ELECTROLYTIC REDUCTION OF ORGANIC COMPOUNDS

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I. INTRODUCTION

This review covers solely the electrochemical reduction of organic compounds at the cathode. Other related types of reduction such as polarographic reduction (360) are not discussed, nor is the interesting area of anodic reductions.

While no pretense is made to include all of the literature on the subject, the authors have attempted to present complete coverage of the subject since 1940. Where it is necessary for complete discussions, reference is made to papers published prior to 1940. The reader is also referred to several excellent books and bibliographies for earlier work (8, 103, 322, 323). Many books, chapters in books, and short reviews on specific aspects of electrochemical reduction are also available (31, 37, 56, 59, 125, 145, 168, 343). Throughout this review the nomenclature of the original authors has been used as much as possible. This practice should assist the reader to locate more readily the specific examples in the original papers, for many of the references contain only one or two examples of electroreduction buried in a large amount of other material.

To conserve space and make the data more available to the reader, much of the information on reductions published since 1940 is presented in the form of tables. Compounds in which more than one functional group have been reduced are, with the exception of some of the more interesting and unusual cases, generally included in one table only. Yields are included where available and where only one product has been obtained. Generally, the yields lie in about the same range as those obtained by other methods of reduction (when these other methods have been applied).

II. GENERAL PRINCIPLES

A. INTRODUCTION TO ELECTROÖRGANIC REDUCTION

1. Cathode reactions

The passage of electricity through two electrodes immersed in an electrolyte results in the deposition of a metal or the evolution of hydrogen from the cathode. Reducing conditions exist at the cathode of sufficient power to enable the electrolytic hydrogen to add to unsaturated organic molecules or to remove oxygen from organic molecules. Unlike the reduction of most inorganic substances, the reduction of organic compounds is sometimes reversible (e.g., quinone–hydroquinone, azobenzene–hydrazobenzene, nitrosobenzene–phenylhydroxylamine). Definitions of many of the terms used are included in earlier reports on electrochemistry (323) and are not discussed here.

2. Theories of reduction at the cathode

Several theories have attempted to account for the reducing action of the cathode. The most reasonable theory, first proposed by Haber (130) and later supported by Creighton (55), states that hydrogen atoms are released at the cathode by the discharge of a proton with an electron. The atomic hydrogen thus formed reacts with the organic compound:

$$H^+ + e \rightarrow H^0$$
$$R + 2H^0 \rightarrow RH_2$$
or
$$RO + 2H^0 \rightarrow R + H_2O$$

The hydride ion has been considered to be the active reducing agent (109). Other workers (51, 368) believe electrolytic reduction to be a phenomenon of simultaneous electrolytic and chemical reduction. Certainly, the electrolytic reduction of an organic compound in a basic solution at a mercury cathode could conceivably be due to the chemical activity of the electrolytically formed amalgam. There may also be the phenomenon of simultaneous electrolytic and catalytic reduction; the activity of platinized platinum and nickelized nickel cathodes probably is due to the catalytic effect of the finely divided cathodic surface. Evidence has been presented (171, 198) that reduction may take place by direct transfer of electrons from the electrode to the substance being reduced; this hypothesis presumes the addition of the highly mobile proton to a negative center. It has been observed (342) that an unstable, benzene-soluble, reducing substance is formed at platinum or lead cathodes. This unknown substance was shown not to be a gas, tritium, or ferrous ion; it was not, however, further identified. Some investigators (115, 186, 337) have stated that the cathode may enter into the electroörganic reduction; they have reported the formation of organometallic compounds, particularly when carbonyl groups were reduced at lead or mercury cathodes.

It appears that to a large extent the mechanism of electroreduction depends upon many factors. In the case of the electroreduction of diphosphopyridine nucleotide (167), it appears that the process involves proton transfers, rather than a direct transfer of hydrogen atoms, since no dependence is found on the use of a variety of electrodes of different overvoltages. Antropov (16) has presented a mathematical treatment which supports the theory that nonpolar groups of compounds such as phenol, acetylene, vinylacetylene, crotonic acid, oleic acid, and sorbic acid are reduced on low-overvoltage cathodes by hydrogen atoms adsorbed on the electrode surface, while polar groups of acetone, acetaldehyde, 1-acetyl-2-propanol, acetophenone, benzophenone, salicylaldehyde, and oxalic acid are reduced on cathodes of high overvoltage by hydrogen ions activated in the double layer. Many other papers have appeared which discuss the mechanism of electroörganic reduction in specific systems (140, 218).

3. Disadvantages and advantages of electroörganic reduction

The two main disadvantages which have been offered for electroörganic reductions (116, 320) are that the reductions are usually of a low velocity and that the process requires careful control of many conditions.

There are several apparent advantages of electroorganic reduction: (*1*) impurities from a reducing agent are not present in the reaction mixture; (*2*) partial reduction may be achieved by altering the reducing conditions; (*3*) selective reduction of certain unsaturated groups in the presence of other groups has been accomplished (208); (*4*) electroörganic reductions have been successful in the presence of compounds that usually poison catalytic reductions, and such substances as mercury, halides, hydrogen sulfide, and arsenic sulfide have been demonstrated to be electrocatalytic (163). Electroörganic reduction can also be developed into procedures suitable for large-scale preparative work (80).

B. FACTORS THAT INFLUENCE ELECTROÖRGANIC REDUCTION

1. The cathode potential

It has been stated (208) that the cathode potential is the factor that determines the success or failure of electroörganic reductions. This fact has long been recognized and conceded by responsible investigators, but very few have described the cathode potential used during reduction. Rather, a host of less important factors have been enumerated and described.

Haber (129, 130) first recognized the importance of controlled cathode potential for electroörganic reductions. He showed that in an alkaline solution at a platinum cathode nitrobenzene was reduced in good yield to pure azoxybenzene when the cathode potential was held at 0.9 v.; a potential of −1.3 v. gave good yields of pure hydrazobenzene. This use of cathode potential has been found to lead to purer products in many cases. In the electroreduction of 8-chlorotheophylline (353), to theophylline the cathode potential was varied until the potential which gave the purest product was found. At all other potentials mixtures of products were obtained. Acetylene has been selectively reduced (32) to ethylene or ethane at a platinum cathode by controlling the cathode potential. Other workers also have stated (10, 12, 80, 207) that the cathode potential was of primary importance for controlled electroörganic reductions, and additional examples will be found later in this review. The electroreduction of nitrobenzene at an empirically established cathode potential of about −1.5 v. has been studied at a number of different cathodes (210). In all cases about 60 per cent yields of azoxybenzene and 40 per cent yields of aniline were obtained at zinc, copper, platinum, tin, and nickel cathodes.

The above work has been reiterated and pushed even further by the determination, polarographically, of the optimum cathode potential for the reduction of 9-(*o*-iodophenyl)acridine to 9-(*o*-iodophenyl)dihydroacridine at a mercury cathode (208). Although all previous methods and attempts to carry out this reduction had failed, because of an excessive reduction that removed the iodine atom, the use of the polarographically determined, constant cathode potential gave the desired product quantitatively. Although other workers (165, 256) also have shown that the potential found in polarographic work is confirmed by electroreductions, it has been pointed out (80, 92) that polarographic data alone do not rigidly demonstrate the efficacy of a preparative method; therefore polarographic data have not been included in this review (see reference 360 for a review of such data).

2. The cathode overvoltage

Two definitions of overvoltage have been presented (58): (*1*) the overvoltage of a gas upon a specific electrode is the polarization involved in the evolution of that gas on that cathode at a specified current density; (*2*) the overvoltage of a gas on a specified electrode is the minimum polarization at which visible evolution of gas occurs, or at which there is a marked increase in current density.

The higher the overvoltage value of any cathode, the greater is the reducing power of that cathode toward any organic depolarizer. Tafel (333, 335) was the first to recognize the relation between high overvoltage and a high reducing power. One of the early examples of this relationship was the inability of a smooth platinum cathode of low overvoltage to reduce cinnamic acid to hydrocinnamic acid; this reduction was accomplished, however, at the high-overvoltage lead and mercury cathodes.

The concept of overvoltage is important, since in an electroörganic reduction when a depolarizer is present, the potential at which hydrogen is evolved as a gas from the cathode marks that potential as the critical point above which the hydrogen is not absorbed by the depolarizer. Below this potential the atomic hydrogen reacts with the depolarizer as fast as it is formed.

Various theories of overvoltage have been discussed in great detail (118). The most acceptable view is that the metals of lower overvoltage function as catalysts for the reaction $H^+ + e \rightarrow H^0$ by decreasing the energy of activation for the process. Metals of high overvoltage have a large energy of activation, and hydrogen atoms formed at a metal of high overvoltage have a much greater potential energy than those liberated at metals of low hydrogen overvoltage.

Considerable study of overvoltages of various metals has demonstrated that the absolute values obtained have little import; only the relative differences in hydrogen overvoltages are of significance. Many of the existing data on overvoltage have been summarized (58, 183). The average overvoltage, obtained by averaging various literature values (49, 58, 183, 335), of hydrogen on various cathodes is presented in table 1. It should be reëmphasized that the absolute values given in this table are of no significance; only the approximate order of arrangement of the cathodes should be considered.

The following factors have been listed as those which affect the overvoltage of hydrogen on metals (58):

TABLE 1

Average overvoltage of hydrogen on various cathodes

Cathode	Overvoltage	Cathode	Overvoltage
	volt		*volts*
Platinized platinum	0.03	Copper	0.67
Tungsten	0.27	Iron	0.71
Smooth platinum	0.29	Graphite	0.77
Antimony	0.43	Aluminum	0.80
Gold	0.48	Mercury	0.89
Nickel	0.56	Tin	0.92
Palladium	0.59	Zinc	0.94
Silver	0.62	Lead	1.00
Carbon	0.64	Cadmium	1.22

(*1*) an increase in current density decreased the overvoltage; (*2*) an increase in temperature decreased the overvoltage; (*3*) an increase in pressure decreased the overvoltage; (*4*) the overvoltage increased with time; (*5*) an alternating current superimposed on a direct current lowered the overvoltage; (*6*) the overvoltage (116) is less in an alkaline solution than in an acid solution.

3. Cathode material and condition

The cathode material and its condition are rather intimately connected with the cathode potential and cathode overvoltage, but several observations on cathode materials properly belong by themselves. In addition to the more specific property of cathode overvoltage, the cathode material and condition have an effect upon electroörganic reductions.

