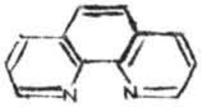
CHAPTER 1

INTRODUCTION

1,10-Phenanthroline or o-phenanthroline (I) is one of diazaphenanthrenes with one nitrogen atom in each of the outer rings (1). It was first obtained by Blau both from O-phenylenediamine and 8-aminoquinoline (2). Most workers (3, 4) have found that when 8-aminoquinoline is starting material the yield is better than that from O-phenylenediamine.



I

1,10-Phenanthroline has a well-marked tendency to combine with various metallic ions, especially with divalent ions of the transition groups. The complex with ferrous ion, known as "ferroin", is considerably importance in analytical chemistry. The relative inertness of phenanthroline toward chemical reactions other than salt-formation or chelation is a significant asset in the analytical application. A correlation between the anionoid and cationoid reactions and the electron distributions in the phenanthroline molecule as calculated by the method of molecular orbitals has been shown by Longeut-Higgins and Coulson (5). The most active positions towards nucleophilic reagents are the 2,9 and 4,7 positions, electrophilic reagents preferentially attack position 5,6 and 3,8 where electron densities are higher. Substitutions of hydrogen by other groups in any of these positions would be expected to produce appreciable alternation in properties.

There are many derivatives of 1,10-phenanthroline, such as 1,10-phenanthroline-1-oxide, 2-carboxy, 2-cyano-, 2-methyl-, 2-methoxy-, 4-nitro-, 5-nitro-1, 10-phenanthroline etc., prepared from 1,10-phenanthroline and 8-aminoquinoline (2).

Millefiore (6) has studied polarographic reduction of azines in acetonitrile, and reported the polarographic reduction potentials and the reduction mechanisms of some mono and diaza compounds in acetonitrile. In addition, polarograms of 1,10-, 1,7- and 4,7-phenanthroline in aprotic solvent have been investigated.(7) Little can be said about the literature concerning electrochemical studies of 1,10-phenanthroline and its derivatives. This was the contributing reason for the present study.

In this study electrochemical properties of 1,10-phenanthroline and its derivatives are interested. The investigation is intended as a polarographic study of the electron transfer mechanism of 1,10-phenanthroline and its derivatives in ca. 67% methanol of various pH, as well as a survey of the effect of substituent groups of 1,10-phenanthroline on the polarographic half wave potentials.

Polarographic analysis is based on the current-potential curve obtained with a polarizable dropping mercury electrode immersing in the solution of electroactive substance and an unpolarizable reference electrode. The current-potential curve shows the sigmoidal form of a wave or of a step, since the electrolytic current reaches a certain limiting value (limiting current) which does not further increase with increasing voltage. There are many types of polarographic limiting currents (8). The most important type of polarographic limiting current used for practical purpose is diffusion current. The magnitude of a diffusion current is limited by the rate of diffusion of electroactive species from the bulk solution to the surface of the mercury electrode. The magnitude of the diffusion current is given by the Ilkovic (9) equation.

$$i_d = 0.627\ nFD^{\frac{1}{2}}m^{\frac{2}{3}}t^{\frac{1}{6}}C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where i_d = the diffusion current (μA)

n = the number of the electron transfer

D = the diffusion coefficient (cm^2/sec)

m = the rate out flow of mercury (mg/sec)

t = the drop time (sec)

C = the concentration of electroactive species (millimole/liter)

For analytical application, the above equation is simplified to

$$i_d = kC \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

To ensure the linear relationship between the diffusion current and concentration, it is necessary to maintain the temperature and mercury pressure constant. Thus the factor k is a constant.

Kinetic current is the polarographic limiting current, caused by an electroactive species other than the substance present in the bulk solution; forming by a chemical reaction in the neigbourhood of the electrode, and consequently undergoes reduction or oxidation at the dropping mercury electrode. In such instances, the rate of a chemical process is slow enough to be the determining step of the electrode process.

Two types of polarographic limiting currents are described as catalytic currents. In the first type the limiting current of an electroactive substance is increased in the presence of a catalyst, which itself is either polarographically inactive or reduce at considerably more negative potential. In the second type, the polarographically inactive catalyst causes a shift in the reduction potential of the polarographically active substance toward more positive potential.

Adsorption current is the limiting current due to some forms of active substance are adsorbed at the dropping mercury electrode. In such instances two waves may be observed on a polarogram, one which corresponds to the reduction or oxidation of the free form and the other of the substance in the adsorbed state.

