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The electrolytic reduction of polynitro compounds to polyamines

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THE ELECTROLYTIC REDUCTION OF
POLYINITRO COMPOUNDS TO POLYAMINES

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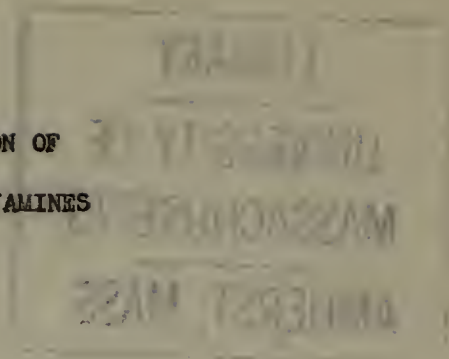


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THE ELECTROLYTIC REDUCTION OF
POLYNITRO COMPOUNDS TO POLYAMINES



FRED WILLIAM JONES

Thesis submitted for
the degree of
Master of Science

MASSACHUSETTS STATE COLLEGE

May 1932

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INTRODUCTION

The original aim which lead to the investigations described in this thesis, was the production of phloroglucinol by means of an indirect electrolytic reduction. Such a procedure, if possible, would be much easier and less expensive than present methods. The problem is of importance because of the usefulness of phloroglucinol in chemical and biological work, especially for the determination of pentosans; and because of its possibilities as an intermediate for the preparation of drugs and dyes. Many interesting possibilities present themselves in the latter field from which phloroglucinol is withheld at the present time because of its cost.

As the work proceeded it was found that in actuality the problem was not one, but two, each of which could be broadened to include not the preparation of a single compound but of a class of compounds. The first problem was the development of a general process for the electrolytic reduction of nitro-compounds by procedures which would give good yields of the corresponding stable amino salts. The free amino compounds in solution are unstable in the presence of atmospheric oxygen and at temperatures often encountered in the reduction or the isolation of such chemical compounds. The second problem was the development of methods for the preparation of corresponding hydroxy derivatives from the amino compounds by relatively simple methods giving good yields. For a time both problems were investigated. However, when it was found that the amino-compounds intermediate to the production of phloroglucinol, could be conveniently

isolated and their yields determined, the second problem was discontinued. The reduction process was extensively studied and a procedure was developed which is of general application for the reduction of various nitro compounds.

REVIEW OF LITERATURE

No attempt can be made here to cover all the work done on the reduction of nitro compounds or even of those compounds with which this paper is concerned. The following review is intended to cover only in general the common methods for the reduction of nitro compounds which yield the less stable amines. The methods closely related to the process investigated and described in this paper are given in greater detail.

For the reduction of some of the nitro compounds with which this thesis is concerned, hydroiodic acid has formerly been used with considerable success (11), but it is a reagent far too expensive for large scale production. Tin and hydrochloric acid serve in general as the best and most used chemical reducing agents for the laboratory. These reagents also are used commercially for such reduced nitro compounds as have been put on the market, for example, diaminophenol (16). The isolation of the amine, usually as the hydrochloride salt, is cumbersome because of the large amount of tin chlorides produced and because the amines often form stable double salts with tin compounds. The method has the disadvantage that in the case of halogen derivatives of the aromatic nitro compounds (e.g.)

pieryl chloride (9) and trinitrodibromotoluene (17), the halogen is often removed from the nucleus. Bradt (2) in carrying out a reduction with zinc dust and hydrochloric acid reports an isolation of 30% of the calculated amount as the 90% pure diaminophenol hydrochloride. There are several other reducing agents which are used to obtain special effects, such as partial reduction, but these are for various reasons, considered inferior to tin and hydrochloric acid for the reductions under consideration.

Until the last few years catalytic hydrogenation of nitro compounds has been largely confined to those compounds which give relatively stable amines. More recently, however, this study has been extended to the production of the less stable amines. Feldmann (8) reports a good yield of the diaminophenol by reduction of the dinitrophenol in water with a nickel catalyst. Bradt (2) in studying the same compound reports a maximum yield of 95.1 per cent of the diamine when the reduction is carried out in absolutelalcohol in the presence of nickel. This result was determined by titration with NaNO_2 . However on actual isolation only 50 per cent, as the 80 per cent pure hydrochloride, was obtained.

The electrolytic method of reduction has been studied from two points of view; the theoretical, in order to ascertain the course of the reduction; and the practical, in order to obtain the products in a way which would make isolation easy. From this later point of view the work has thus far not been as successful as at first expected. The simple amines are produced more easily by chemical methods, and while the reduction of polynitro compounds goes well in many cases, it has been difficult to obtain good yields on isolation (6). Elbs (7) studied the reduction of several polynitro compounds in various solutions (aqueous sulfuric acid and aqueous sodium hydroxide) calculating his yields from the amount of hydrogen evolved, with

apparently no attempt at quantitative isolation. Gattermann (10) using a 50 per cent sulfuric acid solution, reduced nitro compounds to amino phenols, the hydroxyl group being introduced during the reduction. The resulting products were directly precipitated from solution as the sulfates. A number of patents (4), which have had some technical application, were obtained for the production of various aminophenole by this method. It apparently has not developed into the success at first expected since the cost of such products is still high compared to the cost of the raw materials. For example, in April, 1932, (13) diaminophenol was quoted at \$3.80 per pound, dinitrobenzene at \$0.15 1/2, and dinitrophenol at \$0.23.

More recent results on reductions in sulfuric acid solutions have been reported. An excellent paper by Bradt and Brown (3) on the reduction of dinitrophenol gives yields as determined under a variety of conditions employed, such as different concentrations of alcohol, different stirrer speeds and at various cathodes. Although they report a yield as high as 94.4 per cent of the theoretical amount, determined by titration with sodium nitrite, no yield of isolated material is reported. The product isolated is described as "black crystals" whereas the product should be white or gray. It is apparent, therefore, that the isolation of the products, not essentially the reduction, which presents the real difficulty in the preparation of polyamino compounds.

Beehringer (1) has taken out patents for the reduction of nitro compounds at various cathodes in a catholyte of hydrochloric acid to which various salts, such as the chlorides of zinc, tin and iron, or powdered metals have been added. As far as can be determined no attempts were made in his work to maintain a high concentration of hydrogen chloride by its addition continuously during the reduction.

Weyprecht (18) obtained a yield of only 7 per cent of toluylene diamine from 2, 4-dinitrotoluene by the Boehringer method. In attempting to produce chloroanil and other more stable amines, as well as intermediate and substituted products, Lob (14, 15) made reductions in fuming hydrochloric acid to which, in some cases, alcohol was added, and in other cases formaldehyde, or a mixture of formaldehyde and alcohol, in order to obtain certain condensation products. The alcohol added was not saturated with hydrogen chloride nor was hydrogen chloride passed into the mixture so as to saturate the mixed solution. The product was obtained by distilling off the solvents or, in some cases, adding alkali and steam distilling the product. Neither of these methods of isolation would be suited to the more unstable products.

The attempts at electrolytic reduction of trinitrotoluene, picric acid and alkylated polynitro phenols, as far as could be determined from the literature (12, 4) have not resulted in the production of fully reduced amines, but rather of compounds having one or more nitro groups left intact or only partially reduced. No reference could be found to attempts at electrolytic reduction of other polynitro compounds, such as trinitrobenzene, trinitrobenzoic acid, and picryl chloride.