The purity of the cathode is of prime importance. It has been demonstrated (333, 334) that when lead is used as a cathode, its reducing power is nil when there is present as little as 3 mg. of copper, 0.5 mg. of silver, or 0.04 mg. of platinum per square decimeter of lead surface. The difference between 99.9 per cent lead and 99.99 per cent lead is often enough to cause failure in an electroörganic reduction (320). All leads, tabs, and connections of a metal different from the cathode were shown to be deleterious to the cathode activity.

The physical state of the cathode may often play a leading role in an electroreduction. Generally a rough cathode has a lower overvoltage than a smooth one; but since it also has a greater surface area, the depolarizer has more opportunity to react with atomic hydrogen on it. Cinnamic acid failed to undergo reduction at a smooth platinum cathode but reacted at a platinized platinum cathode. It was found (203) that the rate of cathodic reduction of compounds such as aconitic acid and quinoline was increased by continuous renewal of the mercury surface, while the rate of reduction was decreased with naphthalene and anthracene. In these experiments, the surface of the mercury was renewed by motion, and at a high rate of motion reduction was stopped in many cases. It was concluded that if the mercury had a catalytic effect, renewal accelerated the reduction; if the reduction were due to electrolytically produced amalgam, then renewal counteracted the reduction; and finally that if renewal had no effect, as is the case of sorbic acid, then the reduction was truly electrolytic and depended only on the cathode potential.

The history of a cathode is of importance. A case has been cited (320) in which commercial cadmium, presumably of a microcrystalline character, was unfit for use as a cathode until melted and recast. Cathodes which have been used previously as anodes have been shown to have special activity as cathodes.

In addition to the above observations, it has been ascertained that certain cathodes appear to have a definite catalytic effect upon certain reactions which is unexplained in terms of cathode potential or overvoltage. Only platinized platinum, the cathode of lowest overvoltage, reduced aromatic nuclei (24, 25, 102). At a copper cathode, unlike other cathodes, nitrobenzene was reduced completely to aniline in both acid and alkaline solutions.

4. Current density

Current density is usually defined as the amperes of current applied per square decimeter of cathode surface. Too much importance has been placed upon the influence of current density in electroörganic reductions. Its importance lies primarily in the fact that it is a means of controlling the cathode potential. Usually the current density is the major experimental point in the literature (it is sometimes even listed in papers which do not mention what the cathode material is), but it has been shown (10) that the current density is of little value in reproducing work unless everything else is reproduced exactly, and that quite often electroörganic reductions are somewhat independent of current density and applied voltage.

5. Solvent, pH, and concentration

Because of the water insolubility of most organic compounds, a solvent must be used that conducts an electric current and also dissolves organic compounds. Generally this end is attained by adding acetone, alcohol, or lower-molecular-weight organic acids to a water solution of the electrolyte. Organic solvents raise the resistance of an electrolyte and lower the overvoltage of the cathode (116). Another disadvantage is the possibility of reaction of the organic solvent either at the cathode, with the depolarizer, or with the reduction product.

Use of concentrated water solutions of sodium and potassium aromatic sulfonates to increase the solubility of the depolarizer has been found to be of advantage (214, 215). Suspensions of the depolarizer in the catholyte have in many instances been employed successfully. Dispersion has been aided by use of a cellulose ether (278). It has been demonstrated (260) that surface-active agents, as emulsifying aids, decrease current efficiencies during electroörganic reductions.

When the reducible group forms the negative part of a dipole the lowering of the dielectric constant of the solvent, as in the addition of dioxane to water (108), forces the reducible group away from the cathode and thus lowers the reduction efficiency. This has been found to be true with *p*-nitrophenol and nitrobenzene; however, with benzaldehyde and phthalimide the increase in solubility overbalances the change of dielectric constant and the reduction efficiency is increased (108). Other workers (358) have pointed out the importance of the polarity of the organic compound being reduced and emphasized that only the dipole moment of the group being reduced is important. A compound can be reduced if its dipole moment is greater than that of the solvent.

The hydrogen-ion concentration of the catholyte plays an important role in electroörganic reductions. The course of a reduction may be controlled by altering the pH, and the formation of intermediate condensation products may be accelerated with certain pH conditions. As examples of the first effect: (*1*) it has been shown (268) that the reduction of carbon dioxide to formic acid takes place only in a very strong acid; (*2*) aromatic carboxylic acids are reduced to benzyl alcohols in acid solution (224), whereas in alkaline medium a nuclear reduction occurs; and (*3*) reduction of levulinic acid gave the hydroxy acid in acid solution and valeric acid in a basic solution (338).

The reduction of nitrobenzene in a basic solution leads to products with two aromatic rings (89, 90, 137, 211), presumably formed by a base-catalyzed condensation of such intermediates as nitrosobenzene and phenylhydroxylamine. The formation of bimolecular products from the reduction of carbonyl compounds in acid solutions may also be cited (91, 116, 117, 164, 184, 185) as examples of the effect of the pH of the reduction solution.

Generally it has been observed (116, 118) that the rate of reduction is higher in a high concentration of depolarizer than in a low one. High concentrations of depolarizer often give a more rapid reduction, but no increase in yields (84). The effects of the type of compound being reduced can be seen in Section III of this review; compounds which contain unsaturated nitrogen are generally the easiest to reduce, while aromatic benzenoid compounds are by far the most difficult to reduce.

6. Temperature

Temperature influences three factors (116): the cathode overvoltage, the rate of reduction, and the rate of diffusion of the depolarizer to the cathode. In addition, certain side reactions can be influenced by the temperature. The cathode overvoltage loss in most metals amounts to about 0.02–0.03 v. for every ten-degree rise in temperature. Despite this drawback, the rate of reduction in some instances is so low at room temperature that heat is necessary to bring about reduction (267, 336, 339, 359). The increase in reduction, or velocity of reduction, with heat probably is caused by an increase in the rate of diffusion of the depolarizer to the cathode (184). The heating of the cathode itself has been found to be of no value in at least one case (228).

7. Catalysts

Catalysts for electroreduction can be divided into three types (116, 119): (*1*) salts of metals such as copper, tin, lead, and mercury which plate out on the cathode, thereby altering its nature and catalytic action; (*2*) salts of metals such as titanium and vanadium, which are reduced at the cathode from a higher to a lower valence state and in this latter state reduce the organic material; (*3*) finely divided metals with a true catalytic surface, either suspended in the catholyte or fixed to the cathode surface. The influence of catalyst poisons has been studied (295), and it has been found that the addition of arsenic trioxide increased the yields of aniline, but decreased the yields of glyoxalic acid from oxalic acid in electroreduction. From this it was deduced that the reduction of nitrobenzene was based on atomic hydrogen, but that the latter reduction depended on the hydrogen overvoltage.

8. Agitation and miscellaneous factors

As has been mentioned, the rate of diffusion of a depolarizer to the cathode during reduction limits the velocity of reduction. If electrons are supplied to protons faster than the atomic hydrogen is used to saturate the depolarizer, a state of concentration polarization may be attained and gaseous hydrogen evolved. It has been shown (184, 229) that the reaction velocity depends upon the diffusion of the depolarizer to the cathode. In a stirred solution, however, one can reach a point where the velocity of reduction is independent of the rate of diffusion (184).

In a few cases (242, 251) electroörganic reductions have been carried out under a pressure of either hydrogen or carbon dioxide. In many cases the yields are increased at increased pressure, but the results have been variable.

The use of ultrasonics (181) in the reduction of nitrobenzene has been found to give a ten- to fifteen-fold increase in the limiting current.

C. METHODS AND APPARATUS FOR ELECTROÖRGANIC REDUCTIONS

1. Use of diaphragms

The organic depolarizer, cathode, and catholyte must be isolated from the anode section of the electrolytic cell; otherwise the organic compound could diffuse into the anolyte and be oxidized. In most cases this end is accomplished by enclosing or separating the cathode section of the electrolytic cell from the anode section with a partition which conducts an electric current but prevents diffusion of the depolarizer to the anode. Partitions have been constructed of porous clay, alundum, wood, sintered glass, and paper. Because of the high resistance of partitions and their tendency to become impervious, as a result of the formation of tar, such diaphragms are but a poor solution to the problem of anodic oxidation. Many attempts to solve this problem by rendering the anode passive to the depolarizer have met with failure. However, several investigations (95, 96, 265, 277, 298, 299) have been reported wherein an effective separation of the catholyte was accomplished by using either two immiscible solutions, or solutions of considerably different specific gravity. In these cases, of course, the cathode and anode are arranged one above the other. It has been reported (230) that no diaphragm was needed for the reduction of fumaric acid, whereas reduction of maleic acid required a diaphragm.

2. Cathode materials

Cathodes may be prepared from metallic sheets, wire, gauze, rods, or wool. The materials from which cathodes have been made are platinized platinum, platinum, tungsten, antimony, gold, nickelized nickel, nickel, tantalum (386), palladium, silver, carbon, tin, copper, iron, graphite, bismuth, aluminum, mercury, zinc, lead, lead dioxide, gallium (371), cadmium, thallium (385), and amalgams of several of these metals. Platinum, mercury, and lead appear to be the most widely used cathodes. In many instances the pH of the catholyte governs the choice of the cathode.

Although, as mentioned earlier, the purity of the cathode has been shown to be of prime importance, there have been several instances reported in which alloys, amalgams, and plated cathodes have proven of value. The use of the following cathodes has been reported: iron–nickel alloys (115), cadmium–bismuth alloys (263), Monel (215), bronze (215), and amalgamated cadmium. Cathodes have been studied in which tin was plated on copper and lead; lead, copper, zinc, nickel, iron, and silver were plated onto porous graphite; and nickel, tin, and copper were plated onto nickel.

3. The catholyte

The catholyte may consist of either an aqueous or a nonaqueous medium. In the event water is the catholyte, insoluble organic compounds are brought into solution by adding such solubilizers as methanol, ethanol, formic acid, or acetic acid. Concentrated aqueous solutions of sodium or potassium benzene-, toluene-, or xylenesulfonates have been shown (215) to be excellent hydrotropic agents. Some instances have been reported in which the insoluble organic compounds were emulsified in water by adding Igepon T, Nekol BX, sodium lauryl sulfate, cetylpyridinium bromide (260), or a cellulose ether (278).

In order to make aqueous solutions more conductive to an electric current, acids such as sulfuric acid, hydrochloric acid, hydrocyanic acid, and ammonium hydrogen sulfate have been utilized. A basic conducting medium has been attained by adding ammonium hydroxide, sodium hydroxide, or sodium carbonate to water. Nearly neutral aqueous solutions have been prepared by adding ammonium chloride, ammonium sulfate, or sodium acetate to water.

