $E_{1/2}$ about 0.02 v. in a more positive direction for each compound.

**Current-controlling Processes.**—Because of the importance of the nature of the current-controlling process (diffusion, rate or adsorption) relative to the possible origins and reduction mechanisms of the waves, the variations of $i_l$ with both drop-time and temperature were determined in $p$H regions where wave I alone, both waves I and II, wave II alone, and waves II and III were present.

The proportionality of $i_l$ of the first two waves for all three compounds to the square root of the height of the mercury column and the magnitudes of the temperature coefficients of $i_l$ for the same waves indicate that the processes resulting in these waves are diffusion controlled, with the following exceptions: wave II in the region where waves II and III coexist is at least partially kinetic in nature; lack of indication of any kinetic character for wave I may be due to inability to resolve that wave more clearly in the presence of wave II.

Calzolari and Donda[3] found their first, second and fourth neocupferron waves to be diffusion-

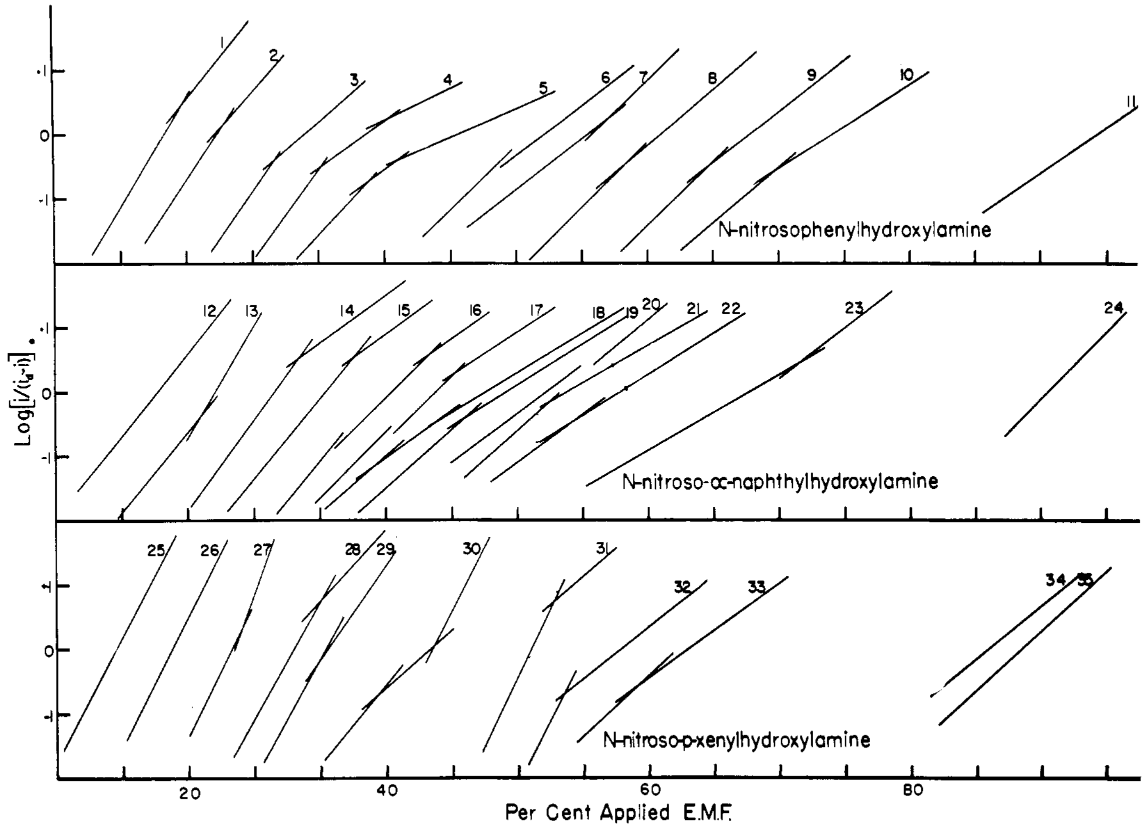

Fig. 3.—Logarithmic analysis of the polarographic waves of aromatic N-nitrosohydroxylamines over $pH$ range −0.4 to 12.

| Cupferron | | Neocupferron | | Phenylcupferron | |
|---|---|---|---|---|---|
| Curve | $p$H | Curve | $p$H | Curve | $p$H |
| 1 | 10% $H_2SO_4$ | 12 | 10% $H_2SO_4$ | 25 | 10% $H_2SO_4$ |
| 2 | 1.02 | 13 | 1.02 | 26 | 1.02 |
| 3 | 1.99 | 14 | 1.99 | 27 | 1.99 |
| 4 | 2.80 | 15 | 2.80 | 28 | 2.80 |
| 5 | 3.78 | 16 | 3.78 | 29 | 3.78 |
| 6 | 4.10 | 17 | 4.10 | 30 | 4.72 |
| 7 | 4.72 | 18 | 4.72 | 31 | 5.69 |
| 8 | 5.69 | 19 | 4.98 | 32 | 6.76 |
| 9 | 6.76 | 20 | 5.20 | 33 | 7.58 |
| 10 | 7.58 | 21 | 5.38 | 34 | 9.81 |
| 11 | 11.73 | 22 | 5.69 | 35 | 11.73 |
| | | 23 | 6.76 | | |
| | | 24 | 11.78 | | |

controlled at $p$H values where only a single wave was observed, *e.g.*, $p$H 1.9, 6.7 and 9.2; measurements made in regions of multiple waves did not yield interpretable results. Kolthoff and Liberti[2] found their first cupferron wave (already identified with the present wave II) to be kinetic controlled at $p$H 8.25 and the second wave to be diffusion controlled; they used the Brdicka–Wiesner equation[5] to calculate the kinetic current and found reasonable agreement between experimental and calculated values.

