CHAPTER I

INTRODUCTION
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The dropping mercury electrode has served excellently well for carrying out reductive voltammetry of almost all inorganic materials as well as a few organic materials which can undergo reduction easily. However, there is a large variety of organic compounds such as aromatic amines, phenols, aldehydes, alcohols as well as various pharmaceuticals and drugs such as phenothiazines, purines, sulpha drugs, antibiotics, local anaesthetics, etc., which can be estimated only through their oxidative voltammetry at comparatively higher positive potentials. Since the dropping mercury electrode fails to operate at potentials more positive than 0.4 V vs SCE, determined efforts were made to replace the dropping mercury electrode by some other micro-electrodes which could operate well at positive potentials. These efforts resulted in the development of a large number of solid micro-electrodes, both metallic and non-metallic. Amongst the metallic electrodes developed for oxidative voltammetry, mention may be made of the rotating platinum electrode (1), the rotating disc electrode (2), the rotating ring-disc electrode (3), the by-pass electrode (4), the vibrating platinum electrode (5), the string electrode (6), the conical electrode (7), the bubbling electrode (8), the dipping electrode (9), the wall jet electrode (10), the
rotating cylindrical electrode (11), the platinum electrode with rotating vessel (12) and the tubular platinum electrode (13). Amongst the non-metallic electrodes, reference may be made to the plain graphite electrode (14), the wax-impregnated graphite electrode (15), the pyrolytic graphite electrode (16, 17), the glassy carbon electrode (18), the carbon paste electrode (19, 20, 21), the polythene graphite electrode (22), the boron carbide electrode (23), the silicone rubber-based graphite electrode (24, 25), the tubular carbon electrode (26) and the tubular graphite electrode (27, 28). The metallic electrodes, however, have not operated so well for oxidative voltammetry of organic compounds. This is because of the fouling of the electrode surface either because of the formation of oxide layers or resistant organic films or both. For organic voltammetry, therefore, the response of the non-metallic electrodes has been decidedly better.

Oxidative Voltammetry of Organic Compounds

The most comprehensive work on oxidative voltammetry of organic compounds on solid micro-electrodes has been carried out by Adams' School of research although valuable contributions have been made in this field by other research groups as well. Most of the work carried out on organic voltammetry has so far remained centred around a study of the oxidative behaviour of aromatic amino and phenolic compounds. Different investigators using different electroanalytical techniques such as conventional d.c. voltammetry, chronopotentiometry, cyclic voltammetry, etc., have tried to peep into the mechanism involved in the anodic oxidation of these compounds.
Anodic Oxidations of Amino Compounds

Mohilner, Adams and Argersinger (29), studied anodic oxidation of aniline in aqueous sulphuric acid at platinum electrode. The oxidation was shown to proceed through a free radical mechanism, the final product being emeraldine. On the basis of the free radical mechanism, the value of \( n \) was found to be 1. However, from the slope of the Tafel lines, the value of \( n \) came out to be 2.

Breitenbach and Heckner (30), studied anodic oxidation of aniline in acetonitrile at rotating platinum electrode and proposed a mechanism involving 1 electron oxidation of \( \text{C}_6\text{H}_5\text{NH}_2 \) to the cation radical \( \text{C}_6\text{H}_5\text{NH}_2^+ \), followed by a rapid deprotonation and finally an oxidation of the \( \text{C}_6\text{H}_5\text{NH} \) radical to give highly condensed ring structures through the formation of benzidine and para amino diphenyl amine.

Mastuda et al (31), studied anodic oxidation of aniline in aqueous alkaline solution at nickel, platinum, lead and graphite electrodes. The oxidation was shown to involve the generation of a cation radical which led to the formation of azobenzene via hydrazobenzene through head-to-head coupling, and para amino diphenyl amine through head-to-tail coupling of the cation radical. The latter product by electron removal gave a polymer with quinonoid structure.

