THE ELECTROLYTIC REDUCTION OF O-NITRODIPHENYL IN ACID, ALKALI AND NEUTRAL MEDIA

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by

PETER PAWLYK

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INTRODUCTION

The electrolytic reduction of aromatic nitro compounds gives an extensive series of reactions. Kendall[1] in 1882 was granted a patent on the reaction in which nitrotoluene and nitrobenzene were cathodically reduced to the corresponding amino derivatives when electrolyzed in a catholyte containing dilute sulfuric acid.

In 1893, much work was done in this field. Investigators like Häusserman[2], Gatterman[3], Noyes and Clements[4], Gatterman and Koppert[5], and Elbs[6] reduced nitrobenzene under varying conditions to obtain a series of products. The brilliant work of Elbs was especially significant.

Since varying the conditions of reductions caused a variation in the products formed, there was need for a theory to account for these products. This theory of what intermediates formed in the reduction of nitrobenzene was satisfactorily established by Haber[7]. This was made possible by the fact that Bamberger[8] reduced chemically by a series of difficult reactions, nitrosobenzene to phenylhydroxylamine. He also was able to reverse this reaction.

Until recently much work has been done on the reduction of mono and dinitro aromatic compounds, however, according to Hartley and Lyons[9] little work has been done on the reduction of o-nitrodiphenyl due to the difficulty of obtaining the product. Now, since diphenyl can be made cheaply and abundantly, it is possible that more work will be done. In 1934, Hartley and Lyons succeeded in reducing o-nitrodiphenyl to o-azoxybiphenyl and the hydrazo compound. It should therefore be possible to reduce the compound in a manner similiar to nitrobenzene in alkaline solution to o-biphenylamine.

The object of this research was to reduce the o-nitrodiphenyl to obtain 2, amino 5, hydroxydiphenyl. By analogy it seemed that this was possible in acid solution. A series of runs were made in acid medium and conditions varied to obtain the desired compound. A series of runs were also made in neutral and alkaline media. In these latter media, very good results were obtained and the chief product formed was o-azoxybiphenyl; in the corresponding acid runs results were for the most part negative. It was possible in some of the acid runs to obtain a few grams of crude crystals. The main difficulty was the separation of the products in the reaction mass.

Experiments were carried out in acid, alkaline and neutral media. The following factors were varied:

(1) acidity or alkalinity
(2) Current density
(3) temperature
(4) choice of electrodes

PART I

EXPERIMENTAL:

The apparatus consisted of; a liter beaker, a porous cup, a mechanical stirrer; lead, and carbon anodes and a monel metal guaze cathode. The solvent for the compound was 95% ethyl alcohol.

In the neutral runs, ten grams of sodium acetate were added to the catholyte. The anolyte in both alkaline and neutral media was saturated sodium carbonate solution. Ten per cent sodium hydroxide was used to vary the alkalinity of the catholyte in alkaline runs.

In the acid runs the anolyte was ten per cent sulfuric acid or ten per cent acetic acid. The laboratory desk switchboard was used and the source of direct current generated by a dynamo.

The experimental procedure consisted of setting up the cell thus; the anode with the anolyte was placed in the beaker containing the catholyte. The monel metal gauze cathode was wrapped about the porous cup and attached to the negative pole by means of a heavy copper wire. The whole cell was placed in a water bath so that the temperature could be regulated.

The mechanical stirrer was inserted into the catholyte and used throughout the reduction.

In neutral runs the catholyte consisted of:

250 ml. of 95% ethyl alcohol
10 grams of sodium acetate
15 grams of o-nitrodiphenyl

In experiment #8 and #9, these variations were made in the catholyte: in experiment #8, thirty grams of o-nitrodiphenyl were dissolved in 250 milliliters of 95% ethyl alcohol; in the ninth experiment, 58.5 grams of o-nitrodiphenyl were dissolved in 450 milliliters of ethyl alcohol.

The anode in these first nine runs was carbon; the anolyte was saturated sodium carbonate. The cathode was a monel metal gauze whose area was approximately 1.83 square decimeters. The cathode current density in each of the first nine experiments was 3.28 amperes per square decimeter.

After the reduction was completed, compressed air was passed through the reduction mass to oxidize any hydrazo compound formed to the azoxy compound. The beaker containing the reduction mass was allowed to stand overnight on an ice bath before filtering off the crude product.

The results obtained are listed in Table I.

TABLE I

REDUCTION OF O-NITRODIPHENYL IN NEUTRAL SOLUTION

Expt.	Time Hr.	Temp °C Cell	Yield (Grams)	% Theo Yield	Theo Amp Hr	Amp Hr Used	C.E.*
1	2.00	40-70	9.5	72.5	4.36	12.00	36.39
2	2.00	50-52	12.0	90.9	5.51	12.00	46.00
3	2.00	48-50	13.5	100.4	6.11	12.00	50.83
4	2.00	50-52	10.0	75.0	4.60	12.00	38.30
5	2.00	70-75	11.2	76.0	5.19	12.00	43.25
6	2.67	50-60	12.5	90.0	5.52	16.00	46.00
7	2.67	40-52	12.5	95.0	5.75	16.00	36.90
8	3.50	50-52	20.0	75.9	9.12	21.00	43.50
9	4.50	50-52	22.0	62.3	14.61	27.00	54.25

* C.E. = Current Efficiency

A second series of runs were made in which the alkalinity and the current density were varied. Since there is a tendency for the carbon anode to flake, a lead anode was used instead. The concentration of the o-nitrodiphenyl in the catholyte was also changed. In the runs tabulated in table II the following factors remained constant throughout this series of runs:

Anode- A lead strip 3.5 cm. wide, .25 cm. thick and
15 cm. long.