**Logarithmic Analysis of the Waves.**—Logarithmic analysis of the polarograms shows a multiplicity of processes to be occurring at the electrode (Fig. 3). Even in strongly acidic solution, the plot of log $[i/(i_d - i)]$ *vs.* $E$ for each wave shows more than one straight-line segment.

The irreversible nature of the electrochemical reduction of aromatic N-nitrosohydroxylamines at the D.M.E. is shown by the values of the reciprocal slopes of the various straight-line segments; in no case does $\alpha$, calculated from the slope as being equal at 25° to $0.059/\alpha$, have a value approaching 2. Likewise, the sum of the $\alpha$ values, when more than one process is involved, is never much greater than 2, although coulometric reduction (*cf.* next section) shows 6 electrons to be involved in the reduction in acidic solution and 4 in alkaline solution.

## Coulometric and Other Macroscale Reductions

**Coulometric $n$ Values.**—Coulometry at $p$H 3.50 show 6 electrons to be involved in the reduc-

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(5) R. Brdicka and K. Wiesner, *Collection Czechoslov. Chem. Communs.*, **12**, 138 (1947).

tion in acidic solution (experimental $n$ values: cupferron—6.1, 5.9, 5.9, 5.9; neocupferron—5.8, 6.0, 5.9, 5.9; phenylcupferron—5.9, 6.0, 5.9, 5.9).

Constant $n$ values were obtained only after correcting the observed values for decomposition and for unreduced compound remaining at the end of the electrolysis period. The former correction was computed by determining the rate of decomposition of the compounds in the coulometer under conditions identical to those during a coulometric run except that no current was passed through the cell. The correction for unreduced nitrosohydroxylamine was found to be necessary when electrolysis rates were measured.

In alkaline solution a correction for decomposition was unnecessary; however, more consistent results could be obtained by determining the residual concentration of reducible material after a fixed period of electrolysis than by carrying the reduction to completion. The number of electrons involved in reduction at *p*H 11.7 was found to be 4 (experimental $n$ values: cupferron—4.2, 3.8; neocupferron—4.1, 4.3, 4.0, 3.7, 4.4, 4.2; phenylcupferron—4.1, 3.8).

**Identification of Reduction Products.**—The chief reduction product or one of its common derivatives was isolated and identified for each aromatic N-nitrosohydroxylamine in both acidic and alkaline solution. The melting points of the isolated benzaldehyde adducts and the coulometric $n$ values show conclusively that in acidic solution aromatic N-nitrosohydroxylamines are reduced by a process or combination of processes involving a total of 6 electrons to the corresponding aromatic hydrazine.

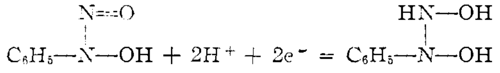
In alkaline solution the results indicate a four-electron reduction to the hydrocarbon. In all runs a strong odor of the aromatic hydrocarbon became apparent shortly after electrolysis began. In the cases of neo- and *p*-phenylcupferron, the naphthalene and biphenyl formed were filtered and recrystallized, and a melting point taken. In several runs the crude product was isolated, dried and weighed; between 40 and 60% of the weight of hydrocarbon anticipated was isolated. Low results could result from a number of factors, *e.g.*, the difficulties inherent in handling such small quantities of precipitate in the large apparatus required for electrolysis, the high vapor pressure of naphthalene and biphenyl coupled with the fact that a rapid stream of nitrogen was passed through the solution during the entire electrolysis period, and the possible reduction of the cupferrons by more than one mechanism resulting in the formation of some soluble reduction product; loss due to entrainment in the nitrogen stream would seem to be the major factor.

Several of the coulometer solutions after electrolysis under alkaline conditions were made strongly acidic and were then extracted several times with ether and chloroform to remove hydrocarbon and unreduced starting material. The resultant aqueous solution failed to give a test for an aromatic amine when tested with bromine water after neutralization, thus eliminating the possibility of reduction by a four-electron or other process to an aromatic amine.

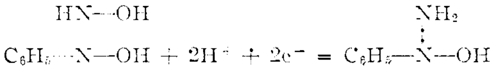
***p*H Change During Electrolysis.**—To examine the consequences of the subsequently proposed mechanism of reduction in alkaline solution, coulometric type runs were made in unbuffered alkaline solution, the purpose of which was to compare the experimentally observed rate of hydroxide ion production relative to hydroxylamine consumed to that predicted by the proposed mechanism. The data (Fig. 4) will be discussed subsequently.