Bacon and Adams (32) made a comprehensive study of anodic oxidation of aniline and a number of ring-substituted
anilines and concluded that anodic oxidation of all the amino compounds follows an ECE mechanism. According to this mechanism, aniline during oxidation loses one electron to produce a monocation which undergoes head-to-tail and tail-to-tail coupling resulting in the formation of para amino-diphenyl amine and benzidine both of which being more readily oxidisable than the parent substance, undergo further oxidation at the same potential forming

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respectively. Similar mechanism was suggested for the oxidation of ring-substituted anilines. While aniline, toluidine, para amino benzoic acid and para nitroaniline were reported to involve a 2-electron oxidation, para anisidine, para phenetidine and para chloroaniline were reported to involve only a single-electron oxidation. Hand and Nelson (33) also made a detailed study of anodic oxidation of aniline and N-alkyl anilines using a variety of electroanalytical techniques including d.c. voltammetry, cyclic voltammetry, coulometry, preparative electrolysis, etc., in aqueous as well as non-aqueous media using platinum and graphite electrodes. The oxidation reaction was shown to follow an ECE mechanism as proposed by Bacon and Adams, resulting in the formation of benzidines and diphenyl
amines as intermediate products through tail-to-tail and head-to-tail couplings of the monocations, the bulk of the alkyl group being the primary factor determining the product distribution.

Lord and Rogers (14) studied anodic oxidations of aniline, toluidines and phenylene diamines at gold, platinum and graphite electrodes in aqueous solutions. In 0.1M HCl and on graphite electrode, both ortho and para phenylene diamines were shown to oxidise in one step at a potential of about 0.5 V vs. SCE. The meta derivative also oxidised in one step but at a considerably higher potential. In buffer of pH 4, the behaviour was different. The para compound gave one wave while the other two isomers showed two oxidation waves. In the case of toluidines, all the three isomers, viz., ortho, para and meta exhibited two oxidation waves.

Kuwana and Strojek (34) studied anodic oxidation of o-toluidine employing cyclic voltammetry, at a plane platinum electrode in aqueous and non-aqueous media. A single 2-electron oxidation wave was obtained at pH 2. At higher pH values the number of waves increased to 2. In acetonitrile also, two oxidation waves were obtained at slightly higher anodic potentials.

Mizoguchi and Adams (35) studied anodic oxidation of N, N-dimethyl aniline at platinum electrode using cyclic voltammetry. The oxidation was shown to lead to the formation
of N,N,N,N'-tetramethyl benzidine and its oxidised quinone as the principal products. In a subsequent publication, Galus and Adams (36) reported anodic oxidation of N,N-dimethyl aniline at stationary and rotated disc carbon paste electrodes and found the data to be consistent with those obtained earlier by Mizoguchi and Adams at the platinum electrode. Galus and Adams (37) also studied anodic oxidation of N-methyl aniline and reported the formation of benzidine as well as a benzidine-imine adduct, the major product being benzidine.

Parker and Adams (38) studied anodic oxidation of phenylene diamines at the rotating platinum electrode using current-scanning technique. In acid solutions, both ortho and para isomers exhibited two oxidation waves involving one electron each. In buffers, however, both the isomers gave only one wave involving a 2-electron change. The meta isomer exhibited only one well-defined wave at a considerably higher potential. Mark and Anson (39) studied anodic oxidation of para phenylene diamine by chronopotentiometry and concluded that the second wave was due to the oxidation of the doubly protonated amine.

Yao et al (40) studied anodic oxidation of phenylene diamine in acetonitrile using a platinum electrode. The oxidation presented two successive 1-electron reversible anodic waves involving the formation of monocation and dication.

Knoblock (41) carried out anodic oxidations of a variety of aromatic amines in anhydrous acetonitrile at
stationary platinum disc electrode employing cyclic voltammetry. The first peak heights in all cases were found to be a linear function of concentration indicating thereby that cyclic voltammetry could be used for quantitative estimations of aromatic amino compounds.

Seo et al (42) studied anodic oxidation of triphenyl amine in acetonitrile and reported the formation of an intermediate monocation which dimerised quickly. These workers reported an interesting observation that the presence of a methoxy group in the aromatic ring stabilised the monocation which, therefore, did not dimerise at all.