Methanol, ethanol, formaldehyde, formic acid, acetic acid, ethyl acetate, hydrogen cyanide, liquid ammonia, and fuming sulfuric acid have served as nonaqueous catholytes. Sodium and potassium acetates have been added to many of the above catholytes to increase the conductivity of the electrolyte.

4. The anode and the anolyte

The anode should be a nonattackable electrode such as platinum, carbon, lead, nickel, or iron. Generally, the anolyte should be of the same material and concentration as the catholyte, for this reduces to a minimum complications that may arise because of diffusion through the diaphragm.

5. Source, measurement, and control of current and potential

Six-volt storage cells are the best source of power for electroörganic reduction. The consumption of current may be measured by an ammeter, and the potential drop across the cell by a voltmeter. A variable resistance must be included in the circuit in order to control the current density at the cathode. Many varieties of power packs and converters are also now available.

The determination of the quantity of electricity (coulombs) passed through a cell may be accomplished by recording accurately the time intervals and the amperes. An easier method is the utilization of silver, copper, or gas coulometers. The silver or copper coulometers are less desirable for routine work, for the gas coulometer visibly evolves gas in direct proportion to the current passed through the reduction cell, and may be referred to with ease as the reduction proceeds. In some investigations the cathode of the reduction cell itself is enclosed so that any gas escaping from it may be measured. If the gas evolved by the coulometer and by the cathode is known, the absorption of hydrogen by the depolarizer may be determined easily. Almost all references contain some description of the apparatus and many include wiring diagrams. The above apparatus has been described in an excellent manner (260).

A determination of cathode potential requires the

TABLE 2

Reduction of carbon–carbon unsaturated compounds

Material to Be Reduced	Reduction Product	Cathode	Yield	References
			per cent	
Aconitic acid	Tricarballylic acid	Hg	60	(202)
Acrylonitrile	Tetrakis(2-cyanoethyl)tin	Sn	60	(349)
Butyl acrylate	Dibutyl adipate	Hg	28	(172)
α-Chloroacrylonitrile	1,4-Dicyanobutane	Hg	68	(172)
Crotononitrile	1,4-Dicyano-2,3-dimethylbutane	Hg	37	(172)
Diethyl maleate and diethyl fumarate	Diethyl 3,4-dicarbethoxyadipate	Hg	7 29	(172)
β,γ-Diphenylmuconic acid	β,γ-Diphenyldihydromuconic acid	Hg	81	(105)
Ethyl acrylate	Diethyl adipate	Hg	52	(172)
Ethyl crotonate	Diethyl 3,4-dimethyladipate	Hg	71	(172)
Ethyl β-methylcrotonate	Diethyl 3,4-dimethyladipate	Hg	31	(172)
Ethyl α-phenylacrylate	Diethyl 2,5-diphenyladipate	Hg	28	(172)
2-Furylacrylic acid	2-Furylpropionic acid	Hg	60–70	(154)
Maleic acid	Succinic acid	Hg	100	(54, 331)
Methyl acrylate	Dimethyladipate	Hg	27	(172)
Methyl α-methylacrylate	Dimethyl 2,5-dimethyladipate	Hg	23	(172)
Propyl acrylate	Dipropyl adipate	Hg	35	(172)
Sorbic acid	Δ^1,Δ^2, and Δ^3-Hexenoic acids and pinacol	Ga, Sn		(371, 372)
p-Aminocinnamic acid	*p*-Aminohydrocinnamic acid	Hg		(123)
Benzoic acid	Cyclohexanecarboxylic acid	Platinized Pt		(247)
o-Chlorocinnamic acid	β,γ-Bis(*p*-chlorophenyl)adipic acid	Hg		(374)
Cinnamic acid	γ-Keto-β,ρ-diphenyl caproic acid, γ-hydroxy-β,ε-diphenylcaproic acid, 2-phenylpropionic acid, 2,3-diphenyladipic acid, and 2-cyclohexanepropionic acid	Platinized Pt, spongy Pt, spongy Ni, Hg, Cu, Pb, PbO_2, Pt		(105, 154, 248, 249, 369, 374)
Cinnamonitrile	1,4-Dicyano-2,3-diphenylbutane	Hg	60	(172)
Cresol (*o*-, *m*-, and *p*)	Methylcyclohexanols and methylcyclohexanones	Pd		(290)
o-Cyanocinnamic acid	β,γ-Bis(*o*-cyanophenyl)adipic acid and β-(*o*-carboxyphenyl)propionic acid	Hg		(374)
N,*N*-Diethylcinnamide	Dimer	Hg	23	(172)
2,3-Dimethoxy-β-methylcinnamic acid	2,3-Dimethoxy-β-methylhydrocinnamic acid	Hg	85	(381)
2,4-Dimethoxy-β-methylcinnamic acid	2,4-Dimethoxy-β-methylhydrocinnamic acid	Hg	82	(381)
2,5-Dimethoxy-β-methylcinnamic acid	2,5-Dimethoxy-β-methylhydrocinnamic acid	Hg	86	(381)
3,4-Dimethoxy-β-methylcinnamic acid	3,4-Dimethoxy-β-methylhydrocinnamic acid	Hg	80	(381)
3,5-Dimethoxy-β-methylcinnamic acid	3,5-Dimethoxy-β-methylhydrocinnamic acid	Hg	85	(381)
2,7-Dimethoxynaphthalene	3,4-Dihydro-2,7-dimethoxynaphthalene	Hg	93	(80)
N,*N*-Diphenylcinnamide	Dimer	Hg	5	(172)
2-Ethoxynaphthalene	3,4-Dihydro-2-ethoxynaphthalene	Hg	96	(80)
Ethyl cinnamate	Diethyl 3,4-diphenyladipate and ethyl β-phenylpropionate	Hg		(172, 248)
Ethyl *p*-nitrocinnamate	*p*-Aminophenylpropionic acid	Hg		(123)
m-Hydroxycinnamic acid	β,γ-Bis(*p*-hydroxyphenyl)adipic acid	Hg		(374)
p-Methoxycinnamic acid	β,γ-Bis(*p*-methoxyphenyl)adipic acid	Hg	55	(374)
o-Nitrocinnamic acid	Dihydrocarbostyril	Hg		(123)
p-Nitrocinnamic acid	β-(*p*-Nitrophenyl)propionic acid	Hg		(123)
ω-Nitrostyrene	Phenylacetaldoxime and phenylethylhydroxylamine	Hg		(220)
Phenylacetic acid	Cyclohexaneacetic acid	Platinized Pt		(247)
Phthalic acid	Cyclohexadienedicarboxylic acid			(54)
2,7,8-Trimethoxynaphthalene	3,4-Dihydro-2,7,8-trimethoxynaphthalene	Hg	95	(80)
Streptomycin	Dihydrostreptomycin	Cd–Hg, Hg, Hg–Pb	85	(85, 236, 303, 350)
2-Aminopyrimidine	2-Aminodihydropyrimidine	Pb, Hg	90	(313)
3-Benzylidene-2-methylphthalimidine	1-Benzyl-2-methylisoindoline	Pb		(306)
3-Benzylidenephthalimidine	1-Benzylisoindoline	Pb		(306)
Dihydrodesoxyvomicine	Dihydrodesoxyvomicidine	Pb	60	(365)
Dihydroquinaldine dimer	Tetrahydroquinaldine dimer and dihydroquinaldine trimer	Hg		(124)
2,6-Dimethylpyridine	*cis*-2,6-Dimethylpiperidine and *cis*-2,6-dimethyl-1,2,5,6-tetrahydropyridine			(98)
9-(*o*-Iodophenyl)acridine	9-(*o*-Iodophenyl)acridan	Hg	90	(208)
Lepidine	Tetrahydrolepidine and dihydrolepidine dimer	Hg		(204)
2-Methylpyridine	2-Methylpiperidine and 2-methyl-1,2,3,6-tetrahydropyridine			(98)
3-Methylpyridine	3-Methylpiperidine and 3-methyl-1,2,3,6-tetrahydropyridine			(98)
4-Methylpyridine	4-Methylpiperidine and 4-methyl-1,2,3,6-tetrahydropyridine			(98)
3-Methylpyridine methiodide	1,3-Dimethyl-1,2,5,6-tetrahydropyridine			(98)
4-Methylpyridine methiodide	1,4-Dimethyl-1,2,5,6-tetrahydropyridine			(99)
1-Methylpyridinium methyl sulfate	1-Methylpiperidine and 1,1′-dimethyl-4,4′-bipyridine	Pb		(231)
8-Methylquinaldine	8-Methyldihydroquinaldine and 8-methyltetrahydroquinaldine	Hg		(202)
Nicotinamide propiodide	Dihydronicotinamide and a dimer	Hg		(254)
4-Nitroquinoline *N*-oxide	1,2,3,4-Tetrahydroquinoline and 4-aminoquinoline	Pb, Cu, Ni		(232)