With these facts in mind, it is apparent that a general procedure giving a high yield of the isolated amine salt of high purity would be very desirable. A high purity is of especial importance as these compounds are very difficult to purify when they have become contaminated with intermediate or decomposition products.

EXPERIMENTAL PART

The Apparatus

The diagram (p. 7) represents the apparatus, as used in the final reductions, with which the best results were obtained. Aside from a tube for the introduction of hydrogen chloride it does not differ essentially from the arrangement ordinarily used for electrolytic reductions. However, several modifications were tried, and it is well, therefore, to explain why the apparatus as given is considered to be best for laboratory reductions.

In a reduction made on trinitrobenzene, in the preliminary work, the catholyte was left open to the air with the result that the only product obtained was a black powder, apparently carbon. When a closed cell was used and the air expelled this decomposition was avoided. The closed cell has been used not only to keep out the atmosphere, but also to retain the hydrogen chloride gas. It is, furthermore, necessary to have a gas tight arrangement in order to measure the amount of hydrogen evolved in the reduction cell.

In the early work, following the common practice, the catholyte was on the inside of the porous cup. It was found difficult by this arrangement to keep the temperature down to the desired level. With the catholyte on the outside, where it is in contact with the cooled walls of the beaker, excellent results were obtained. The heating of the anolyte was of no particular importance in the experimental reductions.

Key to Diagram of Apparatus

- A, Container, an ordinary Pyrex beaker.
- B, Cork stopper paraffined on top and bottom, and sealed to beaker with paraffin.
- C, Porous diaphragm of plain unglazed white porcelain.
- D, Anode of carbon rods connected to ammeter by heavy copper wire.
- E, Glass stirrer, driven by motor not shown.
- F, Mercury seal to prevent passage of gas around the stirrer.
- G, Thermometer.
- H, Cathode, a copper gauze cup.
- I, Glass tube in which the wire leading to the cathode was sealed where it passes through the cork.
- J, Glass inlet tube for hydrogen chloride.
(Hydrogen chloride generator not shown.)
- K, Top of a cut off test tube inserted in cork for introduction of solutions and samples.
- L, Outlet tubing for excess hydrogen chloride and hydrogen.
- M, Constrictions in the tube to prevent water from going back up the tube.
- N, Graduate (500 cc.) for measuring hydrogen evolved.
- O, Water bath for cooling reduction cell.
- P, Ammeter.
- Q, Variable resistance for controlling current.
- R, Source of direct current; batteries, generator or rectifier.

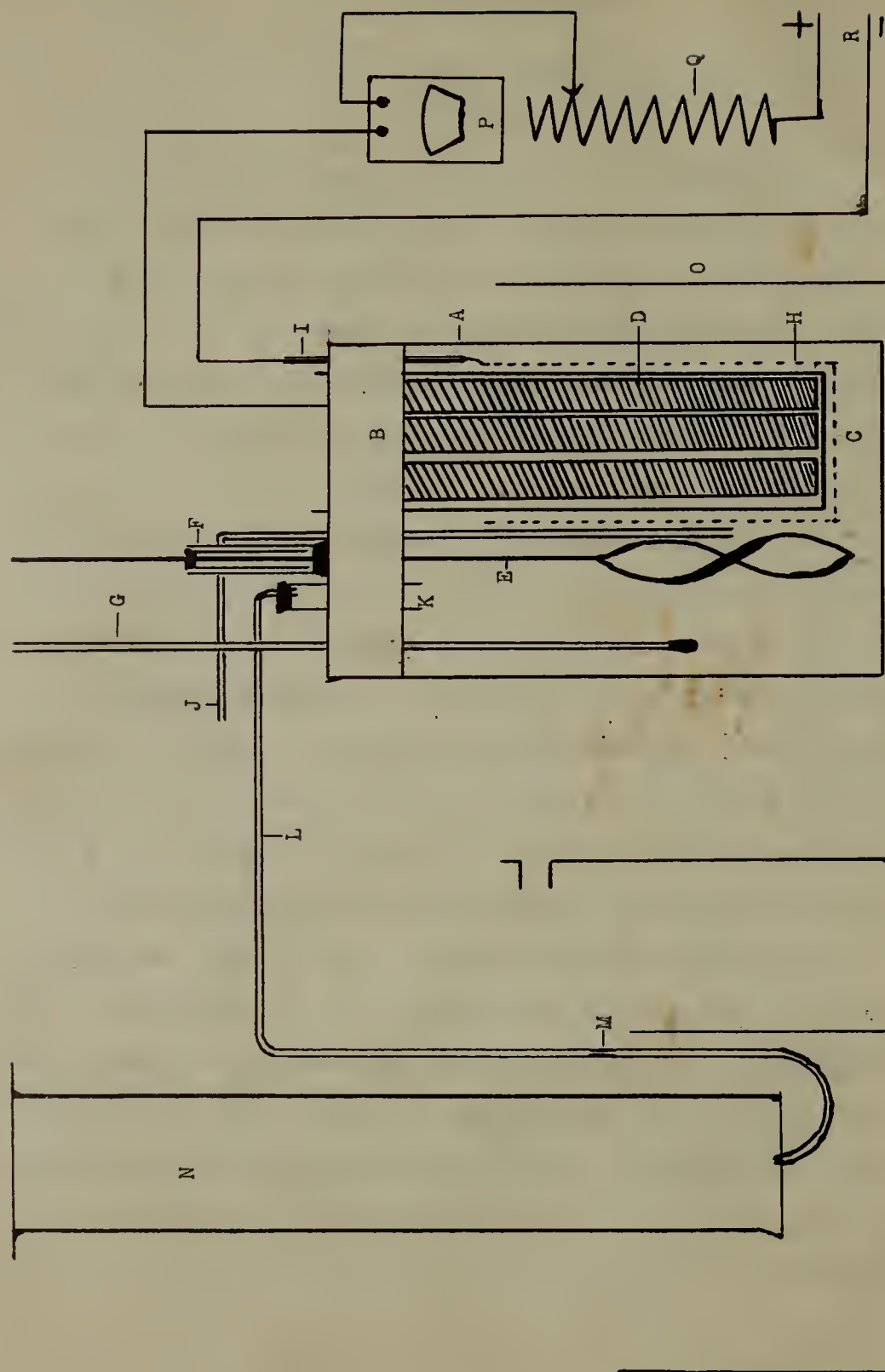


Figure 1: Diagram of Apparatus

For most of the work the porous white porcelain diaphragm was found to work satisfactorily, one cell being used over and over again with no signs of deterioration. In a few instances, with the solution having a very high concentration of alcohol, a more porous diaphragm was used. This consisted of a cardboard diaphragm, paraffined into the beaker, dividing it into two compartments. The cardboard was found to give good results in these cases, and had the advantage of a lower resistance. This diaphragm was also used with a rotating cathode as it made possible an arrangement for cooling the catholyte which was more convenient than with a porous porcelain cup. However, the cardboard would not withstand the treatment with a solution containing greater concentrations of water. A thin wood diaphragm was also tried, but this swelled and cracked, and due to some diffusion tendencies the catholyte passed into the anode compartment under the influence of the current. The porous porcelain also showed this phenomenon to a lesser degree, but in the opposite direction, when using an solution of very high alcoholic concentration. This was not as evident with a solution composed of one-half fuming aqueous hydrochloric acid and one-half fuming alcoholic hydrochloric acid.