Melchior and Maki (43) studied anodic oxidation of phenylene diamines in acetonitrile as well as in aqueous perchlorate solutions and established the formation of stable monocation of para phenylene diamine as a result of 2-electron oxidation. Similar results were reported by Piette et al (44) and Lee and Adams (45).

Masichiro et al (46) studied anodic oxidation of a large number of aliphatic amines through cyclic voltammetry at a glassy carbon electrode in alkaline solutions. Primary amines showed no waves, secondary amines showed one wave while tertiary amines exhibited two waves. The mechanism for the oxidation of tertiary amines involved loss of 2 electrons followed by reaction with water to form a secondary
Adams, McLure and Morris (47) studied anodic oxidations of aromatic amines at platinum electrodes using chronopotentiometry. The measurements were made at different pH values. Aniline gave only a single wave over the entire range of pH. Methyl and dimethyl anilines gave one wave at lower pH values but two waves at higher pH values. The primary process in these oxidations was supposed to be a single-electron reaction giving a free radical species which further interacted with the solvent.

Recently, Hand and Nelson (48) studied in details, the anodic oxidations of a large number of ortho and meta substituted anilines in 6M sulphuric acid at carbon paste and graphite electrodes and reported the formation of substituted benzidines and 4-aminodiphenyl amines by tail-to-tail and head-to-tail coupling of the electro-generated cations. Steric factors were found to hinder or exclude benzidine formation in some systems. The 4-amino diphenyl amines yielded 2-substituted para benzoquinones through hydrolytic degradation. The various products and intermediates were verified by comparison with authentic samples, wherever possible.

Anodic Oxidations of Phenolic Compounds

Gaylor, Elving and Conrad (49) studied anodic oxidations of phenolic compounds on graphite electrodes in aqueous solutions at different pH values. Smooth single waves
were obtained for the oxidation of phenol and hydroquinone. The oxidation of hydroquinone was shown to be a 2-electron oxidation reaction giving quinone as the end product. The oxidation of phenol at pH 1.2 was thought of involving a 4-electron process while at other pH values, a 2-electron process. In the case of 2, 4-dimethyl - 6-tertiary butyl phenol, the number of oxidation waves was determined by the pH of the cell medium. As many as three well-defined waves were obtained at pH 5.2, two waves at pH 8.2 and only one wave at pH 10.

Hendenberg and Freiser (50) also carried out anodic oxidation of ortho, para and meta tertiarybutyl phenols at platinum electrode in aqueous solutions at different pH values. The oxidation was shown to involve a reversible 1-electron process yielding the phenoxide free radical. Gaylor, Conrad and Lander1(15) studied anodic oxidation of mono and dihydric phenols on wax-impregnated graphite electrodes. Phenol and hydroquinone produced double anodic waves when the surface of the electrode was not rubbed with sand paper. Light abrasion of the surface produced single waves.

Bub et al (51) examined anodic oxidation of phenol at gold and carbon paste electrodes in aqueous solutions at different pH values using d.c. and cyclic voltammetry. The cyclic voltammetric curves indicated an ECE mechanism for anodic oxidation. The dependence of oxidation on pH and sweep rate was explained by a potential-determining primary step forming phenoxy radicals. Hawley and Adams (52) studied anodic voltammetry of para methoxy phenol in aqueous sulphuric
acid on carbon paste electrode. The reaction was reported to be an irreversible 2-electron oxidation giving benzoquinone as the ultimate product.

Tsuchima and Kitagawa (53) studied anodic oxidation of catechol at the carbon paste electrode in sulphuric acid solutions of different concentrations (1 to 20 N) using cyclic voltammetry and chronopotentiometry. A single diffusion-controlled anodic wave was obtained in all cases.

Turner and Elving (54) studied anodic oxidation of hydroquinone at pyrolytic graphite electrode in pyridine solution and reported the overall oxidation as an irreversible 2-electron process, probably involving coupling with pyridine. Vetter (55), however, reported the oxidation of hydroquinone as a 1-electron process on platinum electrode. The conclusion that n=1 for the oxidation of hydroquinone was also reached from chronopotentiometric experiments carried out in aqueous solutions by Elving and Krivis (56). Vetter's reaction scheme was also supported by Loshkarev and Tomilov (57).