TABLE 2—*Concluded*

Material to Be Reduced	Reduction Product	Cathode	Yield	References
			per cent	
4-Nitropyridine *N*-oxide	4,4′-Azodipyridine *N*,*N*′-oxide	Cu	78	(232)
Pyridine	Piperidine	Pb, Cd, Sn		(98, 253, 332)
Pyrrole		Pb		(260)
Quinaldine	Dihydroquinaldine and tetrahydroquinaldine	Hg		(201, 202)
Quinoline	Dihydroquinoline and tetraquinoline	Pb, Hg, Zn		(200, 202)
Strychnine	Strychnidine, tetrahydrostrychnine, and dihydrostrychnidine	Na-Hg, Hg		(386)
3-Veratrylidinephthalimidine	1-Veratrylisoindoline	Pb		(173)
Vomicine methosulfate	Salt of methylvomicidine	Pb		(367)
3-(Isoamoxymethoxy)-3-methyl-1-butyne	3-(Amoxymethoxy)-3-methyl-1-butene	Cu-Ag	48	(285)
3-(Butoxymethoxy)-3-methyl-1-butyne	3-(Butoxymethoxy)-3-methyl-1-butene	Cu-Ag	54	(285)
5-Decyne	*cis*-5-Decene	Spongy Ni	75	(47)
Dimethylacetylenecarbinol	2,7-Dimethyl-3,5-octadiene-2,7-diol and dimethylvinylcarbinol	Ni, Pd		(121, 188, 283)
Diphenylacetylene	*cis*-Stilbene	Spongy Ni	80	(47)
3-(Ethoxymethoxy)-3-methyl-1-butyne	3-(Ethoxymethoxy)-3-methyl-1-butene	Cu-Ag	52	(285)
3-(Ethoxymethoxy)-3-methyl-1-pentyne	3-(Ethoxymethoxy)-3-methyl-1-pentene	Cu-Ag	55	(285)
3-Ethyl-1-pentyn-3-ol	3-Ethyl-1-pentene-3-ol	Cu-Ag	80	(190)
1-Heptyne	1-Heptene	Spongy Ni	65	(47)
3-(Methoxymethoxy)-3-methyl-1-butyne	3-(Methoxymethoxy)-3-methyl-1-butene	Cu-Ag	42	(285)
3-(Methoxymethoxy)-3-methyl-1-pentyne	3-(Methoxymethoxy)-3-methyl-1-pentene	Cu-Ag	33	(285)
Methylcyclopropylethynylcarbinol	Methylcyclopropylvinylcarbinol	Cu	70	(122)
Methylethylacetylenecarbinol	3,8-Dimethyl-4,6-decadiene-3,8-diol	Ni		(188)
Methylisobutylethynylcarbinol	3-Hydroxy-3-isobutyl-1-butene	Cu, Cu-Ag		(286)
Methyl-*p*-tolylethynylcarbinol	Methyl-*p*-tolylvinylcarbinol	Cu-Ag		(191)
4-Octyne	*cis*-4-Octene	Spongy Ni	80	(47)
Phenylacetylene	Ethylbenzene and styrene	Spongy Ni		(47)
Phenyl-*p*-tolylethynylcarbinol	Phenyl-*p*-tolylvinylcarbinol	Cu-Ag		(191)
3-(2-Propoxymethoxy)-3-methyl-1-butyne	3-(2-Propoxymethoxy)-3-methyl-1-butene	Cu-Ag	46	(285)
3,4,4-Trimethyl-1-pentyn-3-ol	3,4,4-Trimethyl-1-pentene-3-ol	Ag-Cu	52	(97)

use of a probing electrode, potentiometer, and standard cell; a description of this apparatus has been presented (208). Designs of several pieces of apparatus which can be used to maintain constant cathode potential have been described (3, 107, 207). An apparatus to maintain constant cathode potentials as high as −6 v. has been described in both a micro and a macro form (10). A simple potentiostat, which requires no preliminary adjustment or calibration and which is sensitive to ±0.01 v. up to 25 v., has been reported (207).

6. *Control of temperature*

The temperature of a cell may be controlled by placing the entire cell in an ice bath, on a steam cone, or in a constant-temperature bath. A glass coil in the catholyte may be used to circulate cold or hot water; occasionally the cathodes themselves are hollow tubes through which cold or hot water circulates.

7. *Agitation*

Stirring may be accomplished by the usual types of paddle stirrers, by rotating a cylindrical cathode, or by circulating the liquid by means of a small pump. In some cases bubbling of air or other gas through the catholyte provides sufficient agitation.

III. ELECTROÖRGANIC REDUCTIONS

A. REDUCTION OF CARBON–CARBON UNSATURATED COMPOUNDS

1. *Ethylenic bonds*

Carbon–carbon unsaturation, which is found in isolated ethylenic bonds, is very resistant to electroorganic reduction. The only successful attempts to reduce isolated ethylenic bonds have utilized cathodes with a spongy surface (for example see reference 258). It is to be questioned whether these reductions are bona fide electrolytic reductions, or merely reductions by molecular hydrogen at a catalytic surface. Examples of the reduction of isolated ethylenic bonds as well as other carbon–carbon unsaturation are included in table 2.

Carbon-carbon double bonds conjugated with either another ethylenic group, a carbonyl group, or a nitro group appear to be easier to reduce than isolated ethylenic bonds. Either the use of high-overvoltage cathodes, such as lead or mercury, or of an activated cathode surface, such as platinized platinum or nickelized nickel, is necessary to bring about this type of electrolytic reduction. The diene acid β,γ-diphenylmuconic acid, however, is reduced only to β,γdiphenylhydromuconic acid via 1,4-addition (105).

The olefinic group in acids with a double bond between a benzene ring and the carboxyl group, or between two carboxyl groups, can be reduced using lead or mercury cathodes. In acidic solutions at a mercury cathode certain acids undergo bimolecular reduction to adipic acids (172), but this is not general (374). The electrolytic reduction of 3-nitrocinnamic acid to β-(3-nitrophenyl)propionic acid (293) was very unusual, for the nitro group is generally more easily reduced at the cathode than is the ethylenic group. Reduction of dimethylmaleic and dimethylfumaric acids at a mercury cathode gave racemic acid and *meso*-α,α′-dimethylsuccinic acid, respectively. This is apparently the first clear case of trans addition at an electrode (266).

2. Aromatic unsaturation

A number of carbon-to-carbon double bonds in nitrogen heterocyclic compounds, including some alkaloids, have been reduced. Generally, but not always, either high-overvoltage cathodes or especially activated cathodes were necessary to bring about these electroreductions. Aromatic rings containing a nitrogen atom were reduced with relative ease at high-overvoltage cathodes, particularly lead. A comparison of the activity of heterocyclic and homocyclic rings may be noted in the reduction of quinoline to 1,4-dihydroquinoline and 1,2,3,4-tetrahydroquinoline (200).

Platinized platinum cathodes were required for the complete reduction of the benzene nucleus. Claims that aromatic carboxylic acids were completely reduced in the nucleus under basic conditions at lead or mercury cathodes (223) appear to be ill-founded (224). Several 2-alkoxynaphthalenes have been reduced to 3,4-dihydronaphthalenes by use of a tetrabutylammonium iodide catholyte at a mercury cathode maintained at a constant potential (80).

3. Acetylenes

Nickelized nickel, platinized platinum, and silver-plated copper cathodes served adequately for the reduction of acetylenes to ethylenes or saturated hydrocarbons. Acetylene can be reduced to ethylene by controlling the cathode potential (32). In a number of cases ethynes have been reduced to cis olefins (47).

B. REDUCTION OF CARBON–NITROGEN UNSATURATED COMPOUNDS

Carbon–nitrogen unsaturation has been reduced under electrolytic conditions in a variety of compounds. Ketoximes and aldoximes have been reduced to amines in acid solution, generally at a lead cathode. These, as well as other carbon–nitrogen unsaturated compounds, are presented in table 3.

The reduction of imino ethers to amines involves not only the saturation of a carbon-to-nitrogen double bond, but also the hydrogenolysis of an ethoxy group to give ethanol (362).

Reduction of Schiff bases to secondary amines and related compounds has been carried out at high-overvoltage cathodes of lead or mercury in an acid solution. With some Schiff bases derived from ketones the use of a lead cathode and an alkaline solution has been reported (149). The reduction of a nitro compound in the presence of a carbonyl-containing compound may also lead to a secondary amine, the Schiff base probably being an intermediate.

Carbon–nitrogen unsaturation in heterocyclic compounds has also been reduced electrolytically, in many cases at the same time as carbon–carbon unsaturation (some of these compounds are therefore listed in table 2).

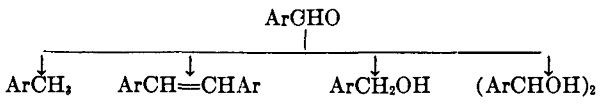
A lead cathode is generally necessary for the reduction of the carbon-to-nitrogen triple bond. Unlike the other carbon–nitrogen compounds, a neutral solution appeared to be the most favorable for the reduction of cyanides to amines. It has been shown (235) that yields of amines by electroreduction of cyanides fell off as the catholyte was made either acidic or basic. In some cases, however, an acidic solution has been used successfully (239). A cyano group attached directly to a benzene ring gives good yields of a benzylamine upon electroreduction, but benzyl cyanide is hardly reduced at all to the corresponding amine (235) (however, see reference 166).

C. REDUCTION OF CARBONYL COMPOUNDS

1. Aldehydes

The electrochemical reduction of carbonyl compounds has been studied almost as extensively as has that of the nitro group. The reduction of saturated aliphatic aldehydes may take several routes. Monomolecular reduction appeared to be favored by an acidic catholyte. Use of a mercury or lead cathode generally gave an alcohol, while at a cadmium cathode, of highest overvoltage, reduction of an aldehyde to a hydrocarbon may take place. An example of bimolecular reduction is the reduction of glyoxylic acid to tartaric acid at a lead or mercury cathode in alkaline, neutral, or acid solution (42). Conjugated unsaturated aldehydes were more easily reduced than the isolated carbonyl groups. The data on the electroreduction of aldehydes are included in table 4.

As with the aliphatic aldehydes, the electrolytic reduction of aromatic aldehydes may take several courses:



ArCHO → $ArCH_3$, $ArCH{=}CHAr$, $ArCH_2OH$, $(ArCHOH)_2$

Most investigators were at odds as to the optimum

TABLE 3

Reduction of carbon–nitrogen unsaturated compounds

Material to Be Reduced	Reduction Product	Cathode	Yield	References
			per cent	
Acetophenone oxime	α-Methylbenzylamine	Pb	17	(328)
Benzophenone oxime	Benzhydrylamine	Pb	11	(328)
Deoxybenzoin oxime	1,2-Diphenylethylamine	Pb		(318)
Diethyl ketoxime	α-Ethylpropylamine	Pb	11	(328)
Dimethylglyoxime	2,3-Diaminobutane, biacetyl, and butylene glycol	Pb, Hg, Zn–Hg		(245)
Oximinoglutaric acid	Glutamic acid	Pb	65	(319)
p-(Carbaldoxime)phenyl ethyl sulfone	*p*-(Aminomethyl)phenyl ethyl sulfone	Pb	63	(226)
p-(Carbaldoxime)phenyl methyl sulfone	*p*-(Aminomethyl)phenyl methyl sulfone	Pb	63	(226)
Cyanamide	Formamidine, formic acid, methylamine, and ammonia	Sn		(233)
Adiponitrile	Hexamethylenediamine			(239)
Benzyl cyanide	β-Phenethylamine	Ni–Pb		(166)
Cyanoacetic acid	β-Aminopropionic acid			(239)
2-Cyanoethanol	3-Amino-1-propanol			(239)
p-Cyanophenylsulfonamide	*p*-Aminomethylphenylsulfonamide	Ni–Pb		(156)
Malononitrile	1,3-Diaminopropane			(239)
Methyl cyanide	Ethylamine	Ni–Pb, Hg	93	(239, 276)
4-Amino-5-cyano-2-methyl pyrimidine	4-Amino-5-(aminomethyl)-2-methylpyrimidine	Ni–Pb, Hg	93	(158, 276)
o-Methylphenyl cyanide	*o*-Methylbenzylamine			(239)
Phenyl cyanide	Benzylamine	Ni–Pb, Pb	96	(239, 276)
Succinonitrile	1,4-Diaminobutane	Pd–Pt		(239)
6-Chloro-7-sulfamoyl-1,2,4-benzothiadiazine 1,1-dioxide	6-Chloro-7-sulfamoyl-3,4-dihydro-1,2,4-benzothiadiazine 1,1-dioxide	Hg		(60)