The anode in all experiments consisted of carbon rods. Graphite would possibly have been better material, but the carbon rods were available in a convenient form and withstood the action of the chlorine very well. They appeared to offer very little resistance to the passage of the current. It would be impossible to use metals since none are available which will withstand the action of nascent chlorine. The most suitable arrangement was found to be a ring of small carbon rods thereby giving a larger surface. These were fastened together by a copper wire.

After fastening the wire it was found necessary to apply a heavy coat of paraffin to it in order to prevent corrosion by the hydrogen chloride and chlorine.

The effect of using different metals for cathode material was investigated to some extent, but not exhaustively. Of those studied none save the pure copper gave good results. Mercury was found to evolve hydrogen in theoretical amounts from the start of the reduction. Nichrome gauze was found to respond in the same way. Amalgamated copper gauze was also found to behave in a similar manner. The cause of this has not been investigated. Lead has not been tried, but it seems likely that it would behave the same as the mercury. Even with large currents aluminum was rapidly dissolved by the acid.

The copper was tried in different forms such as the sheet metal and wire coils. The gauze was found to be the most convenient. The 10-mesh and the 20-mesh were used. Although the 20-mesh actually has a larger surface there seems to be little choice as far as rate of reduction and yield are concerned. The 10-mesh seems to have the advantage in the fact that it is more rugged and allows for freer circulation. The copper was found to be corroded by the catholyte at low current densities, especially with the more soluble nitro compounds, but this trouble was not serious when the higher current densities were employed. The gauze cup was only large enough to leave room for circulation between it and the porous cup, since this cut down the resistance and afforded space for the thermometer, stirrer, etc. It is believed that this had another advantage. Many of the nitro compounds were acid in character and give negative ions in solution which would tend to migrate through the cell if they came into the electric field existing between the anode and the cathode. When the cathode is placed adjacent

to the porous cell only a small portion of these ions would be in the field at any given time while at the same time they would be in close proximity to the reduction source.

The value of vigorous stirring in electrolytic work has long been recognized since the reaction takes place at the cathode surface or very close to it. Bradt and Brown (3) in their work on the reduction of dinitrophenol in sulfuric acid solution have shown that the material yield is favored by increased agitation. The nitro compounds were not highly soluble in the catholyte used in this investigation, hence agitation was necessary not only to circulate the solution around the cathode, but also to keep it in a saturated condition. Good stirring was, therefore, used in all cases. The degree of stirring was limited to some extent by the fact that the space in the beaker did not allow the use of large vanes on the stirring rod. Sometimes the beaker was tilted so that the solid material would settle toward the stirrer and thus be recirculated.

The collection of the hydrogen liberated during the reduction was first attempted in order to determine when total reduction had been accomplished. When it was found that the hydrogen, in some cases, was evolved during the greater part of the reduction process the hydrogen was collected and measured during intervals in order to follow the course of the reduction. Since the chief interest in this work centered on the actual preparation of the compounds no attempt was made to secure very accurate measurements of the current and of the hydrogen evolved. It was considered sufficient to make rough determinations of the current used by taking readings of the ammeter occasionally and multiplying by the time. To obtain more detailed and accurate determinations it would be necessary to have a rather elaborate coulomb meter. These and other

features involved would complicate the work and it is doubted if the results would be of any greater value. The graduate used to collect the hydrogen was arranged so that it could be quickly and easily filled with water by inserting a rubber tube and sucking out the gas. This was necessary because of the large volume of hydrogen evolved.

Catholyte

The catholyte used in all investigations consisted of a water-alcohol mixture saturated with hydrogen chloride. This system differs from that of Lob (14, 15) in that not merely the water, but also the alcohol used was saturated with hydrogen chloride. This difference was carried further in that the concentration of the hydrogen chloride was kept at a high level throughout the reduction by passing in the dry gas. When it is realized that in reducing 15 grams of dinitrophenol, there is removed from the solution approximately 42 grams of hydrogen chloride and that there is formed nearly 6 grams of water, this difference becomes quite striking. Where 300 cubic centimeters of solution are used this amounts to, roughly, one-third of the hydrogen chloride present in the solution at the start of the reduction. As will be shown later this had a very strong bearing on the method of isolation, and it is believed that this has been the most important factor in making the method successful. In preliminary experiments a solution of sulfuric acid in alcohol was employed as the anolyte, but in such cases there was a small diffusion of sulfuric acid through the cell into the catholyte, leading to complications. This practice was, therefore, discontinued and the same solution, viz., water-alcohol mixture saturated with hydrogen

chloride, was used for both catholyte and anolyte, thus avoiding the possibility of complications resulting from diffusion.

The Method of Procedure

The following is a brief account of the process by which the reductions were carried out.

The apparatus was set up as shown, with care to have the cork sealed tight with paraffin, especially around the edge of the beaker. The catholyte was then introduced and the current turned on immediately. The stirrer was started and kept running throughout the reduction as was also the introduction of hydrogen chloride. If a carrier was used, this was next introduced and the current passed until it had been reduced and hydrogen was freely evolved. The temperature was adjusted to the desired level by regulating the passage of water in the water bath. The sample was finally introduced and current regulated. This was necessary since the introduction of the sample usually caused an increase of current. Finally the tube leading to the hydrogen collector was inserted in proper position.

If the reduction was carried out for the purpose of finding the yield of the product only, the current was kept as near constant as possible, by an occasional adjustment of the resistance, until the hydrogen appeared to be evolved in approximately theoretical quantities. The reduction was then discontinued. If the rate of reduction was desired, readings of the ammeter and the volume of hydrogen were taken at definite intervals. Toward the end of the reduction readings were taken when the 500 cc. graduate became filled with gas, and at the same time the graduate was refilled with water. This was continued until it was apparent that

the hydrogen evolved was nearly equivalent to the current, indicating that the reduction was complete.

The cell was then removed from the water bath, the anode was taken from the porous cup, and the anolyte removed with a suction pump and pipette. The cork, along with the porous cup, cathode, etc., were removed from the beaker; the precipitate was removed from the catholyte by filtering through a Buchner funnel, washed with a small amount of 95 per cent alcohol (previously saturated with hydrogen chloride), with ether, and finally with petroleum ether. Washing with this last liquid removed any fine particles of paraffin that may have entered from the stopper. The precipitate was then dried in a vacuum desiccator over calcium oxide.

The cathode and porous cup were washed thoroughly with a small quantity of water, this filtered to remove pieces of copper that were washed from the cathode, and then added to the filtered catholyte. It was then cooled in a cold water bath. The precipitate thus formed was filtered, washed, and dried as above.