Eggins and Chambers (58) studied anodic oxidation of hydroquinone in acetonitrile at platinum electrode through cyclic voltammetry. The cyclic voltammogram showed a single 2-electron wave during anodic sweep and a single 2-electron wave during cathodic sweep. With increase in sweep rate, the current functions decreased and an additional reduction wave appeared. The anodic wave was attributed to the oxidation of hydroquinone to protonated quinone. The first
cathodic wave was assigned to the reduction of protonated quinone and the second to the reduction of quinhydrone.

Parker (59) carried out comprehensive studies on oxidative cyclic voltammetry of hydroquinone in methylcyanide at platinum electrodes in the presence of varying concentrations of perchloric acid. The number of peaks and the peak potentials depended on the concentrations of perchloric acid as well as the pretreatment given to the electrode and the scan rates. The extent of protonation of the anodically generated quinone in the first scan played an important role in deciding the subsequent pathways of voltammetric process. The complexity in the hydroquinone – quinone redox system in methyl cyanide was explained on the basis of the deficiency of protons in solution. Parker and Eberson (60) while carrying out voltammetry at rotating disc electrode reported that anodic oxidation of hydroquinone in acetonitrile occurred through a 2-electron process. The dimerisation scheme put forth by Eggins and Chambers (60) for anodic oxidation of hydroquinone was found to be incorrect by these workers.

Parker (61) made another study on the anodic oxidation of hydroquinone in acetonitrile at platinum electrodes using classical voltammetry, cyclic voltammetry and coulometry. The oxidation of hydroquinone in acetonitrile involved the formation of 2-electron oxidation products as the first observable intermediates. In the presence of small amount of added perchloric
acid, the observable product was monoprotonated benzoquinone. In neutral supporting electrolyte, the product obtained was unprotonated quinone which, however, had a transient existence and reacted sharply with anodically generated protons giving the usual protonated benzoquinone. In the presence of 2,6-lutidine, the product detected was only benzoquinone.

Gorokhovaskii et al. (62) obtained comprehensive data for anodic voltammetry of as many as 28 phenols with a variety of substituents using a rotating graphite electrode in aqueous solutions. Oxidation of alkyl phenols was shown to occur with 1-electron and 1-proton participation. Linear correlations were established between the half wave potentials (obtained at pH 7) and the Hammett's substituent constants of the groups present, on the simple additivity principles.

Popouchado et al (63) studied anodic oxidation pathways of phenolic compounds in aqueous solutions at graphite electrodes. The anodic oxidation was shown to involve one or two electrons depending upon the magnitude of the anodic potential. Phenoxy radicals and phenoxonium cations were supposed to be formed as initial anode products. The former coupled together to give dimers whereas the latter underwent hydroxylation as a predominant follow up reaction.

In addition to aromatic amino and phenolic compounds whose anodic oxidations have been studied most exhaustively, the electro-oxidations of some other organic compounds
including sulphur compounds, aromatic hydrocarbons and heterocyclic systems, etc., have also been studied by several workers in aqueous as well as non-aqueous media. A detailed account of these anodic oxidations in non-aqueous media has been given by Mann and Barnes in their reputed monograph (64). An equally comprehensive account of these oxidations both in aqueous and non-aqueous media has been given by Adams in his own monograph (65). Sasaki and Newby (66) have also given a detailed review of anodic oxidations of various aromatic compounds carried out in aqueous and non-aqueous solvents.