## Nature of Reduction Path

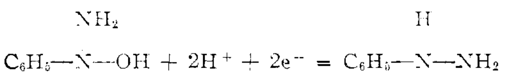
By assuming the diffusion coefficient of N-nitrosophenylhydroxylamine to equal that of benzoate ion and then calculating the number of electrons involved from the Ilkovic equation, Kolthoff and Liberti[2] considered the reduction of cupferron in acidic solution to be a six-electron process and postulated the reduction product to be phenylhydrazine. They proposed a reduction scheme involving three two-electron processes



$$C_6H_5\text{—}\overset{\overset{\displaystyle N{=}O}{|}}{N}\text{—}OH + 2H^+ + 2e^- = C_6H_5\text{—}\overset{\overset{\displaystyle HN\text{—}OH}{|}}{N}\text{—}OH \quad (1)$$



$$C_6H_5\text{—}\overset{\overset{\displaystyle HN\text{—}OH}{|}}{N}\text{—}OH + 2H^+ + 2e^- = C_6H_5\text{—}\overset{\overset{\displaystyle NH_2}{|}}{N}\text{—}OH \quad (2)$$

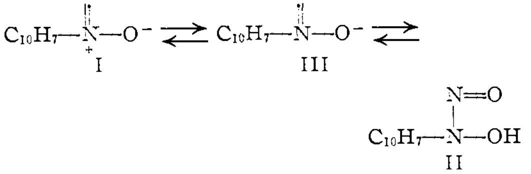


$$C_6H_5\text{—}\overset{\overset{\displaystyle NH_2}{|}}{N}\text{—}OH + 2H^+ + 2e^- = C_6H_5\text{—}\overset{\displaystyle H}{N}\text{—}NH_2 \quad (3)$$

They also concluded that in alkaline solution the reduction involves four electrons inasmuch as the polarographic wave height is two-thirds of that in acidic medium and suggested that the reduction product is an N-aminohydroxylamine.

Calzolari and Donda[3] in their similar neocupferron study suggested that the reduction proceeds in only two stages: a 4e$^-$ reduction of the amine oxide or nitrosohydroxy forms to the aminohydroxylamine (combination of equations 1 and 2) and then a 2e$^-$ reduction to the hydrazine (equation 3). The results of the present investigation, as subsequently discussed, indicate that both mechanisms may be operative in different restricted *p*H regions, but that a third mechanism is operative in the alkaline region.

Kolthoff and Liberti ascribed the first of the two cupferron waves they observed to reduction of the undissociated form of nitrosohydroxylamine and the second wave to reduction of its anion. Calzolari and Donda explain their four waves on the basis of a more complicated picture. The substitution of phenyl by naphthyl is assumed to facilitate the possibility of occurrence of both the amine oxide (I) and nitroso hydroxy (II) forms of neocupferron



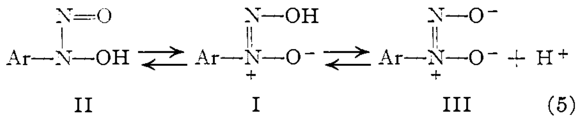
$$\underset{\text{I}}{C_{10}H_7\text{—}\overset{\overset{\displaystyle NOH}{\|}}{\overset{+}{N}}\text{—}O^-} \rightleftarrows \underset{\text{III}}{C_{10}H_7\text{—}\overset{\overset{\displaystyle N\text{—}O^-}{\|}}{N}\text{—}O^-} \rightleftarrows \underset{\text{II}}{C_{10}H_7\text{—}\overset{\overset{\displaystyle N{=}O}{|}}{N}\text{—}OH} \quad (4)$$

They also assume the dissociation constant for the equilibrium, I $\rightleftarrows$ III + H$^+$, to be greater than that for II $\rightleftarrows$ III + $H^+$, I to be more readily reducible than II, and the anion III to be common for both equilibria. Their first wave, assumed due to $4e^-$ reduction of I, decreases with increasing *p*H due to formation of anion III. The latter then recombines with $H^+$ to form the less highly dissociated II whose $4e^-$ reduction results in the second wave. The third wave, which is very ill-defined, is ascribed to the further $2e^-$ reduction of the $4e^-$ reduction products of I and II. The fourth wave which occurs in the alkaline region and is more or less *p*H-independent is assigned to the reduction of III.

### Relation of Wave Pattern to Equilibrium Processes

Since the aromatic N-nitrosohydroxylamines are weak acids, a double polarographic wave observed in the *p*H region corresponding to or somewhat greater than the $pK_a$ of the nitrosohydroxylamine in question may be due to the fact that an acid and its anion are usually reduced at different potentials.[6] The $pK_a$ of cupferron has been estimated[2,7a] as 4.28 in solution of low ionic strength; it is also given as 5.3.[7b] The large extent of acid dissociation has been cited as evidence for the existence of cupferron largely in the amine oxide rather than in the nitroso hydroxy form.[7b] For use in the present investigation, the apparent ionization constants were determined spectrophotometrically at an ionic strength of 1; these $pK_a$ values are 4.11, 3.92 and 3.97 for cupferron, neocupferron and *p*-phenyl cupferron, respectively.[8] Examination of Fig. 1 reveals the appearance of a second polarographic wave for each compound in the *p*H region corresponding approximately to the spectrophotometric $pK_a$.