Results

Reductions in a Catholyte of High Alcohol Concentration

The preliminary work was done with a catholyte of 95 per cent alcohol saturated with HCl for it was thought that success depended on having the nitro compound soluble in the electrolyte. The results in most cases, however, proved less satisfactory than those made in lower concentrations of alcohol. As the work was more or less of a preliminary nature, being completed before the technique for obtaining

maximum yields had been improved, the results will not be described in detail. It was found that it was necessary to regulate the temperature around 20°C. in order to obtain a product which would not darken to a considerable extent, while a temperature above 40° failed to give any precipitate at all. The color of the products in all cases was darker than those obtained later from an electrolyte containing more water. The cell resistance was also quite high and this necessitated the use of a comparatively high voltage which in turn was responsible for an equivalent evolution of heat in the reduction unit. Another disadvantage was encountered in that the electrolyte passed through the porous cup from the anode compartment into the cathode compartment.

It was thought that some of the color imparted to the final product was due to the passage of anolyte containing chlorine into the catholyte resulting in an oxidized product. This was not conclusively settled in the case where a hydrogen carrier was added to the solution. However, it was quite apparent that a better (lighter colored) product was obtained with trinitrobenzoic acid by use of an anodic depolarizer where no carrier was used. Of the compounds studied as chlorine absorbers, it was found that phenol and xylene would remove the chlorine at the anode easily at low temperatures, and that the anolyte would not, in such cases, become strongly oxidizing. Benzene and acetylene failed to absorb chlorine readily. It was found that alcohol would slowly react with the chlorine to give a product which does not have oxidizing properties. However, this reaction was not rapid enough to remove all the chlorine produced. Phenol and xylene gave tarry products which coated on the anode and interfered with the flow of current and were, therefore, undesirable. Sulfur dioxide

was found to keep the solution in a non-oxidizing state. Investigation of depolarizers was discontinued when it was found that the chlorine could be evolved freely at the anode from an electrolyte of higher water concentration with apparently no serious effect on the reduction product.

In the case of compounds whose hydrochloride salts are quite soluble in concentrated hydrochloric acid, the use of a high concentration of alcohol has the advantage that the electrolyte can be removed by vacuum distillation at a fairly low temperature thereby avoiding decomposition. Two compounds prepared which fit this description were o-aminophenol hydrochloride and 2-aminoresorcinol hydrochloride. Of the former a yield, based on the nitrophenol, of 82.5 per cent was obtained as colorless crystals which turned blue-grey on standing. From 10 grams of 2-nitro-resorcinol 5.5 grams of light colored crystals of the amine hydrochloride were obtained and 4.1 grams of darker crystals, making a total yield of 92.5 per cent based on the nitro compound. In both of these reductions no carrier was added to the electrolyte.

Reductions in 50 Per Cent Aqueous and 50 Per Cent

Alcoholic Hydrochloric Acid

A catholyte was made consisting of equal volumes of fuming aqueous hydrochloric acid and 95 per cent ethyl alcohol saturated with hydrogen chloride. This was found to have several advantages over an electrolyte consisting only of 95 per cent alcohol saturated with hydrogen chloride. It gave a product which was generally lighter in color, and therefore believed to be purer. The electrolyte also did not tend to diffuse from the anode compartment into the cathode compartment to any great extent so that it was not necessary to use an anode depolarizer. The conductivity was considerably greater which made it possible to employ a higher amperage with less heat production in the reduction cell.

Table I gives the results of several reductions carried out with this electrolyte. The samples 3 and 4 were the pure chemicals obtained from Eastman Kodak Company. The others, excepting No. 7, were recrystallized and the melting points checked before use. No. 7 was a commercial sample containing about 15 per cent water.

Products and Analysis

The products were without doubt the hydrochloride salts of the amines corresponding to the fully reduced nitro compounds. Except for the triaminochlorobenzene of which no mention could be found, the properties and color reactions checked those given in the literature. As an additional check on the products, and as an estimate of the purity, determinations were made of chlorine (ionic). These were made on the product obtained, with no attempt at further purification, except in the case of triaminophenol hydrochloride the sample was dissolved in 200 to 300 cc. of water, a small amount of nitric acid added and the silver nitrate poured into the solution. Without raising the temperature of the solution the precipitated silver chloride was coagulated by stirring for a short time. It was filtered off on a Gooch crucible, washed and dried in the usual manner. This method carried out in artificial light gave a precipitate of good color.

Triaminophenol, even in acid solutions, was too strong in its reducing action to be treated in this manner. In order to prevent reduction of silver chloride and remove any partially oxidized products, the chlorine was precipitated by adding silver nitrate to an acid (with nitric acid) solution of the amine and the amine then oxidized by gentle heating with about half strength nitric acid. The total chlorine was determined on triaminochlorobenzene trihydrochloride by a Parr bomb

fusion with sodium peroxide.

While it is possible that the low results obtained in the chlorine determinations of Nos. 1, 3 and 4 were due to a small amount of non-chlorine containing material, it seems most likely that these results were due to the loss of some of the combined hydrochloric acid. The compounds when first filtered off were white or very light grey. The triaminotoluene trihydrochloride and the triaminobenzoic acid trihydrochloride turned light yellowish brown, and the triaminophenol trihydrochloride, grey with a tinge of blue, upon drying in the dessicator over calcium oxide. Since the other compounds, which underwent only a very slight change in color on drying, contained almost precisely the amount of chlorine required by theory, it is believed that the discoloring effect must be connected with a loss of hydrochloric acid. When thoroughly dry these compounds color only very gradually.

Table I

Reductions in 50 per cent Aqueous and 50 per cent Alcoholic Hydrochloric Acid

Cell, a 600 cc. beaker. Porous cup, 5 cm. diameter, 10 cm. high. Area of gauze, 3.2 sq. dm. (This is the over all area of both sides, not total area of wires.) Catholyte 300 cc. with 5 grams of FeCl_3 as hydrogen carrier.

No.	Compound	Sample Size gms.	Current Density amp/dm ²	Current amp-hrs.		Yield gms.		Analysis % Chlorine	
				Theory	Passed	Theory	Obtained	Theory	Obtained
1	Picric acid	5	.70	10.5	12	5.4	5.1	94	42.9
									40.6
									40.4
2	Picryl chloride	15	.76	29.3	28	16.2	13.4	82	39.7
									39.6
									39.8
									(total 52.85)
									(53.11
									53.08)
3	Trinitro-toluene (2,4,6)	20	1.25	42.5	64	21.7	20.9	96	43.3
									41.1
									41.0
4	Trinitro benzoic acid (2,4,6)	10	1.25 (hrs) .45 "	19.5	67	10.8	9.3	86	39.9
									37.6
									37.9
5	Picryl chloride	15	.86	29.3	33	16.2	14.9	92	--
									--
6	Picric acid	10	1.87	21.1	32	10.9	9.0	82	--
									--
7	Dinitro-phenol (Com'l)	15	.98	(26.2)	29.6	(16.1)	11.8	(73)	36.0
									35.9
									36.2
8	Dinitrophenol (2, 4)	15	.78	26.2	32	16.1	14.9	92.6	36.0
									35.9
									35.8
9	Dinitrophenol (2, 4)	15	2.10	26.2	35.7	16.1	14.5	90	36.0
									35.9
									36.1

The temperature, except for No. 6, was about 20°, for No. 6, 23°.
The first 4 were with 20 mesh gauze, the rest with 10 mesh gauze.