Anolyte- Saturated sodium carbonate solution.

Cathode- Monel metal gauze.

Catholyte- 25grams of o-nitrodiphenyl
250 ml. of 95% ethyl alcohol

Temperature of cell- 50-2°C.

To vary the alkalinity of the catholyte, volumes of ten per cent sodium hydroxide were measured out with a pipette and added to the catholyte. When the volume of sodium hydroxide added caused the catholyte to separate into two distinct layers, the following procedure was used; forty per cent in the corresponding amounts required. Hence in the tenth and eleventh runs in this series one hundred milliliters of 40% sodium hydroxide and two hundred milliliters

TABLE II

REDUCTION OF O-NITRODIPHENYL IN ALKALINE SOLUTION

Expt	Cathode C.D.*	Time Hr.	Vol 10% NaOH ml	Yield Grams	% Theo Yield	Theo Amp Hr	Amp Hr Used	C.E.*
1	3.28	3.5	---	12.5	56.9	5.75	21.00	27.40
2	3.28	3.5	10	12.7	57.9	5.85	21.00	27.85
3	4.37	2.80	20	11.0	50.0	5.05	22.40	22.45
4	4.37	2.80	---	11.2	51.0	5.15	22.40	25.67
5	4.92	2.50	25	16.0	72.9	7.35	22.50	32.67
6	5.47	2.40	50	22.0	100.0	10.10	24.00	42.09
7	5.47	2.40	100	15.5	70.6	7.13	24.00	29.71
8	5.47	2.40	150	12.5	56.9	5.75	24.00	23.96
9	5.47	2.40	200	14.5	66.0	6.65	24.00	27.70
10	5.47	2.40	100**	16.0	72.9	7.35	24.00	30.63
11	5.47	2.40	200**	14.0	63.7	6.43	24.00	26.29

* C.D. = Current density in amperes per square decimeter

C.E. = Current efficiency

**40% sodium hydroxide solution was used in the last two experiments.

of 40% sodium hydroxide were used respectively, in place of four hundred and eight hundred milliliters of 10% sodium hydroxide. Results in this series are recorded in Table II.

In this second series of runs both the alkalinity and the current density were varied to determine the effect upon the yield.

A third series of runs was then made. The object of these runs was to determine whether or not another current density could be found with which we could parallel or obtain better results than those of the sixth run in the second series. In this third series of runs the following conditions were held constant:

Anode- A lead strip as in series number 2.

Anolyte- Saturated sodium carbonate.

Cathode- Monel metal gauze.

Catholyte- 250 ml. of 95% ethyl alcohol
25 grams of o-nitrodiphenyl
50 ml. of 10% sodium hydroxide

Temperature of cell- 48-50°C.

In this series only the cathode current density was varied. The results of these experiments are recorded in Table III.

TABLE III

REDUCTION OF O-NITRODIPHENYL IN ALKALINE SOLUTION

Expt.	Cathode C.D.*	Time Hr.	Grams Yield	% Theo Yield	Theo Amp Hr	Amp Hr Used	C.E.*
1	2.19	6.00	11.0	50.0	5.02	24.00	20.91
2	3.28	2.60	22.0	100.0	10.10	21.60	46.75
3	4.37	2.80	20.0	90.9	9.18	22.40	39.19
4	5.48	2.40	22.0	100.1	10.10	24.00	42.09
5	6.58	2.00	16.5	75.1	7.58	24.00	31.57
6	7.75	1.72	17.5	79.5	8.02	24.08	33.40
7	8.75	1.50	17.5	79.5	8.02	24.00	33.40

* C.D. = Current Density

C.E. = Current Efficiency

This third series of runs concluded the research on reduction in neutral and alkaline medium.

The crude product obtained from these reductions was treated in the following manner. Air was bubbled through the mass to oxidize any of the hydrazo compound formed. The crystals were then filtered by suction and washed two or three times with hot water. When dry they were light orange in color and a series of melting points on different runs showed a melting point of 140-2°C.

One recrystallization of the crude product from a mixture of carbon tetrachloride and ethyl alcohol yielded slightly golden tinted crystals melting at 154.5°C. One recrystallization from acetone yielded golden plates melting at 153-154°C.

The product was identified, after being purified by the conventional qualitative organic methods. The pure compound was found to be soluble in cold concentrated sulfuric acid and since it contained nitrogen it was listed as an "indifferent compound."