The following equilibrium between the nitroso hydroxy form (II), amine oxide (I) and anion (III), which is a radical revision of that (equation 4) postulated by Calzolari and Donda,[3] is, as subsequently discussed, in harmony with the data of Figs. 1 and 3, and furnishes a basis for the formulation of the reduction mechanism



$$\underset{\text{II}}{\text{Ar—}\overset{\text{N=O}}{\overset{|}{\text{N}}}\text{—OH}} \rightleftarrows \underset{\text{I}}{\text{Ar—}\underset{+}{\overset{\text{N—OH}}{\overset{\|}{\text{N}}}}\text{—O}^-} \rightleftarrows \underset{\text{III}}{\text{Ar—}\underset{+}{\overset{\text{N—O}^-}{\overset{\|}{\text{N}}}}\text{—O}^-} + \text{H}^+ \qquad (5)$$

**Waves I and II.**—Since no decrease in diffusion current accompanies the first wave split, the latter would seem to result from the two acid forms of the cupferron which can exist in tautomeric equilibrium. Additional support for this postulate comes from the *p*H dependence of waves I and II, and the expected relative ease of reduction and the acidic strengths of the two forms. The apparently diffusion controlled nature of wave I may result from a relatively slow rate of interconversion of the two forms, as well as from failure to resolve waves I and II clearly. The present authors tend, in common with others, to favor the amine oxide being the predominant form in solutions varying from neutral to slightly acidic (*p*H 4); in more strongly acidic solution (*p*H 1–2) the nitroso hydroxy form appears to predominate.

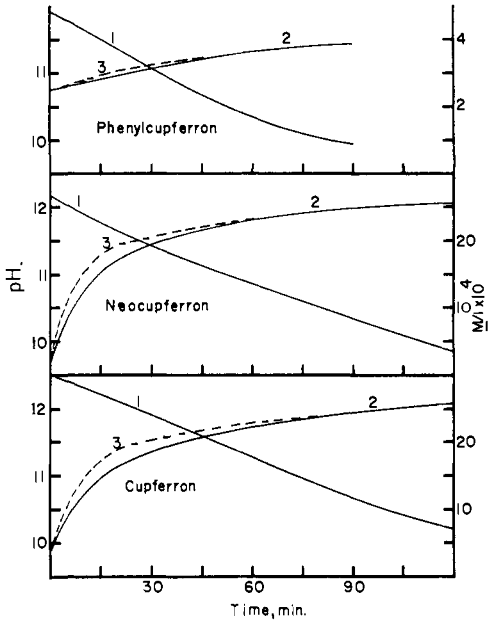
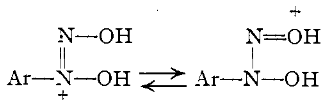


Fig. 4.—Rates of electrolysis and of increase in *p*H during the electrolysis of aromatic N-nitrosohydroxylamines in unbuffered alkaline solution: 1, rate of electrolysis; 2, calculated rate of increase in *p*H for liberation of 5 moles of hydroxide ion per mole of compound reduced; 3, measured rate of increase in *p*H.

The present assignment of wave I to the nitroso hydroxy form and of wave II to the amine oxide form is contrary to that of Calzolari and Donda, but is in harmony with the facts cited. The mechanism for the interconversion of I and II in acidic solution rather than proceeding through a common anion as postulated by Calzolari and Donda more likely occurs through the cyclic form resulting from hydrogen bonding or through a protonated species



$$\text{Ar—}\underset{+}{\overset{\text{N—OH}}{\overset{\|}{\text{N}}}}\text{—OH} \rightleftarrows \text{Ar—}\overset{\overset{+}{\text{N=OH}}}{\overset{|}{\text{N}}}\text{—OH} \qquad (6)$$

The polarographic waves of the two tautomeric forms of cupferron coexist over a very narrow *p*H region; the height of the wave is the same before and after the first wave split (Fig. 1). For these reasons, an unfortunate choice of a buffer interval from *p*H 3.1 to 4.4 (at which the first wave has virtually disappeared) resulted in the failure of the previous investigators[2] to find an equilibrium corresponding to I $\rightleftarrows$ II. They postulated, and quite correctly for their data, a very large kinetic current for cupferron in the *p*H range of 4 to 8. However, on the basis of the present investigation it appears that their second wave actually corresponds to the third cupferron wave and that the *p*H of 7.2 reported by them as that where the two cupferron waves are equal, actually refers to the second and third waves. Quite commonly the apparent polarographic *pK* of an acid is found to lie from a few

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[6] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1952.

[7] (a) I. V. Pyatnitokii, *Zhur. Anal. Khim.*, **1**, No. 2, 135–139 (1946); *C. A.*, **41**, 725 (1947); (b) L. F. and M. Fieser, "Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1956, pp. 606–607.