Table IIReduction of Dinitrophenol at High Current Density

Sample, 15 grams of dinitrophenol in 300 cc. of catholyte. Current strength, 7 amps or 2.18 amps/sq. dm. of cathode during first of reduction and 5.4 amps. or 1.68 amps/sq. dm. of cathode during last of reduction. Temperature, about 20°C. Five grams of ferric chloride as carrier.

Current Passed Amp-hrs.	Current Equivalent of H ₂ Amp-hrs.	Per cent Current Used	Total Current Used	Remarks
4.1	0	100	4.1	
4.3	0	100	8.4	
7.7	.7	91	15.4	
1.6	.3	81	16.7	
3.9	1.1	72	19.5	
2.7	1.1	59	21.1	
3.0	1.2	60	22.9	It became necessary to change to source of current which would give only about 5.4 amps.
2.4	1.3	46	24.0	
1.6	1.1	31	24.5	
1.7	1.1	35	25.1	
1.3	1.1	15	25.3	
1.4	1.1	21	25.6	

Yield, 14.5 grams of 90% of theory. Color, very light grey, product crystalline. Cathode attacked very slightly. Material reduced as calculated from current used, 97.7%. Material reduced isolated, 92%. Current efficiency, 69%.

Table IIIReduction of Dinitrophenol at Low Current Density

Sample, 15 grams of dinitrophenol in 300 cc. of catholyte.
Current strength, 2.5 amps or .78 amps/sq. dm of cathode. Temperature about 20°C. Five grams of ferric chloride as carrier.

Current Passed Amp-hrs.	Current Equivalent of H ₂ Amp-hrs.	Percent Current Used	Total Current Used	Remarks
3.5	0	100	3.5	
2.5	0	100	6.0	
3.1	0	100	9.1	
2.5	.2	92	11.4	
3.9	.1	97	15.2	
3.0	.3	90	17.9	
1.0	.1	80	18.7	
3.5	.8	77	21.4	
.9	.3	67	22.0	
2.0	1.1	45	22.9	
1.9	1.1	42	23.7	
1.5	1.1	27	24.1	
1.3	1.1	15	24.3	
1.2	1.1	8	24.4	

Yield, 14.9 grams or 92.6% of theory. Color, very light grey, product crystalline. Cathode attacked to some extent. Material reduced, as calculated from current used, 93.2%. Material reduced isolated, 99%. Current efficiency 76%.

Table IVReduction of Dinitrophenol without Hydrogen Carrier

Sample, 15 grams of dinitrophenol in 300 cc. of catholyte.
 Current strength, 2.5 amps or .78 amps/sq.dm. of cathode.
 Temperature, about 20°.

Current Passed Amp-hrs.	Current Equivalent of H ₂ Amp-hrs.	Per cent Current Used	Total Current Used	Remarks
2.5	0	100	2.5	
2.5	0	100	5.0	
5.0	0	100	10.0	
2.5	0	100	12.5	
2.5	0	100	15.0	Solution gradually became some- what dark.
3.3	0	100	18.3	
2.6	.6	77	20.3	
1.2	.5	58	21.0	
1.4	1.1	21	21.3	
.7	.6	14	21.4	
.9	.8	9	21.5	
1.1	1.1	0	21.5	

Yield, 9.6 grams of 60% of theory. Color, very light grey.
 Product crystalline. Cathode, attacked to considerable extent.
 Material reduced, as calculated from current used, 82%. Reduced
 material isolated, 73%. Current efficiency 73%.

Table VReduction of Picric Acid with Hydrogen Carrier

Sample, 10 grams of picric acid in 300 cc. of catholyte.
 Current strength, 6 amps or 1.87 amps/sq. dm. of cathode.
 Temperature, about 23°C. Five grams of ferric chloride as carrier.

Current Passed Amp-hrs.	Current Equivalent of H ₂ Amp-hrs.	Per cent Current Used	Total Current Used	Remarks
6.0	.2	97	5.8	
3.0	.2	89	8.5	
2.5	.6	78	10.4	
3.2	1.1	66	12.5	
2.4	1.1	55	13.8	
2.1	1.1	49	14.8	
1.8	1.1	40	15.5	
1.9	1.1	42	16.3	
1.6	1.1	30	16.8	
1.6	1.1	30	17.3	
1.4	1.1	24	17.6	
1.4	1.1	21	17.9	
1.2 ⁺	1.1	--	18.0	+Approximate due to change of battery.
1.3	1.1	17	18.2	
1.2	1.1	18	18.3	

Yield, 9.0 grams or 82% of theory. That directly obtained from catholyte a bluish-grey, that reprecipitated from cathode washings a very light grey. Cathode attacked only very slightly. Catholyte, directly after filtering, a light brown. Material reduced as calculated from current used, 87%. Reduced material isolated 94.5%. Current efficiency, 56.5%.

Table VI

Reduction of Picric Acid without Hydrogen Carrier

Sample, 10 grams of picric acid in 300 cc. of catholyte.
 Current strength, 6 amps, or 1.87 amps/sq.dm. of cathode.
 Temperature, about 23°C.

Current Passed Amp-hrs.	Current Equivalent of H ₂ Amp-hrs.	Per cent Current Used	Total Current Used	Remarks
6.0	.4	94	5.6	Solution became dark, getting darker during run to a bluish- black which remained to end of reduc- tion.
3.9	.7	82	8.8	
2.9	1.1	62	10.6	
1.9	1.1	42	11.4	
1.7	1.1	35	12.0	
1.6	1.1	31	12.5	
1.5	1.1	27	12.9	
1.4	1.1	21	13.2	
1.4	1.1	21	13.5	
1.3	1.1	15	13.7	
1.3	1.1	15	13.9	
1.0	.9	11	14.0	

Yield, 4.7 grams, 43% of theory. That directly obtained from catholyte was dark brown. That reprecipitated from cathode washings, light grey. Catholyte was very dark. Material reduced as calculated from current used, 66.4%. Reduced material isolated, 65%. Current deficiency 50%.