**Oxidative Voltammetry of Pharmaceuticals and Drugs**

Most of the pharmaceuticals and drugs known at present happen to contain phenolic and/or aromatic amino groups in their structures. Thus antibiotics, antiseptics, anti-inflammatory agents, antimicobacterial agents, antiparkinsonism drugs, analgetics, gastrointestinal drugs and even some vitamins and hormones contain amino/phenolic groups in their molecules. Similarly, sulpha drugs, petridines, local anaesthetics and some antimalarials contain the amino group in their structures. There are a number of pharmaceuticals and drugs which contain both amino and phenolic groups. Some such materials are para aminosalicylic acid (PAS) and its derivatives, salvarson, etc. Because of the presence of these easily oxidisable functional groups, these compounds are prone to easy anodic oxidations.
There are also some biologically active heterocyclics which do not contain phenolic or amino groups, yet they are susceptible to easy anodic oxidations. This is because of the presence of electron-rich heteroatoms and easily attackable ring structures in their molecules. Important amongst these are phenothiazines and purines. However, only a limited amount of work on the oxidative voltammetry of these compounds appears to have been done so far. The only compounds in respect of which some systematic work has been done, include sulpha drugs, phenothiazines and purines. In the case of others, the work is merely of a scattered nature.

Anodic oxidations of sulpha drugs were carried out mainly by Voorhies and Adams (67) using voltammetry and by Voorhies and Furman (68) using chronopotentiometry, at platinum electrodes. The site of oxidation in these substances was shown to be the primary aromatic amino nitrogen.

Oxidative voltammetry of N-substituted phenothiazines was carried out by Billon (69) in non-aqueous media and by several other workers in aqueous media (70-75). The anodic oxidation of each phenothiazine derivative was established to proceed through the formation of a monocation as an intermediate product, the final product being the corresponding sulphoxide.

Work on anodic oxidations of purines including
xanthine, N-methylxanthine, caffeine, theobromine, guanine, adenine, uric acid, etc., was done fairly exhaustively by Dryhurst and co-workers (17, 76-83) at pyrolytic graphite electrode in aqueous media. The oxidation reaction in each case was shown to involve a 2-electron attack at the - N\_\text{= C} - double bond to give the appropriate uric acid, which being more easily oxidisable than the parent compound, oxidised readily in a further 2-electron process forming a 4,5-diol species. Work on anodic oxidation of some purines was also carried out by Yao et al (84, 85) using graphite electrodes. The mechanism involved anodic oxidation of these compounds has been well illustrated. Good amount of work on the analytical utilisation of voltammetric data of purines and pyrimidines was done by Smith and Elving (86) and of sulphur-containing purines by Dryhurst (76). A comprehensive review of electro-oxidation of the various biologically important purines has been given by Dryhurst in Fortschr Chem. Forsch (78).

Other biologically active substances whose oxidative voltammetry has been studied with some success include ascorbic acid (87-90), dopa (91), methyldopa (92), tyrosine (93), tocopherols (94), vitamin K\_\text{a} (95), bilirubin (96), flavinemononucleotide (97), catecholamine (98) and a few other compounds (99-105). Pungor et al (106-108) reported voltammetric determinations of some drugs including
ascorbic acid, chlorpromazine, diethazine, morphine, papverine, etc., using silicon rubber-based graphite electrode securing accuracy of a very high order. Similarly, Mason (91) claimed that the voltammetric method for the estimation of dopa involving the tubular carbon electrode was superior to the common colorimetric method used for the purpose. Likewise anodic oxidation of ascorbic acid was tried by various workers primarily with a view to establishing the validity of the voltammetric technique for the estimation of this material. Anodic voltammetry of some other compounds was also tried with a similar objective in view.

Proksa and Molnar (109) recently reported a voltammetric method for the determination of morphine in poppy seeds, crude morphine and in pharmaceutical preparations. The method based on electro-oxidation of morphine at a stationary graphite or platinum electrode showed good reproducibility.

Cheng, Strope and Adams (110) made comprehensive electrochemical studies on the oxidation pathways of apomorphine in aqueous buffers. The compound was shown to undergo an intial 2-electron and 2-proton oxidation followed by an irreversible chemical reaction resulting in the formation of a new redox couple. This new redox couple was shown to exhibit properties of electrocatalysis for the oxidation of ascorbic acid.
A recent publication by Chatten et al (111) described anodic oxidation of tetracyclines employing cyclic voltammetry in buffer solutions using stationary platinum electrode. Totally irreversible waves were obtained for all tetracyclines excepting minocycline.