TABLE 4

Reduction of aldehydes

Aldehyde	Reduction Product	Cathode	Yield	References
			per cent	
Acetaldol	1,3-Butylene glycol	Hg		(380)
Acrolein	Allyl alcohol	Cu, Pb, Zn, Hg–Pb	50	(36)
Butyraldehyde	1-Butanol	Hg		(357)
Fructose	Sorbitol and mannitol	Pb, Hg	30–55 50–92	(255)
Glucose	Formaldehyde, pentoses, mannitol, sorbitol, a dodecitol, and a polyhydric alcohol	Pb, Hg, Ni–Al, Pb–Hg, Zn–Hg		(26, 43, 57, 132, 133, 134, 138, 142, 144, 255, 264, 308, 376–379)
Hexoses	Hexitols			(44)
Lactose	Lactositol	Pb–Hg, Zn–Hg		(133)
Mannose	Mannitol	Pb, Hg	50–92	(255)
Sugars	Polyhydric alcohols			(22)
p-Acetamidobenzaldehyde	4,4′-Bis(*p*-acetamido)hydrobenzoin	Hg	80	(12)
Benzaldehyde	Dibenzylmercury	Hg		(21)
	Hydrobenzoin	Hg		(357)
p-Dimethylaminobenzaldehyde	4,4′-Bis(dimethylamino)hydrobenzoin	Hg	58	(2, 357)
p-Hydroxybenzaldehyde	4,4′-Dihydroxyhydrobenzoin	Hg	95	(4)
m-Tolualdehyde		Cu		(260)
p-Tolualdehyde		Cu		(260)
o-Vanillin	2,2-Dihydroxy-3,3′-dimethoxyhydrobenzoin	Pb	70	(257)

conditions for the electroreduction of aromatic saturated aldehydes. An acidic catholyte and high-overvoltage cathodes appeared to be most desirable, although good yields also were reported from basic solutions. It has been stated (287) that copper, the cathode of lower overvoltage, favors bimolecular reduction.

2. Ketones

The electrolytic reduction of keto groups to methylene groups in aliphatic compounds has been reviewed by Swann (324). This reduction generally takes place only in acid solution; an amalgamated zinc cathode appears to be the most active. Reduction of aliphatic ketones at cathodes of high overvoltage, generally in alkaline solution, tends to lead to pinacol formation, although this reaction is not general for all aliphatic ketones. A host of other products have been isolated from the electroreduction of aliphatic ketones. Table 5 contains a summary of the electroreduction of various ketones. Generally the reduction of aldehydes can be accomplished a little more readily than the reduction of ketones.

Acetone has been reduced to isopropyl alcohol and pinacol in aqueous solution at a mercury cathode (141). It is believed that the acetone is first adsorbed on the mercury, forming a covalent bond. This may then dissociate as a free radical to form pinacol, or may first add a proton and then dissociate from the mercury surface as an ion, which adds a second proton to give the alcohol.

In certain cases an electroreduction of an ethylenic bond in an aliphatic unsaturated ketone may occur selectively. Also, with α,β-unsaturated ketones, a bimolecular reduction may occur (187).

TABLE 5

Reduction of ketones

Ketone	Reduction Product	Cathode	Yield, %	References
Acetone	Propane, pinacol, and 2-propanol	Pb, Hg, Cu, Pb-Cu		(50, 131, 141, 160, 174, 234, 294, 296, 373)
1-Acetyl-2-propanol	2-Pentanol	Cd	50	(64)
Carbon monoxide	Formaldehyde	Pb	trace	(100)
4-Dibutylamino-2-butanone	4-Dibutylamino-2-butanol	Pb	69	(346)
Dimethylaminoacetone	Dimethylamine	Cd	25	(193)
4-Dimethylamino-2-butanone	4-Dimethylamino-2-butanol	Pb	62	(304)
Methyl ethyl ketone	2-Butanol, butane, and a pinacol	Zn		(326, 329)
Methyl propyl ketone	Pentane	Cd-Bi	55	(263)
n-Propyl ketone	No reduction	Graphite		(329)
Acetophenone	Methylphenylcarbinol, ethylbenzene, *sym*-dimethyldiphenylglycol, and bis(α-methylbenzyl ether)	Pb, Cu, Pt, Hg, graphite		(81, 110, 225, 260, 272, 325, 329)
p-Acetamido-α-dimethylaminopropiophenone hydrochloride	3,4-Bis(*p*-acetamidophenyl)-1,6-bis(dimethylamino)-3,4-hexanediol	Hg	32	(12)
3-Acetylpyridine	2,3-Bis(3-pyridyl)-2,3-butanediol	Hg	68	(2, 9)
4-Acetylpyridine	2,3-Bis(4-pyridyl)-2,3-butanediol	Hg	98	(9)
2-Acetylpyridine	2,3-Bis(2-pyridyl)-2,3-butanediol	Hg	68	(9)
p-Aminoacetophenone	*p,p'*-Diamino-α,α'-dimethylhydrobenzoin	Hg, Sn	63	(7, 10, 83, 196)
p-Aminopropiophenone	*p,p'*-Diamino-α,α'-diethylhydrobenzoin		57	(11)
p-Carboxyacetophenone	2,3-Bis(*p*-carboxyphenyl)-2,3-butanediol	Hg	96	(6)
p-Dimethylaminoacetophenone	2,3-Bis(*p*-dimethylaminophenyl)butane-2,3-diol	Hg	82	(5)
p-Dimethylaminopropiophenone	Two isomers of α,α'-di(2-dimethylaminoethyl)hydrobenzoin	Hg	6 and 11	(12)
Hexanoylresorcinol	Hexylresorcinol	Zn-Hg	71	(146)
p-Hydroxyacetophenone	*p,p'*-Dihydroxy-α,α'-dimethylhydrobenzoin	Hg		(2)
4-Methoxyacetophenone and 4-aminoacetophenone	Mixed pinacol	Hg	23	(14)
4-Methoxyacetophenone and 4-dimethylaminoacetophenone	Mixed pinacol	Hg	38	(14, 205)
p-Methoxypropiophenone	α,α'-Diethyl-4,4'-dimethoxyhydrobenzoin			(147)
1-Piperonylidene-2-heptanone	1-(3,4-Methylenedioxyphenyl)-3-octanone	Cu-Ni		(157)
Benzophenone	Benzhydrol	Graphite	75	(39, 327)
α-Methyldeoxybenzoin	Erythro-1,2-diphenyl-1-propanol	Hg		(218)
Androsta-1,4-dien-17-β-ol-3-one	A pinacol	Hg	85	(212)
Androstenedione	A pinacol (mixture)	Hg	60	(212)
Δ^4-Androstene-3 17-dione	Testosterone	Pb, Ni, Cu, C, Pt		(128, 180)
1-Azabicyclo[6.4.0]dodecan-7-one	1-Azacyclododecan-7-ol	Pb	42	(197)
1-Azabicyclo[5.4.0]hendecan-6-one	1-Azacyclohendecan-6-ol	Pb	71	(197)
Benzo[*c*]-7-oxo-1-azobicyclo[4.4.0]decane	Benzo[*c*]-1-azabicyclo[5.3.0]decane, benzo[*c*]-7-hydroxy-1-azabicyclo[4.4.0]decane, and benzo[*c*]-7-hydroxyazocyclodecane	Pb		(195)
Bezno[*j*]-7-oxo-1-azabicyclo[6.4.0]dodecane	Benzo[*c*]-1-azabicyclo[5.5.0]dodecane, or benzo[*j*]-1-azabicyclo[6.4.0]dodecane and (maybe) benzo-[*c*]-7-hydroxyazacyclododecane	Pb		(195)
Benzo[*c*]-7-oxo-1-azabicyclo[4.3.0]nonane	Benzo[*c*]-1-azabicyclo[4.3.0]nonane, and benzo[*c*]-7-hydroxy-1-azabicyclononane or benzo-7-hydroxyazacyclononane	Pb		(195)
Benzo[*i*]-6-oxo-1-azabicyclo[5.4.0]undecane	Benzo[*c*]-1-azabicyclo[5.4.0]undecane and benzo[c]-7-hydroxyazacyclohendecane	Pb		(195)
4-Cholesten-3-one	Bi(3β-hydroxy-4-cholesten-3α-yl) and bi(3,5-cholestadien-3-yl)	Hg	40–51	(34, 212)
3-(2-Diethylaminoethyl)-4-oxo-4*H*-octahydroquinolizine)	3-(2-Diethylaminoethyl)octahydroquinolizine	Pb	35	(238)
2,6-Dimethylcyclohexanone	2,6-Dimethylcyclohexanol (trans)	Hg, Pb		(18)
	(cis)	Cu		
	(mixed)	Ni		
Estrone	Estradiol	Pb, C		(279)
2-Ethyl-1-methyl-3-piperidone	2-Ethyl-1-methyl-3-piperidinol, 1-methyl-2-propylpyrrolidine, 1-methyl-2-ethyl-3-piperidinol, *N*-methylheptylamine, and 1-methyl-2-propyl-Δ^1-pyrroline	Cu, Cd, Pb		(193)
1-Butyl-3-pyrrolidone	Dibutylamine, 1-butyl-3-hydroxypyrrolidine, 1-butylamino-3-butanol, 1-butyl-3-hydroxypyrrolidine, and 1-butylamino-3-butanol	Cd		(193)
1-Methyl-4-piperidone	1-Methylpiperidine	Cd	59	(193)
Hexahydro-1(2*H*)pyrrocolinone	Azacyclononan-4-ol and azacyclononane	Pb		(194)
Hexahydro-8(5*H*)pyrrocolinone	Acyclononan-5-ol and octahydropyrrocoline	Pb		(194)
5-Methyl-4-oxoheptanoic acid	5-Methylheptanoic acid	Pb	72	(301)
Octahydro-1*H*-quinalizin-1-one	Azacyclodecan-5-ol and 1-azabicyclo[5.3.0]decane	Pb		(194)
7-Oxo-5-cholesten-3β-yl acetate	A pinacol	Hg		(34)
20-Oxo-5,16-pregnadien-3β-yl acetate	Mixture incl. bi(3β-hydroxyoxo-5-pregnen-16-yl)	Hg		(34)
Δ^4-Pregnene-3,20-dione	Δ^4-Pregnen-20-ol-3-one	Pb, Ni, Cu, C, Pt		(128, 180)
Progesterone	A pinacol	Hg	65	(212)
2,2,4,4-Tetraphenyl-3-oxetanone	2,2,4,4-Tetraphenyl-3-oxetanol and (possibly) 1,1,3,3-tetraphenyl-2-propanol	Hg		(259)