Figure II: Reduction at High and Low Current Density

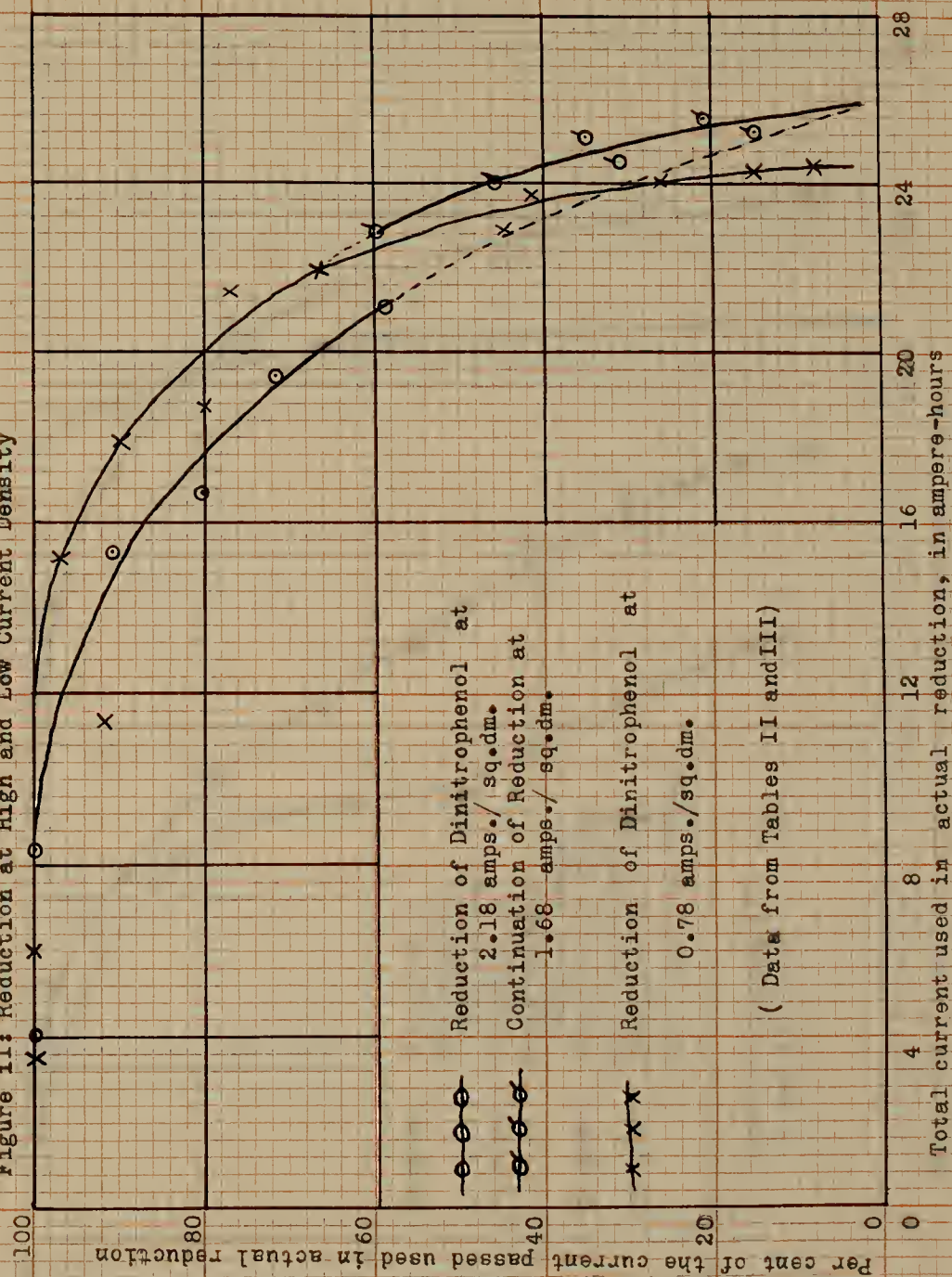
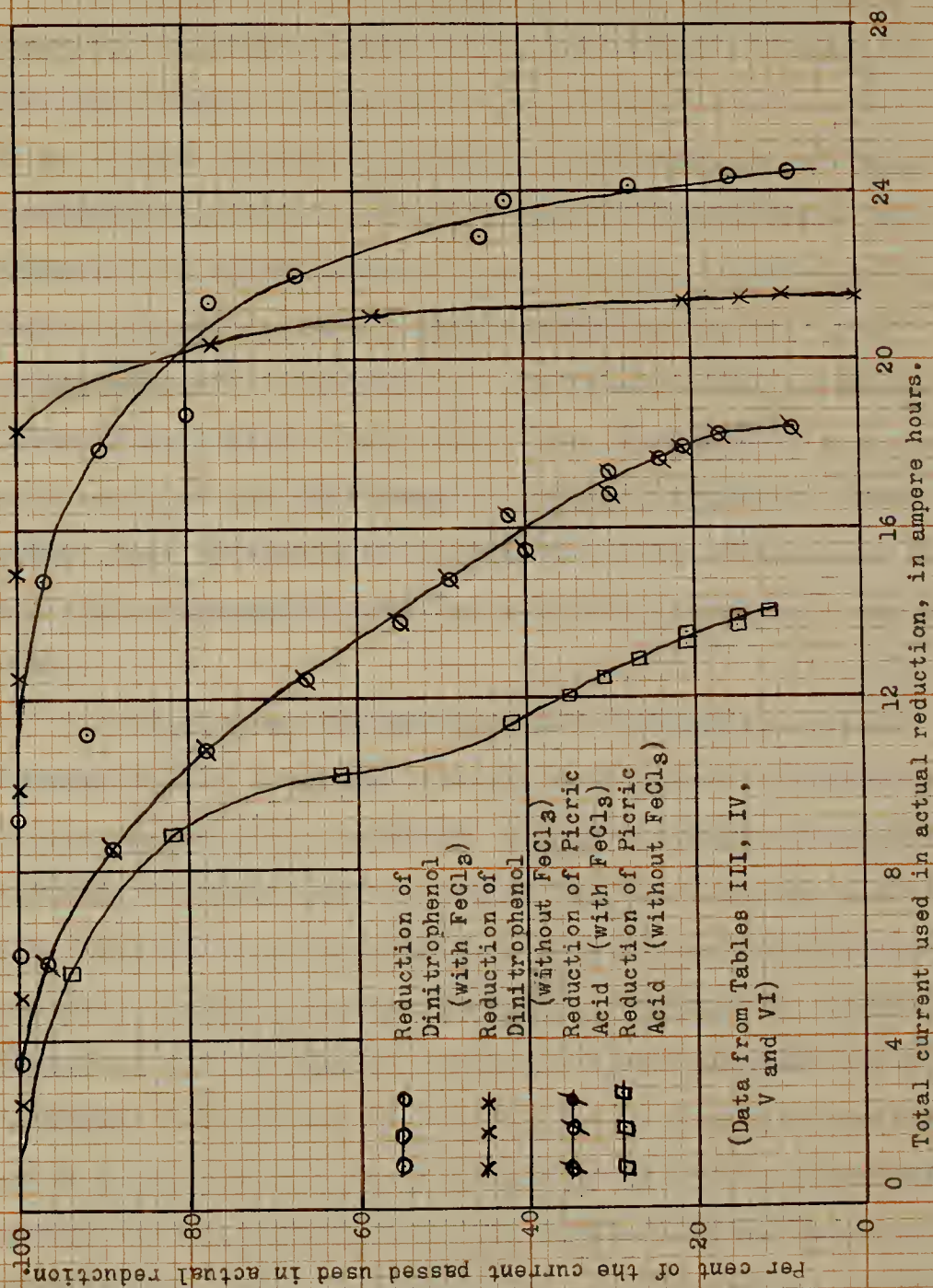


Figure III: Effect of Hydrogen Carrier (FeCl_3) on Reduction.

Effect of Current Density and of the Hydrogen Carrier

When it was found that hydrogen was evolved from the cathode before the reduction was entirely completed it became desirable to study the effect of a variation in current density and the effect of the addition of ferric chloride on current efficiency. In these experiments the hydrogen evolved was measured and reported as the electrical equivalents in ampere-hours. In these reductions all other factors involved were kept as nearly constant as possible. This applies especially to the stirring. The reduction cell for these experiments was a 600 cc. beaker. The cathode consisted of 10 mesh copper gauze having an area (both sides) of 3.2 square decimeters. Three hundred cubic centimeters of the mixed 50 per cent alcoholic and 50 per cent aqueous hydrochloric acid, was used as the catholyte in each reduction.