[8] P. J. Elving and E. C. Olson, This Journal, **78**, 4206 (1956).

tenths to several $pH$ units higher than the values determined by conductance or potentiometric methods because of the kinetics of the acid-anion process at the electrode surface.

**Calzolari and Donda's Third Wave.**—If allowance is made for the transition from the first to the second $pH$-dependent wave inadvertently missed in the earlier cupferron study, the present general wave picture reconciles those encountered in the two previous polarographic studies[2,3] of the aromatic nitrosohydroxylamines. A major difference is the reported $4e^-$ neocupferron wave followed by an ill-defined $2e^-$ wave in the acidic region,[3] as compared to the $6e^-$ wave calculated on the basis of analogy for cupferron[2] and found experimentally by coulometric measurement for all three cupferrons in the present study. The conclusions of Calzolari and Donda[3] relative to the number of electrons involved in their neocupferron waves were based solely on the relative magnitudes of the waves and on the opinion that the polarographic reduction of the aromatic nitrosohydroxylamines was a $6e^-$ process. The presence of their ill-defined third wave was probably due to the rather complicated buffer systems employed which resulted, as $pH$ was changed, in considerable variation not only in ionic strength but also in the relative amounts of the various phosphate, citrate and borate species, many of which may interact with the reducible organic functional grouping to alter its ease of reduction and perhaps even to affect its polarographic wave pattern by separating the potentials required for the various steps in the over-all reduction process, *e.g.*, the sequence of three steps described in equations 1 to 3.

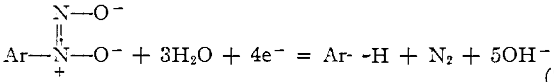
On the basis of the preceding discussion, it is interesting to compare the wave patterns found by Calzolari and Donda with the logarithmic analysis of the waves (Fig. 3); within the $pH$ region in which they observed the appearance and disappearance of their third wave, the slope analyses show a change from three to two straight-line segments.

## Reduction Mechanism

Logarithmic analysis of the polarographic waves of the compounds over $pH$ range 1 to 12.5 (Fig. 3) indicates that, even in the steeply rising region of the polarographic wave which was the region analyzed, marked changes occur. Neo- and $p$-phenylcupferron show a single straight line in very strongly acidic media, but at $pH$ 2 there are in all cases two distinct straight-line segments to the log plot. As the $pH$ is increased, three straight-line segments appear in every case in the $pH$ region immediately preceding the first wave split. After appearance of the second wave, analysis of the first wave gives only a single straight line, but analysis of the second wave again produces two straight lines. Only two straight lines are formed after the disappearance of the first wave.

Therefore, there seems to exist a $pH$ region, *ca.* 2 to 7, in which the reduction proceeds *via* three $2e^-$ steps, as suggested for cupferron by Kolthoff and Liberti,[2] and $pH$ regions, *ca.* 0 to 2 and *ca.* 7 to 10, in which a $4e^-$ reduction is probably followed by a $2e^-$ reduction, as suggested for neocupferron by Calzolari and Donda.[3] In very strongly acidic solution the reduction of the $\alpha$-naphthyl and $p$-xenyl derivatives appears to take place in a single $6e^-$ step; no such region was found for the phenyl compound.

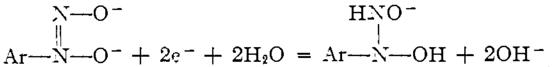
**Wave in Alkaline Solution.**—The third wave at higher $pH$ represents the $4e^-$ reduction of the anion to the aromatic hydrocarbon. Inasmuch as logarithmic analysis of the polarographic waves after the second wave split gives only a single straight line, reduction in alkaline solution occurs in an effectively single $4e^-$ step, *i.e.*, the processes involving the transfer of all four electrons are controlled by a single step



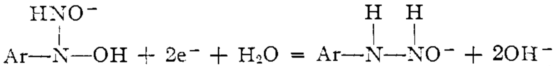
$$\mathrm{Ar{-}\underset{+}{\overset{\overset{N-O^-}{\|}}{N}}{-}O^- + 3H_2O + 4e^- = Ar{-}H + N_2 + 5OH^-} \qquad (7)$$

If equation 7 is correct, 5 moles of hydroxide ion should be produced for each mole of aromatic N-nitrosohydroxylamine reduced. By carrying out the reduction at controlled potential in unbuffered alkaline solution, it was possible to follow both the increase in $pH$ of the solution and the decrease in concentration of N-nitrosohydroxylamine. On comparing the measured $pH$ as a function of time with that calculated from the measured decrease in concentration of reducible compound on the basis of 5 moles of hydroxide ion produced per mole of N-nitrosohydroxylamine consumed (Fig. 4), good agreement is found except in the region corresponding to the beginning of the electrolysis. Furthermore, by calculating the $pH$ assuming production of 4 and 6 moles of hydroxide ion per molecule reduced and plotting the experimental and calculated curves on an enlarged scale, it is apparent that the experimental curve corresponds much more closely to the curve calculated for 5 hydroxyl ions per mole of reduced N-nitrosohydroxylamine than to either of the other curves.