Reduction of saturated aromatic ketones at a lead cathode in slightly basic solutions gave high yields of secondary alcohols. An acidic catholyte generally produced a mixture of the pinacol and the benzhydrol; if the catholyte was strongly acidic, rearrangement to the pinacolone sometimes occurred. *o*-Nitrobenzophenone was reduced in alkaline solution at a lead cathode to *o*-hydroxylaminobenzohydrol, which loses water to form 1,2-dihydroanthranil (23.) To reduce aromatic ketones to hydrocarbons it is generally necessary to use amalgamated zinc cathodes. The reductive coupling of 4-methoxyacetophenone with 4-amino- and 4-dimethylaminoacetophenones to yield mixed pinacols is achieved by electrolysis at a mercury cathode (14). It is of interest to note that 2,3-bis(*p*-aminophenyl)-2,3-butanediol can be obtained only by electrolytic reduction of the appropriate ketone in an aqueous hydrochloric acid medium at a mercury cathode (10, 11). The usual chemical methods gave only the carbinol. It is also of interest to note in regard to the reduction of *p*-aminoacetophenone that using an aqueous hydrochloric acid solution at a mercury cathode with a reference potential of −1.1 v. gave the carbinol, while a reference potential of −1.5 v. (10, 11) or a tin cathode (196) gave the pinacol. A number of Mannich bases also have been reduced to pinacols (12). Depending upon the reference potential used, either a low-melting or a high-melting form of the pinacol was obtained from *p*-dimethylaminoacetophenone (5).

An acid solution with a high-overvoltage cathode, such as lead or mercury, is best for the reduction of cyclic ketones. Alcohols, pinacols, pinacolones, and hydrocarbons have been isolated from the electroreduction of cyclic ketones. Reduction of 2-methylcyclohexanone at a mercury or lead cathode gave pure *trans*-2-methylcyclohexanol, at a nickel cathode a mixture was obtained, at a copper cathode pure *cis*-2-methylcyclohexanol was obtained, and at a platinum cathode no reduction took place (18). The reduction of 2-ethyl-1-methyl-3-piperidone has been reported to give products such as 1-methyl-2-propylpyrroline, 2-ethyl-3-hydroxy-1-methylpiperidine, *N*-methylheptylamine, and 1-methyl-2-propyl-2-pyrroline (193) depending on the cathode and the temperature. Thus reductions, and rearrangements of the Clemmensen type, can be obtained by electrolysis.

Reduction of keto acids and keto esters may take several courses. Generally an acidic catholyte allowed complete reduction to hydrocarbons with hydrogenolysis of the ester group. A basic catholyte usually gives a less reduced product than an acidic catholyte.

Quinones are reduced easily at the cathodes of lowest overvoltage in acid solution. For example, the following gave the corresponding hydroquinones: anthraquinone (244), 3,6-bis(1,4-dihydroxyphenyl)-1,4-benzoquinone (127), naphthoquinone (243), and quinone (1, 170).

3. Carboxylic acids, esters, and lactones

An acid solution at a lead or mercury cathode was preferred for the electroreduction of aliphatic carboxylic acids to aldehydes, alcohols, or hydrocarbons. With these cathodes, ethyl oxalate in ethanolic sulfuric acid has been reduced to ethyl glyoxylate ethyl hemiacetal (252). The products of the electroreduction of carboxylic acids, esters, and lactones are presented in table 6.

Aromatic carboxylic acids are reduced to alcohols in a sulfuric acid catholyte using a lead or mercury cathode. It is possible to reduce certain aromatic acids to aldehydes in alkaline solution in the presence of the borate ion at a mercury cathode (227). Isonicotinic acid has been reduced to 4-picoline at an amalgamated lead cathode (364).

Aromatic carboxylic acid esters have been reduced to the corresponding ethers or alcohols in an acid catholyte at mercury or lead cathodes.

4. Amides, imides, and related compounds

The reduction of amides to amines has been carried out in acidic catholytes (some aliphatic amides have been reduced in basic solutions) at lead cathodes. The more substituted the amide nitrogen, the better the yield of amine; a phenyl group attached to the amide group increases the yield of substituted benzylamine. In fact, any aryl group linked directly to the carbonyl function gave good results, indicating that the greater the electron-donating effect of substituents on the amide nitrogen and the α-carbon atom, the greater the ease of reduction. A few instances of hydrogenolysis of the nitrogen compound to give ammonia or a simple amine have been reported. These reductions of amides, as well as the reduction of imides and related compounds, are included in table 7. Attempts to reduce *p*-aminobenzanilide have been without success at many cathodes (38).

Imides of dibasic acids have been reduced to cyclic lactams and cyclic amines in acid solution. Generally a lead cathode is used, but cadmium and amalgamated zinc have been useful in some cases. Occasionally the ring has been opened by hydrogenolysis. In the case of many aliphatic imides the product from the reduction of only one carbonyl group may be isolated in good yields, while electroreduction of both carbonyl groups gave poor yields of the corresponding cyclic amine. *N*-substituted tetrachlorophthalimide can be reduced to a hydroxyphthalimide at a palladium cathode and a potential of −0.68 v. This hydroxyphthalimide can then be reduced further to an isoindoline at a reference potential of −1.10 v. (13). The mechanism of this reduction has been discussed in some detail (8).

TABLE 6

Reduction of carboxylic acids and derivatives

Material to Be Reduced	Reduction Product	Cathode	Yield	References
			per cent	
Butyric acid	Butyl alcohol		6	(221)
α-Hydroxypropionic acid	Lactaldehyde	C	40	(82)
Oxalic acid	Glyoxylic acid, glycolic acid, formaldehyde, and tartaric acid	Pb. Ni, Hg. Cd, Tl		(106, 154, 159, 209, 182)
Oxalic acid and hydroxylamine sulfate	Glycine	Pb	75	(382)
Diethyl oxalate	Ethyl glyoxalate	Hg. Pb	53	(252)
Anthranilic acid	*o*-Aminobenzyl alcohol	Pb	78	(53)
6-Benzyl-3-carbomethoxy-2-hydroxy-4-methylbenzoic acid	6-Benzyl-3-carbomethoxy-2-hydroxy-4-methylbenzaldehyde			(227)
Isonicotinic acid	4-Picoline	Hg. Pb	31	(364)
Phthalic acid	Phthalide and 2,5-dihydrophthalic acid	Hg		(246)
2-Pyridinecarboxylic acid	2-Picoline	Hg, Pb	33	(364)
Salicylic acid	Salicylaldehyde and phenol	Cu. Hg. Cu-Hg		(79, 222, 351, 352)
Acetylsalicylic acid	Acetylsalicylaldehyde	Brass	30	(222)
Methyl isophthalate	*m*-Carboxybenzyl alcohol	Hg		(246)
Methyl phthalate	Phthalide			(246)
α-D-Glucoheptono-γ-lactone	α-D-Glucoheptose	Hg	60	(274)
Lactones of monosaccharides	Monosaccharides	Hg		(153)
D-Mannono-γ-lactone	D-Mannose	Hg	60	(274)
N-Methylcarbamylmeconin	1,3-Diketo-2-methyl-7,8-dimethoxy-1,2,3,4-tetrahydroisoquinoline	Pb	40	(356)
Polyhydroxycarboxylic acid lactones	Sugars	Hg		(148)
D-Ribono-γ-lactone	D-Ribose	Hg	60	(29, 275)
D-Talono-γ-lactone	D-Talose	Hg	60	(274)
Benzoic acid	Benzyl alcohol and benzaldehyde	Pb. Hg		(251)
Phenylacetic acid	Phenethyl alcohol	Pb. Hg. Zn-Hg		(250)

D. HYDROGENOLYSIS OF ALCOHOLS

Aside from the possible reduction of carbonyl groups to methylene groups that may conceivably proceed through the alcohol, there are very few examples known of the hydrogenolysis of an alcohol to the methylene compound. A few of these have been included in other tables. In the case of leucopterin the hydrogenolysis of all the hydroxyl groups does not take place, and the product is 2-amino-7-hydroxypteridine (366). The hydrogenolysis of hydroxysparteine to sparteine (112) may also be cited in this section.

E. REDUCTION OF NITROGEN–OXYGEN UNSATURATED COMPOUNDS

1. *Hydroxylamines*

A nickel cathode and a basic catholyte were preferred for the reduction of aromatic hydroxylamines to azoxy compounds or to amines. Liquid ammonia has been used as a solvent in the reduction of phenylhydroxylamine to benzenediazoic acid (289).

2. *Nitroso compound*

The reduction of a nitrogen–nitroso compound to the corresponding hydrazine was best carried out in an acidic catholyte at cathodes of copper, lead, mercury, and cadmium, while a nickel or platinum cathode and a basic catholyte were preferred for the reduction of a carbon–nitroso compound to the corresponding amine. For example, 1,1-dimethylhydrazine was obtained in 90 per cent yield by the electroreduction of *N*-nitrosodimethylamine in aqueous sulfuric acid at a lead cathode (152) and 2,4,5-triamino-6-hydroxypyrimidine was obtained in 80–85 per cent yield by the reduction of 2,4-diamino-6-hydroxy-5-nitrosopyrimidine in dilute alkali (383), or by the reduction of the 5-isonitroso compound in aqueous hydrochloric acid or 1 per cent sodium hydroxide (28).

3. *Azoxy compounds*

The reduction of azoxy compounds to azo, hydrazo, or amino compounds took place quite readily in an acid solution. In this manner, azoxybenzene gave azobenzene, hydrazobenzene, benzidine, and aniline (30).