**Oxidative Voltammetry At the Tubular Graphite Electrode**

Sharma et al (112-121) have studied extensively the anodic oxidations of a wide variety of aromatic amino and phenolic compounds at the tubular graphite electrode in aqueous and non-aqueous media employing d.c. as well as cyclic voltammetry. As a result of comprehensive experimentation, the following observations have been made:

1. All aromatic amines, irrespective of the nature of the medium (whether aqueous or non-aqueous) undergo anodic oxidation through the formation of a monocation.

2. In aqueous medium, the monocation formed undergoes, through its resonance structures, dimerisation involving tail-to-tail, head-to-tail and even head-to-head coupling. The products formed being more easily oxidisable than the parent substance in each case, undergo further oxidation at the same potential so that the overall oxidation involves a one-step two-electron process.
3. In non-aqueous medium, the monocation formed does not undergo any dimerisation through coupling reactions. Retaining its identity, the monocation undergoes further oxidation at a higher potential forming a dication. Thus in non-aqueous medium, aromatic amines undergo oxidation in two steps involving one electron in each step.

4. The N-alkyl anilines oxidise in two steps instead of one even in aqueous medium. This is attributed to the fact that the electron-releasing alkyl groups attached to the N-atom disperse the positive charge on the cation and thus partially render it stable. The stabilised fraction of the cation undergoes further oxidation at a higher potential forming a dication. This accounts for the formation of the second oxidation step.

5. The dication formed in aqueous as well as in non-aqueous medium combines with a neutral molecule of the parent compound forming hydrazobenzene or its analogue as an intermediate product, the final product being azobenzene or its analogue.

6. Ortho and para anisidines (in 0.1 M H₂SO₄) exhibit an unusual behaviour and undergo anodic oxidation in as many as three steps involving one electron in each step. At the first oxidation step, the products formed are the usual dimers which result from the permissible couplings of the electro-generated monocation. At the
second oxidation step, the major product formed is orthoquinone in the case of the ortho anisidine and paraquinone in the case of para anisidine. At the third oxidation step, the main product is orthoquinone-imine cation in the case of ortho anisidine and para quinone-imine cation, in the case of para anisidine.

The above mentioned unusual voltammetric behaviour of ortho and para anisidines has been explained on the basis of resonance-stabilisation of the monocations and the dications owing to the presence of the typical methoxy group in ortho and para positions.

7. Unlike aromatic amino compounds, the phenolic compounds, in general, oxidise in one step involving 2 electrons not only in aqueous but also in non-aqueous media. One-step 2-electron oxidation clearly indicates that the oxidation of phenolic compounds involves elimination of one full pair of electrons at a time.

8. The d.c. voltammetric data have been utilised, in conjunction with Levich equation (13, 129), for an easy and reliable determination of diffusion coefficients of a variety of organic compounds, in aqueous and non-aqueous media. Interestingly enough, the diffusion coefficients of all substances, differing so much in their chemical constitution, happen to approximate to $0.65 \times 10^{-5} \text{cm}^2 \text{sec}^{-1}$ in 0.1 M $\text{H}_2\text{SO}_4$ and to $2.30 \times 10^{-5} \text{cm}^2 \text{sec}^{-1}$ in acetonitrile, at 25° C. This interesting observation has led to the derivation of a
simple empirical correlation which permits one-step direct
determination of the concentration of any organic compound
(with a known value of n) without the use of even a reference
solution.
CONCLUSIONS AND PLAN OF WORK

From the survey of literature given above, it is amply clear that while oxidative voltammetry of aromatic amino and phenolic compounds has been studied fairly comprehensively, only a limited amount of work appears to have been done on oxidative voltammetry of pharmaceuticals and drugs although most of them contain easily oxidisable amino and/or phenolic groups in their structures. The two series of biologically important compounds whose voltammetry has been carried out systematically and conclusively are the sulpha drugs and the purines, the former containing an easily oxidisable amino group and the latter containing an easily oxidisable ring structure. As a result of careful experimentation, the pathways involved in the anodic oxidations of these compounds have been properly elucidated.