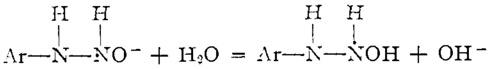
It is possible to postulate a stepwise reduction to an aromatic hydroxyhydrazine followed by rearrangement in alkaline solution to the hydrocarbon, nitrogen and water since this rearrangement is known to occur in the presence of alkali[9]



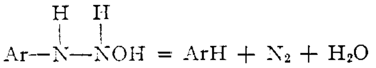
$$\mathrm{Ar{-}\underset{+}{\overset{\overset{N-O^-}{\|}}{N}}{-}O^- + 2e^- + 2H_2O = Ar{-}\overset{\overset{HNO^-}{|}}{N}{-}OH + 2OH^-} \qquad (8)$$



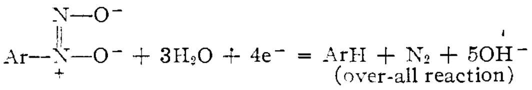
$$\mathrm{Ar{-}\overset{\overset{HNO^-}{|}}{N}{-}OH + 2e^- + H_2O = Ar{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{H}{|}}{N}O^- + 2OH^-} \qquad (9)$$



$$\mathrm{Ar{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{H}{|}}{N}O^- + H_2O = Ar{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{H}{|}}{N}OH + OH^-} \qquad (10)$$



$$\mathrm{Ar{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{H}{|}}{N}OH = ArH + N_2 + H_2O} \qquad (11)$$



$$\mathrm{Ar{-}\underset{+}{\overset{\overset{N-O^-}{\|}}{N}}{-}O^- + 3H_2O + 4e^- = ArH + N_2 + 5OH^-} \qquad \text{(over-all reaction)} \quad (12)$$

The over-all reaction (equation 12) is obviously identical with that previously proposed (equation 7).

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(9) F. D. Chattaway, *J. Chem. Soc.*, **93**, 270 (1908).

**Relative Ease of Reduction.**—The general pattern for the waves of all three compounds is that of phenylcupferron being the most easily reducible and neocupferron the most difficultly reducible. This pattern correlates with the *p*-xenyl group being the most electron-withdrawing and the naphthyl group the least.

## Possible Analytical Applications

**Determination of an Individual Cupferron.**—Since single well-defined polarographic waves are obtained for the aromatic N-nitrosohydroxylamines only below about *p*H 3.5 (Fig. 1), only the diffusion current constant values below *p*H 4 are pertinent for their polarographic determinations (Table I). The direct proportionality of diffusion current to concentration permits the ready determination of the individual compounds. The analytical precision ranges from about ±2 for cupferron to ±4 for neocupferron. The rapid decomposition of neocupferron in acidic solution is probably the major cause of the lack of precision in its polarographic determination.

The potential regions subtended by the polarographic waves of these compounds in acidic solution below *p*H 4 are so low, *i.e.*, $-0.4$ to $-0.8$ v. *vs.* S.C.E., that there should be few interferences among the organic compounds usually associated with the aromatic N-nitrosohydroxylamines.

$E^{1}/_{2}$ values for the various cupferrons are sufficiently close to one another at a given *p*H to make the individual determination of any one cupferron in the presence of any other impossible, except perhaps by derivative polarography.

**Basis for Amperometric Titration.**—The previous discussion indicates use of aromatic N-nitrosohydroxylamines as reagents for titrations employing amperometric detection of the equivalence point to be practical. Kolthoff and Liberti[10] described the use of cupferron in the amperometric titration of Fe(III) and Cu(II), although the titration was preferably performed at potentials at which only the reduction current due to the metal ion was measured.

Use of neocupferron as a titrant is somewhat limited by its extremely rapid rate of decomposition in strongly acidic solution, as indicated by failure of the straight-line relation between concentration and $i_l$ at *p*H 2.80 to pass through zero current at zero concentration (Fig. 2). Use of neocupferron is also limited by the fact that oxygen-free aqueous solutions of neocupferron decompose much more rapidly than do similar solutions of cupferron or phenylcupferron.

The use of *p*-phenylcupferron is restricted to the titration of minute amounts of metals since the solubility of the reagent is much less than that of either cupferron or neocupferron. An aqueous solution of the ammonium salt of N-nitroso-*p*-xenylhydroxylamine, saturated at 25°, contains only about 0.65 mg./ml. (approximately $3.1 \times 10^{-3}$ *M*). The solubility of the free acid is, however, much less, being about one-fiftieth of this value. Oxygen-free aqueous solutions of this compound are considerably more stable than those of either cupferron or neocupferron. This increase in stability would be advantageous for the titration of very low concentrations of metals as would the lower solubility of the metal salts of *p*-phenylcupferron.[8]

Because of the low solubility of *p*-phenylcupferron and the instability of neocupferron, cupferron is considered best suited of the three N-nitrosohydroxylamines for the development of general titration procedures in spite of the somewhat greater solubility of its metallic salts. Procedures for amperometric titration of Group IVB metal ions with cupferron have been published.[11]

## Experimental

**Cupferrons.**—G. F. Smith Chemical Co. reagent grade cupferron (ammonium salt of N-nitrosophenylhydroxylamine) was recrystallized twice from ethanol after treatment with Norit and finally once more from ethanol; the dried crystals (m.p. 162.5–163.5°) so purified are essentially 100.0% pure.[11a] Neocupferron (ammonium salt of N-nitroso-α-naphthylhydroxylamine) was prepared essentially by Smith's method[12] (m.p. 124–126°).