Other polarographic currents are the charging and migration current. Current owing to the charging of the electrode to the respective potential is called the charging or condenser current. It is observed even in pure supporting electrolyte. In absence of any supporting electrolyte, if charged electroactive particles are present in the solution, the migration of these charged particles in the electric field between the two electrodes takes placed, and resulting migration currents. In polarographic study, migration currents are undesired and are eliminated by adding a supporting electrolyte. Normally, the molar concentration of a supporting electrolyte is more than twenty times higher than that of the substance studied.

Another important characteristic of a polarogram is the reversibility of electrode reaction. A reversible electrode process can be symbolized as:

$$\mathrm{Ox} + ne \rightleftharpoons \mathrm{Red}$$

For such system, if the value of D_{Ox} and D_{Red} are equal and f_{Ox} and f_{Red} (f is activity coefficient) are the same the half wave potential is proportional to the standard free energy change ΔG^{o} (10)

$$E_{1/2} = -\frac{\Delta G^{o}}{nF} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

An irreversible electrode process can be written as:

$$\mathrm{Ox} + ne \rightleftharpoons \mathrm{Red}$$

In this case the half wave potential is a function of the free energy of activation, $\Delta G^{\ddagger}$, provided that the changes in αn are known (10)

$$E_{1/2} \sim \frac{\Delta G^{\ddagger}}{\alpha nF} + \frac{RT}{\alpha nF} \ln 0.886\sqrt{\frac{t}{D}} \quad \ldots\ldots\ldots\ldots \quad (4)$$

where α = electron transfer coefficient.

Whenever possible the polarographic waves of both the oxidized form and reduced form of a given system should be compared. For a reversible process, if the oxidized form alone is present in the solution, the cathodic half wave potential, at which the current is equal to one half of the diffusion current, is given by (10)

$$E_{1/2} = E^{o} - \frac{RT}{nF} \ln \sqrt{\frac{D_{Ox}}{D_{Red}}} \quad \ldots\ldots\ldots\ldots\ldots (5)$$

On the other hand, when only the reduced form is present in the solution, the half wave potential of the anodic wave is also given by equation (5). Finally, when both the oxidized and the reduced form are present in the solution, the half wave potential is again given by equation (5). Since in all three cases the ratio D_{Ox}/D_{Red} is not vary considerably from unity, the value of the second term on the right hand side of equation (5) is negligible and

$$(E_{1/2})_{Ox} = (E_{1/2})_{Red} \cong E^{o}$$

Practically, the half wave potential of the oxidized and reduced form are measured; if the half wave potential differs by less than about 10 - 20 mV, the system may be deduced to be reversible.

In polarography, the relationship between potential and current is generally described as (10)

$$E = E^{o} - \frac{RT}{nF} \ln \frac{\bar{i} - (\bar{i}_d)_a}{(\bar{i}_d)_c - \bar{i}} \sqrt{\frac{D_{Ox}}{D_{Red}}} \quad \ldots\ldots\ldots\ldots (6)$$

where $(\bar{i}_d)_a$ is the anodic diffusion current and $(\bar{i}_d)_c$ is the cathodic diffusion current. When only the oxidized form is present in the solution, $(i_d)_a = 0$, equation (6) is simplified to

$$E = E^{o} - \frac{RT}{nF} \ln \frac{\bar{i}}{(\bar{i}_d)_c - \bar{i}} \sqrt{\frac{D_{Ox}}{D_{Red}}} \quad \ldots\ldots\ldots\ldots (7)$$

On the other hand, when only the reduced form is present, $(\bar{i}_d)_c = 0$, equation (6) becomes to

$$E = E^{o} - \frac{RT}{nF} \ln \frac{\bar{i} - (\bar{i}_d)_a}{\bar{i}} \sqrt{\frac{D_{Ox}}{D_{Red}}} \quad \ldots\ldots\ldots\ldots\ldots (8)$$

To proof the system is reversible and that it follows one of the above equations, the mean diffusion current $\bar{i}_d$ is measured first. Then the mean current $\bar{i}$ is measured at each of several potentials E on the rising portion of the polarogram. The value of $\log (\bar{i}_d - \bar{i})/\bar{i}$ is computed for each point and plotted against the corresponded E. For a reversible system, they will give a linear graph with the slope of -2.303 RT/nF which is -59/n mV at 25°C.