4. *Aliphatic nitro compounds*

The reduction of aliphatic nitro compounds was carried out in an acidic catholyte at a wide variety of cathodes. Generally, the cathodes of lower overvoltage such as copper, tin, or nickel, permitted partial reduction of the hydroxylamine (which can be reduced further under certain conditions as mentioned above), whereas the cathodes of higher overvoltage, such as mercury and lead, favored the complete reduction of the nitro group to the amino group. Table 8 includes the various aliphatic and alicyclic nitro compounds that have been reduced electrolytically since 1940.

A number of 2-aminoethyl compounds have been prepared by the reduction of α,β-unsaturated nitro compounds at a lead cathode in hydrochloric acid.

5. *Aromatic nitro compounds*

The aromatic nitro group is perhaps the easiest of all

TABLE 7

Reduction of amides, imides, and related compounds

Material to Be Reduced	Reduction Product	Cathode	Yield	References
			per cent	
Acetanilide	*N*-Ethylaniline	Pb	39	(321)
Benzamide	Benzylamine and benzyl alcohol	Hg. Cd. Pb		(175, 176)
1,4-Dibenzyl-2,5-dioxopiperazine	1,4-Dibenzylpiperazine	Pb	70	(384)
Diketopiperazine	Piperazine	Hg	92	(175)
1,4-(3,4-Dimethoxybenzyl)-2,5-dioxopiperazine	1,4-(3,4-Dimethoxybenzyl)piperazine	Pb	70	(384)
N,N-Dimethylbenzamide	Dimethylbenzylamine	Pb. Hg	100	(175)
N,N-Dimethylphenylacetamide	*N,N*-Dimethyl(2-phenethyl)amine	Zn. Hg	100	(175)
N,N-Dimethylvaleramide	*N,N*-Dimethylamylamine	Pb	56	(321)
1,4-Di(2-phenethyl)-2,5-dioxopiperazine	1,4-Di(2-phenethyl)piperazine	Pb	70	(384)
Hippuric acid	*N*-Benzylglycine	Pb	97	(176)
Leucylleucine	Diisobutylpiperazine	Hg	90	(175)
N-Methylbenzamide	Methylbenzylamine	Pb, Hg	95	(193)
1-Methyl-2-ethyl-3-piperidone	1-Methyl-2-propylpyrrolidine, 1-methyl-2-ethyl-3-hydroxypiperidine. *N*-methylheptylamine. and 1-methyl-2-propyl-Δ^2-pyrroline	Sn. Cu. Cd. Pb		(193)
1-Methyl-4-piperidone	1-Methylpiperidine	Cd	59	(193)
N-Methylphenylacetamide	*N*-Methyl(2-phenethyl)amine	Hg	93	(175)
3-Benzylidene-2-methylnaphthalimidine	1-Benzyl-2-methylisoindoline	Pb		(306)
3-Benzylidenephthalimidine	1-Benzylisoindoline	Pb		(306)
N-(2-Diethylaminoethyl)succinimide	*N*-(2-Diethylaminoethyl)pyrrolidone	Pb–Hg		(237)
N-(2-Dimethylaminoethyl)succinimide	*N*-(2-Dimethylaminoethyl)pyrrolidone	Pb–Hg		(237)
Hexahydro-4-pyrrolo[1,2-α]-pyrrol-3-one	Pyrrolizidine	Pb		(113)
1-Methylisatin	1-Methyldihydroxyindole. 1-methylhydroxyindole. and 1-methyldihydroindole	Pb. Hg, Zn–Hg		(270)
Phthalimide	Dihydroisoindole, phthalimidine. 3-hydroxyphthalimidine, isoindoline. and 1-(2-phthalimidyl)-3-oxoisoindoline	Pb. Zn–Hg		(86. 87. 88. 271)
3,4,5,6-Tetrachloro-*N*-(2-dimethylaminoethyl)-phthalimide	4,5,6,7-Tetrachloro-2-(2-dimethylaminoethyl)-3-hydroxyphthalimidine. 4,6,7-trichloro-2-(2-dimethylaminoethyl)isoindoline. and 4,5,6,7-tetrachloro-2-(2-dimethylaminoethyl)isoindoline	Pb		(13)
3-Veratrylidinephthalimidine	1-Veratrylisoindoline	Pb		(173)

TABLE 8

Reduction of aliphatic and alicyclic nitro compounds

Nitro Compound	Reduction Product	Cathode	Yield	Reference
			per cent	
Chloropicrin	Methylamine. methylhydroxylamine. dichloroformoxime. di- and trichloronitrosomethanes	Pb. Cd. Hg. Sn		(41. 217. 260)
3,4-Diethoxy-α-(1-nitroethyl)benzyl acetate	*N*-(3,4-Diethoxy-β-hydroxy-α-methylphenylethyl)acetohydroxamic acid			(177)
2,5-Dimethoxy-β-nitrostyrene	2,5-Dimethoxyphenylethylamine	Pb	52	(307)
1-(3-Methoxy-4-ethoxyphenyl)-2-nitropropyl acetate	1-(3-Methoxy-4-ethoxyphenyl)-2-acetamido-1-propanol	Hg	76	(46)
Various nitroalkanols	Hydroxylaminealkanols	Sn		(297)
Various nitroalkanols	Aminoalcohols	Pb		(216)
5-Chloromethyl-3-nitro-2-oxazolidone	3-Amino-5-chloromethyl-2-oxazolidone	Hg	20	(114)
4,4-Dimethyl-3-nitro-2-oxazolidone	3-Amino-4,4-dimethyl-2-oxazolidone	Hg	45	(114)
Nitroguanidine	Aminoguanidine, nitrosoguanidine, and guanidine	Pb. Sn. Pb–Hg		(288, 302. 314. 316, 317)
3-Nitro-4-heptanol	3-Amino-4-heptanol	Pb		(111)
Nitroisobutylglycerol	Tris(hydroxymethyl)methylamine	Pb		(40)
β-Nitroisoelemicin	α-Methylmescaline	Pb	47	(143)
β-Nitrosafrole	α-Methylhomopiperonylamine	Pb		(45)
Nitromethane	Methylhydroxylamine and methylamine	Cu. Pb. Ni		(162. 192. 284)
2-Nitro-1-(*p*-methoxyphenyl)propyl acetate	2-Nitroso-1-(*p*-methoxyphenyl)propyl acetate		21	(178)
1-(Nitromethyl)cyclohexanol	1-(Aminomethyl)cyclohexanol	Pb	83	(35)
2-Nitro-1-(3,4-methylenedioxyphenyl)propyl acetate	2-Nitroso-1-(3,4-methylenedioxyphenyl)propyl acetate			(178)
2-Methyl-2-nitro-1-propanol	2-Methyl-2-hydroxylamine-1-propanol	Sn	78	(297)
3-Nitro-2-oxazolidone	3-Amino-2-oxazolidinone	Hg	50	(114)
1-Nitropropane	*N*-Propylhydroxylamine	Pb	60	(192)
2-Nitropropane	*N*-Isopropylhydroxylamine	Pb	60	(192)
Nitrourea	Semicarbazide	Sn. Hg	69	(33, 155. 302)

unsaturated groups to reduce electrolytically. The platinum cathode has been principally used to bring about this reduction, but procedures have been described for the reduction of aromatic nitro compounds at almost all other known cathodes. Data for the electroreduction of aromatic nitro compounds are summarized in table 9.

The pH of the catholyte is of prime importance in controlling the product of the electroreduction of an aromatic nitro compound; in fact, several chapters of a

TABLE 9

Reduction of aromatic nitro compounds

Nitro Compound	Reduction Product	Cathode	Yield	References
			per cent	
2-Chloromethyl-4-nitrotoluene	Xylidine and 2,6-bis(chloromethyl) derivative	Zn. Pb. Ni. Cu. Sn. Hg		(27)
o-Chloronitrobenzene	4-Amino-3-chlorophenol. *o,o'*-dichlorohydrazobenzene. and *o*-chloroaniline	Cu. Pb		(63. 64. 71. 135. 241, 370)
2-Chloro-6-nitrotoluene	4-Amino-2-chloro-*m*-cresol	Monel. Cu	72	(48. 135. 370)
4-Chloro-2-nitrotoluene	4-Amino-6-chloro-*m*-cresol	Monel. Cu	82	(370)
2.5-Dichloronitrobenzene	4-Amino-3,5-dichlorophenol. 2.2'.5.5'-tetrachlorohydrazobenzene. and 2.2'.5.5'-tetrachloroazoxybenzene	Cu. Fe. Pb. Monel. Ni		(65. 66. 135. 370)
1.3-Dinitrobenzene	1.3-Diaminophenol. 3-nitrophenylhydroxylamine. and *m*-phenylenediamine	Cu		(30, 67. 77. 150. 169)
2.4-Dinitrophenol	Aminonitrophenol and diaminophenol	Pt. Ni. Zn. Cu. Pb		(73. 76)
o-Ethylnitrobenzene	4-Amino-*m*-ethylphenol	Cu	68	(135. 136)
Ethyl *p*-nitrobenzoate	Ethyl *p*-aminobenzoate	Sn. Pb		(292)
1-Methoxy-2-(*p*-nitrophenoxy)-ethane	4.4'-Bis(2-methoxymethoxy) azobenzene	Pb. Ni	45	(362)
o-Nitroaniline	*o*-Phenylenediamine	Pt. Ni. Cu. Monel. Pb. Zn. bronze. Hg. Sn. Fe	92	(344. 345. 347. 348)
m-Nitroaniline	2.4-Diaminophenol	Ni. Cu. Pt. Monel. bronze	69	(30. 78)
p-Nitroaniline	*p*-Phenylenediamine	Pt. Ni. C	95	(30, 225)
o- and *p*-Nitroanisoles	*p*-Anisidine. azoxyanisole. hydrazonanisole. *o*- and *p*-anisidines. *o*-aminophenol. 1.2-bis(*o*-methoxyphenyl)hydrazine. and *p.p'*-azoxybisanisole	Pb. Zn. Hg		(30, 63. 75)
Nitrobenzene	Aniline. hydrazobenzene. benzidine. azobenzene, azoxybenzene. *p*-aminophenol. and *p*-phenetidine	Fe. Pb, Zn. Ni, Hg. Cu. Au. Sn. Pt. Cd		(17. 20, 30, 61, 62, 219. 225. 280. 281. 282. 300. 310. 311. 370)
m-Nitrobenzenesulfonic acid	Benzidine-3,3'-disulfonic acid	Ni. Fe	60	(126)
o-Nitrobenzoic acid	Anthranilic acid and 5-hydroxyanthranilic acid	Cu. Pt. Pb. Sn. Zn		(72. 161)
m-Nitrobenzoic acid	*m*-Aminobenzoic acid and 5-aminosalicylic acid	Pt. Pb. Sn. Cu. Zn		(72, 161)
p-Nitrobenzoic acid	*p*-Aminobenzoic acid	Sn. Hg, Pb. Zn	98	(30, 126. 161, 262)
2-Nitro-4-chloroanisole	Dichlorohydrazoanisole. 4-chloro-*o*-anisidine. 1.2-bis-(5-chloro-2-methoxyphenyl)hydrazine	Fe		(65)
2-Nitro-4-chlorophenetole	2.2'-Dichloro-5.5'-diethoxyhydrazobenzene and 1.2-bis(5-chloro-2-phenoxyphenyl)hydrazine	Fe		(70)
m-Nitrodimethylaniline	Tetramethyl-*m*-diaminoazobenzene. *m*-aminodimethylaniline, and tetramethyl-*m*-diaminohydrazobenzene	Ni		(30)
p-Nitrodimethylaniline	*p*-Azodimethylaniline and *p*-aminodimethylaniline	Pb		(30)
1-Nitronaphthalene	1-Aminonaphthol and 1-aminonaphthalene	Ni, Cu		(135)
p-Nitrophenetole	*p*-Phenetidine	Pt. Ni. Pb. Zn, Cu		(19)
o-Nitrophenol	*o*-Aminophenol and dianilinoquinoneanil	C. Pt, Ni. Pb. Zn. Hg. Fe		(355. 361)
m-Nitrophenol	*m*-Aminophenol and *m*-hydroxylamine derivative	Pt. Ni, Hg		(30. 355)
p-Nitrophenol	*p*-Aminophenol and dianilinoquinoneanil	Pt. Ni. Pb. Zn. Cu		(30. 355)
o-Nitrophenylcyclohexane	*o*-Cyclohexylaniline	Hg	85	(213)
m-Nitrophenyldiphenylmethanol	3.3'-Bis(α-hydroxybenzohydryl)azobenzene	Pt		(375)
4-Nitropyridine *N*-oxide	4.4'-Azodipyridine *N.N'*-oxide	Cu	78	(232)
4-Nitroquinoline *N*-oxide	4-Aminoquinoline and tetrahydroquinoline	Pb. Cu. Ni		(232)
p-Nitrosalicylic acid	*p*-Aminosalicylic acid	Pb. Sn. Pt	82	(151. 225. 305)
o-Nitrotoluene	Hydrazotoluene, *o*-toluidine. 4-amino-*m*-cresol. and *o,o'*-azotoluene	Zn. Ni. Cu. Monel. Fe, bronze. Pb. Pt		(63. 68. 135. 370)
m-Nitrotoluene	4-Amino-*m*-cresol and *m,m'*-azotoluene	Hg. Monel		(69. 74. 135)
p-Nitrotoluene	*p*-Toluidine. diaminophenyltolylmethane. *p.p'*-hydrazotoluene, and *p.p'*-azotoluene	Pt. Pb. Zn		(30)
4-Nitrotropolone	4-Aminotropolone	Hg		(30)
Picric acid	Triaminophenol	Pt. Pb	97	(206, 240)
2.4,6-Trinitrobenzoic acid	2,4.6-Triaminobenzoic acid	Pb	76	(206)
Trinitrotoluene	Triaminotoluene	Pb	97	(206)