The oxidative work which has been done in the case of other biologically important compounds is so far only of an exploratory nature. Amongst these compounds, the N-substituted phenothiazines (which are important tranquillizers) appear to present a highly fascinating system for systematic voltammetric studies. These compounds contain two electron-rich elements (viz., N and S) which are in a position to lose electrons when exposed to appropriate potentials. These compounds thus provide two sites for anodic attack. Further, because of the existence of a bridge structure in their
molecules, there is ample provision for resonance as a result of which the electro-generated species may become prone to easy follow up reactions. This situation can be helpful in elucidating the mechanism involved in anodic oxidations of these substances - a subject which is of great biological importance (122). In spite of this, only an inadequate attention appears to have been given to this important aspect. Some workers did try to investigate the character of oxidation of these compounds employing chemical means (123-126), but by far and large the investigations have remained inconclusive.

It has, therefore, been thought of interest to carry out systematic studies on the oxidative voltammetric behaviour of N-substituted phenothiazines employing d.c. voltammetry, chronopotentiometry and more comprehensively cyclic voltammetry with a view to elucidating the exact mechanism involved in these anodic oxidations. All measurements would be made at the Tubular Graphite Electrode, which is reputedly known (28, 112, 116, 118) for its capacity to yield highly reproducible results.

The following plans of work have been drawn to carry out the investigations contemplated as above.

1. **Study of d.c. Voltammetric Behaviour**
   
   D.C. Voltammetry of all the available N-substituted
Phenothiazines will be carried out in solutions of sulphuric acid of different concentrations varying from 0.001 M to 4M as well as in buffers of different pH values varying from 2 to 12. The number of oxidation waves obtained would indicate the number of steps involved in a given oxidation reaction. If the oxidation steps are reversible and involve the same number of electrons, then the heights of the waves would give an idea about the relative stability of the species generated in the steps involved. Thus appearance of two waves of equal heights would indicate complete stability of the species generated at the first step of oxidation.

2. **Study of Chronopotentiometric Behaviour**

Chronopotentiometry of all the phenothiazines will be carried out in all the background solutions mentioned above. Measurements would be made using different concentrations of the key materials employing different current densities. The data thus obtained would first be utilised in checking the validity of the Sand equation for the tubular graphite electrode used in the present investigations. The potential-time curves obtained in chronopotentiometry would give authentic information in respect of the number of steps involved in a given oxidation reaction and the number of electrons involved in each step for a reversible oxidation. The heights of the steps can also give information about the relative
stability of the electro-generated species in a given oxidation.

3. **Study of Cyclic Voltammetric Behaviour**

Cyclic Voltammetry of all the phenothiazines will be carried out in all the background solutions mentioned in (1) above, in stationary state. Cyclic Voltammograms would be able to yield most comprehensive information with respect to the intermediates formed in a given oxidation process. This, in turn, would help considerably in defining the pathways involved in that oxidation reaction. Very precise information about the stability of the electro-generated species is likely to be obtained through cyclic voltammetry by judiciously fixing the scan potentials.

4. **Isolation and Identification of Products of Electrolysis**

After getting indications, from cyclic voltammetry, about the formation of particular species as intermediates or as final products of oxidation, preparative electrolysis of the parent compound would be carried out at precisely controlled potentials for appropriate time periods. The product or products formed would be isolated (through column chromatography, if necessary), purified by following standard methods (127) and then identified through ESR, IR, and NMR spectroscopy. Identification of the intermediates and
the final products of electrolysis would certainly help in establishing conclusively the mechanisms involved in these oxidation processes.

In addition to the above comprehensive investigations it was also considered desirable to study cyclic voltammetric and chronopotentiometric behaviour of some other pharmaceuticals and drugs including antibiotics, vitamins, local anaesthetics, antifertility drugs, plant hormones, etc., in order to see if some useful information in respect of the mechanisms involved in their oxidations was coming forth.