By equation (7) another criterion of reversibility has already been employed, that is, $E_{1/4} - E_{3/4}$ should equal +56/n mV at 25°C in the reduction (11).

Finally, the third general technique used to distinguish the reversibility of an electrode process is to obtain curves showing the dependence of instantaneous current on time during the life of a single drop (i - t curves) (12). These are preferably recorded on the first drop, immediately after the voltage has been applied. The curves are recorded in the form

$$\begin{aligned} i &= kt^{\beta} \\ \text{or} \quad \log i &= k + \beta \log t \end{aligned} \quad \ldots\ldots\ldots\ldots\ldots (9)$$

where β is the coefficient factor.

When comparing the plot of log i against log t at various potentials on the rising portion of the polarographic curve, reversible process in which both the oxidized and reduced form are soluble in the studied solution shows for t greater than 0.5 second at all potentials and a linear dependence with a mean value of the slope of 0.192.

For irreversible process the logarithmic plot departs from linearity.

A number of organic compounds behave in the reversible manner. Thus, the Nernst equation is satisfied.

$$E = E^{o} - \frac{RT}{nF} \ln \frac{a_{Red}}{a_{Ox}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

However, a **more** complicated form of this equation must be derived, owing to the fact that in most case hydrogen ion take part in the over-all reaction, the most common reaction being represent as (16)

$$Ox + ne + mH^{+} \rightleftharpoons Red$$

hence $$E = E^{o} - \frac{RT}{nF} \ln \frac{a_{Red}}{a_{Ox}\, a_{H^{+}}^{m}} \quad \ldots\ldots\ldots (11)$$

or $$E = E^{o} + m\frac{RT}{nF} \ln a_{H^{+}} + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Red}}$$

In most cases, direct proportionality of concentration (C) to activities (a) can be assumed, and the following equation are obtained.

$$E = E^{o} - 2.303m\frac{RT}{nF} pH + 2.303\frac{RT}{nF} \log \frac{C_{Ox}}{C_{Red}} \quad \ldots\ldots (12)$$

This equation shows that the oxidation-reduction potential is a linear function of pH, even for a constant ratio of the oxidized and reduced form

$$\frac{\Delta E}{\Delta pH} = \text{const} - m\,\frac{RT}{nF}\ (\text{Volt/pH}) \ldots\ldots\ldots\ldots\ (13)$$

From this slope $\Delta E/\Delta pH$ the proton consumed in the reaction can be computed, if n is known. With most heterocyclic compounds, the number m does not remain constant over the whole pH-region, and depends on the structure of the species taking part in the reactions and their dissociation constants.

The polarographic half wave potentials of organic compounds are also influenced by their substituents. The substituent possessing a + I ($-CH_3$) or + T effect (I = Inductive effect, T = mesomeric effect) shifts the half wave potential to more negative value, while half wave potentials of substances with a -I substituent (Cl, -Br, or I) or a - T substituent ($-NO_2$, or -COOH) are shift to more positive values as compared to the unsubstituted substance (12).

The half wave potentials of reversible systems are affected mainly by the static effects, including inductive effects (I_s) and mesomeric effects, and those of reversible systems by dynamic effects, including inductomeric effects (I_d), and electromeric effects (E). The above term "I effect" includes both inductive (I_s) and inductomeric (I_d) effects, and the term "T effect" has been chosen somewhat arbitarily for mesomeric (M) and electromeric (E) effects, since here static and dynamic effects can not be distinguished from each other. These effects express the electronic shift in the molecule caused by the substituent.

Apart from these general effects, there are also specific effects of the heterocyclic nuclei due to the presence of the heteroatom in the nucleus. In the usual qualitative treatment in six-membered nuclei the nitrogen atom in the pyridine nucleus may be looked up on as a strong-T substituent in benzene nucleus (13).