The tables II and III show the results obtained with greatly different current densities. The rate of absorption of electricity is shown graphically in figure II. While these curves are not essentially different in general shape, it is seen that the low current density was more economical in current utilization since the per cent of the current involved in reducing the nitro compound was greater. The per cent of utilization also remained at a higher level when nearer the end of the reduction. On the other hand, the high current density is more economical of time as there was still considerably more current being used in reducing the compound during a given period than in the low current density case in spite of the lower percentage utilization. The high current density gave a slightly lower yield, and, of course, required a higher voltage with greater amount of heat developed in the solution.

The discrepancy in the total current used is probably due to the accumulated error obtained by adding the total currents for the short intervals. This error for any short interval could not be very great, however, so that the general shape of the curve would not be effected. The method of obtaining the total current makes only approximate the figures given for the percent of material reduced as calculated from the current used, and also those given for the per cent of the reduced material that was isolated.

Tables III and IV show the results of reductions of dinitrophenol with and without the addition of ferric chloride and tables V and VI indicate similar results with picric acid. The expected lower rate of reduction was not found in the reduction without ferric chloride, as shown in figure III. On the contrary, there was actually a higher percentage utilization in the case of dinitrophenol. However, it is to be noted that the total amount of current used was considerably smaller (more than could be accounted for as an error in current measurement). The most striking results were found in the lower per cent yields and the lower per cent of reduced material that was isolated in the reduction without the carrier. This result correlated with the fact that a colored solution was produced during the reduction without the carrier, has lead to the conclusion that the carrier has a tendency to prevent side reactions which result in the formation of colored compounds that are not easily and completely reduced.

The compounds studied, especially the picric acid, are among those which show the greatest tendency to form intermediates. With some of the other compounds it is not expected that the absence of ferric chloride would make so great a difference in the yield. It is possible that the copper which dissolves from the cathode when the current density is low serves as a hydrogen carrier in such cases.

The Effect of Temperature

While no reductions have been made to determine exactly the effect of increased temperature of the catholyte, keeping other factors constant, it was observed in the preliminary studies that higher temperatures were always detrimental. It is believed that the lower yield shown for picric acid in table I, No. 6, as contrasted with No. I, was largely due to the average of about 3 degrees higher temperature. Since colored compounds were always formed at higher temperatures it is believed that side reactions took place which were suppressed at the lower temperatures. A temperature of about 20°C. was used in these reductions which could be conveniently maintained with tap water as a cooling medium.

The Course of the Reduction

The best reductions always took place with very little formation of colored compounds. The solution generally would take on the yellowish color (depending on the color of the compound and its solubility in the catholyte) due to the nitro compound. This color would remain practically unchanged during the course of the reduction while the character of the suspended material would change from the yellowish nitro compound to the fine white crystals of the hydrochloride salt of the amine. Toward the end of the reduction the yellow color of the solution mostly disappeared leaving a nearly colorless solution with a white or grey crystalline precipitate.

No attempt was made to ascertain the exact course which the reduction takes. It is thought, however, that the reduction does not take place in definite stages (as is often pictured for the reduction of nitro compounds), but rather that each molecule is completely reduced soon after the first step in the reduction

has taken place. This is borne out by the fact that the suspended material gradually changes in character without giving a clear solution and if some is withdrawn at an intermediate point of the reduction, part (crystals of the amine hydrochloride) will go into solution in water leaving undissolved crystals of the nitro compound.

Other Catholytes

The use of moderate concentrations of alcohol has the advantage in laboratory reductions that it can be filtered through ordinary filter paper without difficulty. Also the amine salts are generally less soluble in alcoholic than in pure aqueous hydrochloric acid. Time limitations have not allowed a detailed study of salt solubilities in various concentrations of alcoholic-hydrochloric acid. A reduction in 25 per cent by volume of 95 per cent ethyl alcohol saturated with hydrogen chloride, the other 75 per cent being aqueous concentrated hydrochloric acid, gave very good results with dinitrophenol, except for the isolation. It was found necessary in this case to allow the precipitated amine salt to settle, decant the electrolyte, and then add alcohol saturated with hydrogen chloride to the salt so that the solution would not disintegrate the filter paper. A reduction of trinitrobenzoic acid, using absolute methyl alcohol saturated with

hydrogen chloride as an electrolyte, also gave very good results. These reductions show that good yields may be obtained with widely varying conditions so far as alcohol concentration is concerned.

The electrolytes with a low concentration of alcohol show higher conductivity. On the other hand, a majority of nitro compounds are more soluble in solutions containing a higher concentration of alcohol. In Table I it is seen that for picric acid, picryl chloride and dinitrophenol only a little more current was used than that required by theory. Trinitrotoluene and trinitrobenzoic acid, on the other hand, required an excess of current. In these cases hydrogen was evolved during most of the reduction and it was necessary to determine complete reduction of the nitro compound by withdrawing a little of the suspended matter and testing its solubility in water. This difference, no doubt, was due to the small solubility of the trinitrotoluene and trinitrobenzoic acid in the electrolyte. For such compounds it might be advantageous to sacrifice conductivity for solubility and use an electrolyte having higher alcohol concentration.

Reduction of s-Hexanitrodiphenyl

Because of its insolubility in the catholyte, even when 95 per cent ethyl alcohol, saturated with hydrogen chloride, was used the reduction of s-hexanitrodiphenyl offered more difficulty than any other aromatic nitro compound upon which reduction was attempted. For this reason and because no mention of its reduction by any method could be found in the literature, it is given special mention here.

The attempt to carry out the reduction of hexanitrodiphenyl with the same apparatus, and in the manner described for the other compounds mentioned, resulted in the evolution of hydrogen in amounts nearly equivalent to the current passed from the beginning of the reduction. However, when the precipitate (mostly unchanged hexanitrodiphenyl) was extracted with water and the extraction liquid added to the filtered catholyte a small amount of precipitate was obtained which had the characteristics of an amine salt. This made it apparent that the hexanitrodiphenyl could be reduced by this method, but on account of the small solubility the reduction would have to be carried out at slower speed with the use of a large excess of current.

A cell was constructed exactly like the one used in the previous reductions except that it was smaller in size, using a 400 cc. (instead of a 600 cc) beaker and everything correspondingly smaller. Ten grams of hexanitrodiphenyl was used in a catholyte of about 200 cc. of 50-50 alcoholic and aqueous hydrochloric acid mixture with 5 grams of ferric chloride as a hydrogen carrier. A Tungar rectifier was used as a source of current. The reduction was

continued at 1.8 to 2.0 amperes over a period of about 28 hours. During the first of the run the current was largely used in the reduction, but later hydrogen was evolved freely. At the end of the period nearly all of the hexanitrodiphenyl had disappeared. The precipitate was filtered off, dissolved in a small amount of water and the aqueous solution, along with the filtered washings from the cathode, added to the catholyte. The precipitate thus obtained was filtered off, washed with ether and dried over lime in a vacuum dessicator. The product which was at first white turned yellowish on drying. Yield 7.7 grams.

The analysis corresponds to hexaminodiphenyl tetrahydrochloride though further study is necessary to prove this.