*p*-Phenylcupferron (ammonium salt of N-nitroso-*p*-xenylhydroxylamine) is a new compound which was prepared as follows: 10 g. of *p*-nitrobiphenyl was dissolved in a mixture of 500 ml. of 95% ethanol, 60 ml. of water and 6 g. of $NH_4Cl$; 10 g. of zinc dust was then added in one-gram portions with vigorous mechanical stirring and continuous cooling with tap water. After the reaction was complete, as indicated by a decrease in temperature of the reaction mixture, stirring was continued at room temperature for 30 min. The solution was then filtered into 30 ml. of glacial acetic acid, which appears to stabilize the hydroxylamine[13]; the resulting solution was then poured into a liter of cold water. The *p*-xenylhydroxylamine was filtered by suction and dissolved at once in 300 ml. of ether. After being dried over anhydrous sodium sulfate, the ether layer was filtered, cooled to 0° and saturated with ammonia gas. Freshly prepared *n*-butyl nitrite[14] was rapidly added dropwise, with vigorous mechanical stirring and passage of a rapid stream of ammonia, until 0.56 g. of butyl nitrite had been added for each gram of *p*-xenylhydroxylamine. The amonium salt of N-nitroso-*p*-xenylhydroxylamine which precipitated as very pale yellow platelets was filtered, washed with several portions of ether, and dried (m.p. 177–179°); yield was 64% of theory.

*Anal.* Calcd.: C, 62.13; H, 5.41; N, 18.23. Found: C, 62.33; H, 5.63; N, 18.23.

All three cupferrons were stored in the dark over ammonium carbonate; solutions of desired concentrations were prepared immediately before use by dissolving weighed portions of the crystalline salts in oxygen-free water.

**Other Reagents.**—Eastman Kodak white label grade tetramethylammonium bromide was purified by recrystallization. The salt was dissolved in the minimum amount of boiling reagent grade methanol and filtered, while hot, into an equal volume of reagent grade acetone. The mixture was then cooled to 0°; the crystals which formed were filtered, washed with cold 1:1 methanol–acetone and dried. This procedure gave a salt of sufficient purity to be used as a polarographic background electrolyte for potentials as negative as $-2.2$ v. *vs.* S.C.E.

A stock solution of tetramethylammonium hydroxide was prepared from purified bromide and freshly precipitated silver hydroxide.[15]

Nitrogen used for purging solutions of oxygen was first passed through chromous sulfate solutions to remove residual oxygen, then through distilled water to remove spray and finally through a portion of the solution to be purged

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[10] I. M. Kolthoff and A. Liberti, *Analyst*, **74**, 635 (1949).

[11] (a) E. C. Olson and P. J. Elving, *Anal. Chem.*, **26**, 1747 (1954); (b) P. J. Elving and E. C. Olson, *ibid.*, **27**, 1817 (1955); **28**, 251, 338 (1956).

[12] G. F. Smith, "Cupferron and Neocupferron," G. F. Smith Chemical Co., Columbus, Ohio, 1938.

[13] H. Gilman and J. E. Kirby, THIS JOURNAL, **48**, 2190 (1926).

[14] A. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943.

[15] E. S. Peracchio and V. W. Meloche, THIS JOURNAL, **60**, 1770 (1938).

in order to obtain vapor pressure equilibration. All other chemicals, including those used in buffer preparation, were of reagent or C.P. grade and were used without further purification; they were "polarographically pure."

**Apparatus.**—A Sargent Model XXI Polarograph, a Leeds & Northrup Model E Electro-Chemograph and a Fisher Elecdropode were used; potentials were checked with a Leeds & Northrup Type K potentiometer. A thermostated, jacketed H-type polarographic cell[16] containing a saturated calomel reference electrode was used. When changing from one temperature to another (20, 25 or 30 ± 0.1°), at least 24 hr. was allowed for the S.C.E. to reach thermal equilibrium. Capillaries, prepared from Corning marine barometer tubing, had $m^{2/3}t^{1/6}$ values at open circuit in water at 25° at 68 cm. mercury head of (1) 2.06, (2) 2.17 and (3) 2.04 mg.$^{2/3}$ sec.$^{-1/2}$; one capillary used only in drop-time studies had $m^{2/3}t^{1/6}$ = 1.75 at 81 cm.

The coulometric apparatus was a modification of that of Lingane,[17] employing a water-jacketed (25 ± 0.1°) electrolysis cell, a stirred massive mercury electrode, a large external silver anode and an oxygen–hydrogen coulometer. The cathode potential was measured against S.C.E. with the Type K potentiometer.