The effect of substituents can be expressed quantitatively by means of empirical equations of organic chemistry. The effects of substitution on the free energy of activation change or on the standard free energy change must be resolved into independent contributions of polar, resonance, and, if necessary, steric effects (12). According to Taft (14) the influence of the individual contribution to the reaction rate in a homogeneous reaction may be written as

$$\log k = P + S + M \quad \ldots\ldots\ldots\ldots\ldots\ldots (14)$$

where P denotes the polar, S the steric and M the mesomeric contribution. Koutecky (15, 16) derived the relationship between the half wave potential and the rate constant of the electrode process as

$$E_{1/2} = \frac{RT}{nF} \ln 0.886\, k_f \left(\frac{t_1}{D}\right)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (15)$$

The meaning of the symbols used here is obvious. By combining equation (14) and (15) the following relation results

$$\Delta E_{1/2} = P + S + M \quad \ldots\ldots\ldots\ldots\ldots\ldots (16)$$

where $\Delta E_{1/2}$ is $(E_{1/2})_X - (E_{1/2})_R$, $(E_{1/2})_X$ and $(E_{1/2})_R$ is the half wave potential of the substance with substituent X and the reference substance bearing a H atom instead of X.

The values of P, S, M are independent and can not be directly determined. The solution of the whole problem can be attained by starting a reaction series in which only P is operative and continuing with those compounds in which two effects are supposed, such as P + M or P + S.

A simple form of the above relation with respect only to the polar effect is the modified Hammett equation

$$E_{1/2} = P = \rho_{\pi,R} \cdot \sigma_x \qquad \text{.................} \ (17)$$

where σ_X is the total polar constant characteristic of the nature and orientation of the substituent, or of the type of aromatic system. Then constants are independent of the electroactive group and of polarographic conditions. $\rho_{\pi,R}$ is the reaction constant expressed in volts, typical of the electroactive group attached to a given nucleus. Although independence of the other substituents, this value is strongly affected by the external experimental conditions. The reaction constant is a measure of the half wave potential shift for a given substituent. The sign of the reaction constant is of utmost importance; a positive value points to a nucleophilic mechanism of the electrode process (electron uptake as the potential determining step) and a negative value is characteristic of a dissociation mechanism (analogous to S_N 1) or of a radical mechanism.

A further equation of this type for reaction series with prevailing polar effects has been prepared as a polarographic form of the Taft equation (12)

$$\Delta E_{1/2} = P = \rho_{\pi,R^*}\sigma_{X^*} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (18)$$

Here, the meaning of all the symbols is analogous to that in equation (17) with the exception that the reference X is CH_3. In reaction series of this type, the electroactive group is not separated from the substituent, but the steric effects are considered constant for the whole series.

All the relationship mentioned above should enable the investigator to determine both the heterocyclic ring bearing the electroactive group and the nature of the substituent on the heterocyclic ring.

The determination of the heterocyclic nucleus in a reducible compound is exceptional. The heterocyclic nucleus in a reducible compound can be solved by measuring the half wave potential of several compounds bearing the same electroactive group on various nuclei H with known values of σ_H. From these measurements the reaction constant $\rho_{\pi,R}$ is determined. Then in a graph the value of σ_H of the unknown compound is found which corresponds to the obtained value of $E_{1/2}$. The heterocyclic nucleus is identified by means either of tabulated σ-values or of values obtained in kinetic measurements or in measurements of dissociation constants.

Closely related to the Hammett equation and to similar relationship and based on the same principles is the Dimroth equation (17). Originally, this equation, derived for reactions of two members of a dynamically homologous series possessing the same reaction group, relates the oxidation-reduction potential to the rate constant of the chemical reaction k for a reversible process the equation is as the following:

$$\log k_1 - \log k_2 = b(E_1 - E_2) \quad \ldots\ldots\ldots\ldots\ldots \quad (19)$$

and for irreversible process is as

$$\log k_1 - \log k_2 = B \;\; (E_{1/2})_1 - (E_{1/2})_2 \quad \ldots\ldots\ldots\ldots \quad (20)$$

where 1 and 2 refer to the oxidation and reduction respectively.

b = the constant for the reversible reaction, and b = $\frac{nF}{RT}$ (2.3)(m + 1).

B = the constant for the irreversible reaction, and it has the value similar as b.

m = the symmetry exponent.

The validity of this equation has been proved in classic potentiometry with several reaction series of aromatic compounds. In heterocyclic chemistry excellent agreement has also been observed.

In the present investigation, the diffusion controlled process for any reaction is shown by the linear variation of the limiting current with both concentration and square root of the height of mercury reservoir (see equation (1) and (2)). The reversibility of any system at DME is tested by equation (7). The number of electrons transferred in a system are determined from the slope of the plot of $E_{d.e}$ V.S $\log i/i_d - i$ for a reversible process the slope is $-2.303 \frac{RT}{nF}$ and n is an integer.