book (42) have been devoted to the reduction of aromatic nitro compounds in basic, neutral and acidic catholytes.

Briefly, the effect of the pH of the catholyte upon the reduction of aromatic nitro compounds may be divided into four classes. In a basic catholyte bimolecular products, the azo-, azoxy-, and hydrazo-compounds, predominate. Presumably this is due to the base-catalyzed condensation of such intermediate reduction products as the nitroso- and hydroxylamine compounds.

The reduction to azoxy compounds is general except for *o*- and *p*-nitrophenols, nitroanilines, and nitro-*N*- and -*N*,*N*-substituted anilines, and certain hindered nitro compounds. Generally a cathode of low hydrogen overvoltage, such as nickel, and an alkaline solution are used. The low hydrogen overvoltage prevents the azoxy compound from being reduced. The azoxy compound is insoluble in the catholyte and precipitates out. In order to prepare the azo compound the azoxy compound must be kept in solution. Generally the addition of alcohols or salts of aromatic sulfonic acids aids this solubility. A nickel cathode is most generally used at a temperature near the boiling point of the catholyte for the formation of azo compounds. In order to form hydrazo compounds the conditions for the formation of an azo compound are followed and then the cathode current density is lowered.

In a neutral or weakly acidic medium it is sometimes possible to isolate the aromatic hydroxylamine and nitroso compounds. The reduction of aromatic nitro compounds to *p*-aminophenols has been known for some time. At a smooth platinum cathode in sulfuric acid the reduction of aromatic hydroxylamines does not proceed rapidly; rather, in the acid medium they rearrange to the *p*-aminophenols. In the case of 3-nitrophthalic acid the hydroxylamine, as formed, reacts with the carbonyl group to give benzisoxazolone-4-carboxylic acid (120).

In strong acid solutions amines result from the reduction of nitro compounds, while in a very strongly acidic catholyte benzidine may be obtained, probably through the acid-catalyzed benzidine rearrangement of intermediate hydrazo compounds.

An excellent procedure for the preparation of 3-chlorotoluquinone has been described (48). 6-Chloro-2-nitrotoluene is reduced electrolytically to the *p*-aminophenol, and the reaction mixture is oxidized directly to the quinone in good yield.

As can be noted, by examining the reduction of aromatic nitro compounds shown in table 9, it is often possible to reduce the nitro group without further reducing other groups present in the molecule.

F. REDUCTION OF NITROGEN–NITROGEN UNSATURATED COMPOUNDS

1. Azo compounds

Azo compounds were reduced easily to the corresponding hydrazo compounds, or cleaved to two molecules of the corresponding amines, in either basic or acidic catholytes at many different cathodes, including platinum. Azobenzene, for example, has been reduced to hydrazobenzene, benzidine, and aniline (30, 328). Coke has been found to be an efficient cathode for this reduction (328).

2. Diazonium salts

A few diazonium salts have been reduced at a number of high-overvoltage cathodes in acidic catholytes to the corresponding substituted phenylhydrazines. In this manner phenylhydrazine (269) and *o*- and *p*-methoxyphenylhydrazines (101) have been obtained in good yield; in the case of the methoxy compounds the yields are better than those obtained by conventional chemical methods.

G. REDUCTION OF SULFUR-CONTAINING ORGANIC COMPOUNDS

Reduction of the sodium or potassium salts of sulfonic acids at a lead cathode resulted in cleavage of the sulfonic acid residue from the organic molecule.

In an acid solution at a lead cathode aromatic sulfonyl chlorides may be reduced to sulfinic acids, disulfides, sulfoxides, or thiophenols, depending upon the duration of the electroreduction (340, 341).

Sodium thiosulfates are reduced to disulfides in neutral or alkaline catholytes at a platinum cathode.

TABLE 10

Reduction of miscellaneous organic compounds

Material to Be Reduced	Reduction Product	Cathode	Yield	Reference
			per cent	
2-Amino-4-chloro-6-methylpyrimidine	2-Amino-6-methylpyrimidine	Zn, Pb	60	(309, 312)
2-Amino-4-chloropyrimidine	2-Aminopyrimidine	Cd, Pb	60	(312, 313)
8-Chlorotheophylline	Theophylline	Hg	91	(353)
Dibromoacetic acid	Bromoacetic acid	Magnetite		(139)
α,α'-Dibromosuccinic acid	Fumaric acid	Hg		(93)
Dichloroacetic acid	Chloroacetic acid	Magnetite		(139)
Ethyl α,α'-dibromosuccinate	Fumaric acid	Hg		(93)
9-(*o*-Iodophenyl)acridan	9-Phenylacridan	Hg	95	(208)
Chlorotetracycline	Tetracycline	Sn		(261)
Trichloroacetic acid	Chloroacetic acid	Magnetite		(139)
3-Amino-4-hydroxybenzenearsonic acid	3-Amino-4-hydroxyphenylarsenic oxide, 3,3'-diamino-4,4'-dihydroxyarsenobenzene, 3-amino-4-hydroxyphenylarsine, and $HO(3\text{-}NH_2\text{-}4\text{-}HOC_6H_3As)_nOH$	Hg, Pb		(179, 354)
7-Keto-1-azabicyclo[6.4.0]dodecane	7-Hydroxyazacyclododecane	Pb	42	(197)
6-Keto-1-azabicyclo[5.4.0]hendecane	6-Hydroxyazacyclohendecane	Pb	71	(197)
1-Ketoöctahydropyrrocoline	Azacyclononane and 4-hydroxyazacyclononane	Pb		(194)
8-Ketoöctahydropyrrocoline	Octahydropyrrocoline and 5-hydroxyazacyclononane	Pb		(194)
1-Ketoquinolizidine	1-Azabicyclo[5.3.0]decane and 5-hydroxyazacyclodecane	Pb		(194)

Even with very long periods of electroreduction no mercaptans or thiophenols were ever isolated.

By the use of a lead or an amalgamated aluminum cathode and an acidic catholyte, thioacetamides are reduced to the corresponding amines with complete removal of the sulfur.

Reduction of nitrated aromatic thiocyanates, in which the two groups were adjacent to one another, resulted in interaction of the reduced forms to give a thiazole (104).

Reduction of disulfides in an acid solution at a lead cathode resulted in reductive cleavage of the molecule between the two sulfur groups to give the corresponding mercaptans (291). Homocystine has been converted to homocysteine by use of a mercury cathode and a basic catholyte (15). Thiolactams were reduced to the corsponding cyclic amines at a lead cathode in an acidic catholyte.

H. REDUCTION OF MISCELLANEOUS ORGANIC COMPOUNDS

Hydrogenolysis of organic halogen compounds has been found to take place in either acidic or basic catholytes at palladium, lead, copper, mercury, and amalgamated zinc cathodes. Generally better yields, in a shorter period of time, were obtainable in an acid catholyte. The reduction of 9-(*o*-iodophenyl)acridine to (*o*-iodophenyl)acridan and then to 9-phenylacridan at a mercury cathode can be performed selectively by controlling the potential (208). The removal of an aromatic halogen cannot always be predicted (see reference 13).

Arsenic compounds in an acid catholyte were reduced to arseno or arsinic type compounds; generally a high concentration of acid favored the former. The results of various miscellaneous electrolytic reductions, including the scission of carbon-to-nitrogen bonds and the scission of cyclic ethers, are included in table 10.

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