	Obtained	Calculated
Chlorine, ionizable,	36.6%	36.4%
	36.4	

The compound is very soluble in water and not soluble in organic solvents. The dilute water solution made alkaline slowly becomes dark in color. Attempts made to prepare the acetyl derivative by refluxing with acetic anhydride and sodium acetate with and without the addition of glacial acetic acid have met with failure, apparently due to decomposition of the amine.

Studies on Triaminochlorobenzene

The common methods for the reduction of picryl chloride yield triaminobenzene instead of triaminochlorobenzene. The method given here is of interest as it does not remove the chlorine atom from the benzene nucleus and produces triaminochlorobenzene. As no description of this latter product was found in the literature a few studies were made on it, which are given here.

Hydrochloride Salt. The hydrochloride salt, as obtained by the reduction was a definitely crystalline product which was nearly white when first filtered off, but took on a slight yellow tinge during drying. It is completely soluble in water, but not soluble in common organic solvents. The water solution slowly turned dark on standing in the air, and colored more rapidly when ferric chloride was added.

Analysis of the hydrochloride salt gave the following:

	Obtained	Theoretical
Chlorine, ionizable	39.6% 39.8	39.7%
Chlorine, total (by Parr bomb)	52.85 53.08	53.11%

Free Amine. When the dilute solution of the hydrochloride was made alkaline no change was noted at first, but the solution gradually became dark. A more concentrated solution of the hydrochloride gave a gelatinous dark precipitate with sodium hydroxide. No further attempts were made to isolate the free amine.

Picrate. In attempting to prepare the picrate results were obtained which lead to some question as to the nature of the product. A warm solution of the triaminochlorobenzene trihydrochloride treated when warm with a solution of picric acid and then cooled gave a precipitate of red needles. This was found to dissolve easily in hot water, losing the red

color and giving a pale yellow solution. On cooling it reformed the colored crystals which, after drying, decomposed at 180° before melting.

Analysis of the product gave the following results:

	Obtained	Calculated for monopicrate
Chlorine (by Parr bomb)	9.15%	9.25%
	9.92	

In attempting to prepare more of the picrate 250 cc. picric acid solution was added to 2.5 grams of the triaminochlorobenzene trihydrochloride dissolved in a small amount of water. Both solutions were cooled to room temperature. In a few seconds yellow crystals appeared and in a short time the solution became thick with long silky yellow needles. These were filtered off with suction washed a few times with water. The mass of crystals in the form of a fibrous mat was then placed in a desiccator under reduced pressure. After about 2.5 hours red spots appeared in the mat and these gradually grew until nearly all of it had been changed to the red color. On opening the desiccator it was found that the crystal form had completely changed, the mass of crystals no longer being fibrous, and appeared more moist than when placed in the desiccator. The drying was then completed. Yield, 3 grams. The product recrystallized from water the same as the first product obtained, giving red crystals. This behavior lead to the belief that the picrate first formed might undergo internal oxidation and reduction which would mean that the product was not a true picrate. No attempt has been made to ascertain whether this is the case or whether the change was merely one of crystalline form with possibly the loss of water of crystallization.

Acetyl Derivative. Five grams of triaminochlorobenzene trihydrochloride was refluxed for about 3 hours with 15 grams of acetic anhydride, 10 grams of sodium acetate, and enough glacial acetic acid to afford a

solution. Upon cooling crystals separated. The mixture was poured into a large volume of water, the precipitate filtered, dried and recrystallized from a mixture of glacial acetic acid and toluene. A white bulky product was obtained which on drying in a steam oven weighed 4.9 grams and had a constant melting point at 274° . A second preparation was made using only the amount of sodium acetate needed to react with the ionizable chlorine and using an excess of acetic anhydride with no glacial acetic acid. Practically the same yield of crude product was obtained. This material was recrystallized from water-alcohol mixture and gave a constant melting point of 274° the same as that obtained with crystallization from glacial acetic acid-toluene mixture.

Hydrolysis. The triaminochlorobenzene trihydrochloride refluxed in aqueous solution or a slightly alkaline solution gave only a dark brown gelatinous precipitate. When a solution of equal weights (nearly equal molecular quantities) of triaminochlorobenzene trihydrochloride and stannous chloride was made neutral to litmus with sodium carbonate and refluxed for 12 hours it gave a strong test with vanillin hydrochlorid acid reagent for phloroglucinol. The tin salts were filtered off and the resulting solution concentrated to small volume, acidified with hydrochloric acid and cooled to 0° . The crystals which formed were filtered from the solution and recrystallized from water. After dehydrating in a vacuum desiccator they melted at 217°C . which is the melting point of phloroglucinol. Attempts to repeat this with larger amounts lead to the formation of only 1 gram of the crude product from 10 grams of the triaminochlorobenzene trihydrochloride.

Reaction with NaNO_2 . When a solution of triaminochlorobenzene trihydrochloride was treated with a solution of NaNO_2 at room temperature a reddish-brown precipitate was formed resembling Bismark brown. Attempts to prepare the tetrachlorobenzene through the diazo compound were unsuccessful.

Reaction with Formaldehyde. When a solution of the triaminochlorobenzene trihydrochloride was treated with 40 per cent formaldehyde a red coloration appeared. When this red solution was made alkaline a gelatinous red precipitate was obtained. Similar colorations and reactions were shown by the hydrochlorides of triaminotoluene, triaminobenzoic acid and triaminophenol.

Acetyl Derivative of Triaminotoluene

The ease with which the acetyl derivative of triaminochlorobenzene could be made lead to the preparation of the corresponding derivative of triaminotoluene, which was not found described in the literature. Preliminary studies indicated that this reaction took place much more difficultly than with triaminochlorobenzene, hence the refluxing was continued over a greater period of time.

Five grams of triaminotoluene trihydrochloride, 15 grams of acetic anhydride, and 10 grams of sodium acetate were mixed with enough glacial acetic acid to cause solution. The solution was then refluxed for about 12 hours. On cooling the mixture it became nearly solid with a mass of crystals. The product was poured into water, washed on a Buchner funnel, dried and then recrystallized twice from glacial acetic acid, - toluene mixture. After drying in a steam oven the white fibrous crystals weighed 2.5 grams and had a melting point at 293°C .

SUMMARY

A method has been developed for the electrolytic reduction of nitro compounds yielding amines and amine salts which, due to their instability, are difficult to isolate in the pure form by ordinary methods of reduction. The essential points of this process are; maintenance of a high concentration of hydrogen chloride in the catholyte and the keeping of a low temperature during the reduction. Very satisfactory yields of the amine hydrochlorides of a high degree of purity have been obtained and isolated in crystalline form.

A study of the current density and alcohol concentration in the catholyte have lead to the conclusion that good results may be obtained under a variety of conditions, provided that the temperature is kept at 20°C. or below.

A study of the effect of ferric chloride as a hydrogen carrier has led to the conclusion that this substance (and those which behave like it) frequently increase the yield by preventing side reactions.

s-Hexanitrodiphenyl has been reduced.

Picryl chloride has been reduced directly to triaminochlorobenzene trihydrochloride which is not possible by ordinary methods of reduction.

Preliminary studies have been made on the chemical behavior of triaminochlorobenzene.

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