A Beckman Model G $p$H meter was used to measure $p$H; in the alkaline region a Type E electrode was employed.

**Polarographic Procedure.**—A weighed portion of the reducible compound was dissolved in oxygen-free water and then diluted to the desired concentration with a stock solution of background electrolyte which had also been purged with nitrogen. The polarographic cell was rinsed twice with the test solution and then filled; the capillary was introduced and a rapid stream of nitrogen passed through the cell for 2 to 3 min., during which time the initial potential was set at the desired value. Nitrogen was passed over the solution during the polarographic run. All test solutions contained from 0.01 to 0.02% gelatin as a maximum suppressor. Potentials are reported *vs.* S.C.E. and at 25° unless otherwise noted; cell $iR$ drops were negligible.

Constant ionic strength MacIlvaine buffers (Table II) were used between $p$H 2 and 7.6. Buffers of ionic strength 0.2 and 0.3 for use between $p$H 7 and 12 were prepared by titrating a solution of 0.05 $M$ $H_3PO_4$ with 0.1 $M$ tetramethylammonium hydroxide to the desired $p$H; both the acid and hydroxide solutions were approximately 0.1 $M$ in tetramethylammonium bromide.

**Coulometric and Macroscale Electrolysis Procedures.**—The background electrolyte was deoxygenated in the electrolysis cell with a rapid nitrogen stream which was maintained throughout the experiment. The cathode mercury was then added; the bridge from the reference S.C.E. was adjusted so that it just touched the vigorously stirred mercury surface; the gas coulometer, in which the solution had just been saturated with hydrogen and oxygen,[17] was connected in series with the cell. The potential of the mercury cathode was made several tenths of a volt more negative than that at which the run was to be made; electrolysis was continued until the last traces of reducible impurities had been removed as indicated by the decrease in current.

Without breaking the circuit, the applied potential was reduced until the cathode potential attained the desired value; the coulometer buret was read; the deoxygenated sample solution was added to the cell and the potential readjusted to the desired value which was maintained during electrolysis.

After electrolysis had proceeded for 2.0 to 2.5 hr., the circuit was opened, a sample of the cell solution withdrawn and the residual aromatic N-nitrosohydroxylamine concentration determined polarographically. From the decrease in concentration and the volume of gas evolved, the number of electrons involved in the electrode reaction was calculated after making the necessary corrections,[17] including, if required, those for the homogeneous decomposition of the cupferron. In addition, the main product of the electrolytic reduction was isolated and identified as follows.

In the case of an acidic solution, the solution was drained from the cell and 2 or 3 drops of benzaldehyde was added followed by sufficient ethanol to take the benzaldehyde into solution; the mixture was then set aside. In all cases a precipitate appeared within 15 or 20 min.; however, additional time was allowed for the reaction to proceed to completion. After about 2 hr., an equal volume of water was added and the mixture cooled to 0° in an ice-bath. The precipitate was isolated and recrystallized at least twice from ethanol–water mixture; after drying, its melting point was determined. The benzaldehyde adducts isolated from the solutions of the products formed by electrolysis in acidic solution had the following melting points (literature values in parentheses for the $RHN-NH_2$–benzaldehyde condensation products where R is phenyl, α-naphthyl or $p$-xenyl): cupferron, 156–158° (155–156°); neocupferron, 143–144° (144–145°); $p$-phenylcupferron, 151–152° (153°).

In alkaline solution, the reduction product precipitated from the electrolysis solution and could be isolated by filtration. The product precipitated from neocupferron solution melted at 78–79° (m.p. of naphthalene, 80.2°) and the product from $p$-phenylcupferron solution at 68–69° (m.p. of biphenyl, 69–70°).

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[16] J. C. Komyathy, F. Malloy and P. J. Elving, *Anal. Chem.*, **24**, 431 (1952).

[17] J. J. Lingane, THIS JOURNAL, **67**, 1916 (1945).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# A Spectrophotometric Study of the Indium–Bromide Complex Ions[1]

BY EUGENE A. BURNS AND DAVID N. HUME

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The aqueous bromide complexes of indium have been investigated by means of ultraviolet spectrophotometry. The spectra obtained can best be interpreted by terms of the mono-, di-, tri- and tetrabromoindium ions whose stepwise formation constants have been evaluated at an ionic strength of 4.00 $M$. Analysis of the data by five distinct methods gives average values for the stepwise formation of $InBr^{++}$, $InBr_2^+$, $InBr_3$ and $InBr_4^-$ of 120, 19, 4 and 7, respectively.

In the past three years, fourteen articles have appeared in the literature concerning the nature of indium(III) in halide media, twelve specifically dealing with the bromide system. Table I lists the values of the consecutive formation constants of the indium bromide system observed by these workers, together with the values obtained in this investigation. The considerable lack of agreement among previous workers prompted the present investigation using spectrophotometric methods which are not subject to some of the difficulties in other methods.

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[1] Abstracted from a thesis submitted by Eugene A. Burns in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology, May 4, 1956.