Next a series of tests for functional groups like the hydroxyl and amine were carried out. These tests gave negative results. Then some of the pure compound was subjected to hydrolysis and reduction. It was found that no hydrolysis took place. Reduction did take place with zinc dust and alkali. The compound was also reduced by stannous chloride in an alcoholic solution. Since the compound reduced easily and went through a deep color change in the course of reduction, it was considered an azoxy compound. A derivative, 3, 3'diphenylbenzidine was prepared by treating a hot alcoholic solution of the product with stannous chloride. After several recrystallizations this derivative melted at 150-151°C. The literature gave 151°C as a melting point.

A series of nitrogen determinations using a Kjeldahl method were made. The average of these determinations was 7.98%. The calculated percentage for o-azoxybiphenyl is 8%.

Molecular weight determinations were run by the Beckmann freezing point method. Thiophene free Benzene was used as a solvent. The following results were obtained:

(1) 356

(2) 352

(3) 350

(4) 358

(5) 352

(6) 356

The molecular weight of o-azoxybiphenyl is 350.

PART II

EXPERIMENTAL

The following reductions were carried out in acid medium. The first few runs yielded negative results. Some of the last ones are fairly encouraging.

In carrying out reduction in acid medium the conditions were varied as in the neutral and alkali experiments (see page 3) in an attempt to obtain an appreciable yield of 2 amino, 5 hydroxy-diphenyl.

The catholyte in some of the acid runs was completely miscible; in other cases it was an emulsion. A porous cup was used as a diaphragm throughout these experiments.

Twelve separate experiments were carried out in acid medium. The conditions of the experiments and results obtained on each are tabulated in the following pages.

In addition to these experiments, repeat trials were made on experiments 1,3,5 and 9. In repeating the nineth experiment, the hydrochloric acid was eliminated.

Experiment I

Anode- Nickel metal

Anolyte- Dilute sulfuric acid (10%)

Cathode- Nickel metal--Temp of cell-50°C.

Current density-8 amps/sq. decm.

Catholyte- 15 gm. of o-nitrodiphenyl
200 ml. of 95% ethyl alcohol
200 ml. of concentrated sulfuric acid.

Results- Unreacted o-nitrodiphenyl and approximately 0.5 grams of organic compound. This latter compound seemed to be a mixture.

Experiment II

Anode- Lead

Anolyte- 10% sulfuric acid

Cathode- Nickel

Current Density- 8 amps/sq. decm.

Temperature of cell- 50°C.

Catholyte- 15 gm. o-nitrodiphenyl
100 ml. 95% ethyl alcohol
200 ml. 80% sulfuric acid.

Results- Very little reduction compound. Practically all of the o-nitrodiphenyl was recovered.

Experiment III

Anode- Lead

Anolyte- 20% sulfuric acid

Cathode- Nickel

Current Density- 9 amps/sq. decm.

Temperature of cell- 50°C.

Catholyte- 15 gm. o-nitrodiphenyl
50 ml. 95% ethyl alcohol
250 ml. 40% sulfuric acid
20 ml. 1% gelatine

Results- Some fine white needle like crystals, ether and water soluble; and an unseparable mass of organic and inorganic crystals.

Experiment IV

Anode- Lead

Anolyte- 20% sulfuric acid

Cathode- Nickel

Current Density- 10 amps/sq. decm.

Temperature of cell- 50-52°C.

Catholyte- 15 gms of o-nitrodiphenyl
300 ml. of 20% sulfuric acid
20 ml. of 5% gelatin

Results- No reduction after ten hours. A skin formed on the cathode.

Experiment V

Anode- Carbon

Anolyte- 10% sulfuric acid

Cathode- Monel metal gauze

Current Density- 6 amps/sq. decm.

Temperature of cell- 50-55°C.

Catholyte- 200 ml. of 95% ethyl alcohol
15 gm. of o-nitrodiphenyl
5 ml. of concentrated sulfuric acid

Results- Mixed crystals plus a black viscose oil.

Experiment VI

Anode- Carbon

Anolyte- 10% sulfuric acid

Cathode- Monel metal gauze

Current Density- 6 amps/sq. decm.

Temperature of cell- 50°C.

Catholyte- 15 gm. of o-nitrodiphenyl
100 ml. of distilled water
50 ml. of concentrated sulfuric acid
200 ml. of 95% ethyl alcohol

Results- No reduction.

Experiment VII

Anode- Carbon

Anolyte- 10% acetic acid

Cathode- Monel metal

Current Density- 8 amps/sq. decm.

Catholyte- 25 gm. o-nitrodiphenyl
10 ml. concentrated acetic acid
250 ml. 95% ethyl alcohol

Results- Some organic crystals and a large amount of oil.

Experiment VIII

Anode- Lead

Anolyte- 50% sulfuric acid

Cathode- Monel metal gauze

Current Density- 10 amps/sq. decm.

Catholyte- 25 gm. o-nitrodiphenyl (sulfonated)
250 ml. of distilled water

Results- A large mass of crystals difficult to separate.

Experiment IX

Anode- Lead

Anolyte- 10% sulfuric acid

Cathode- Copper

Current Density- 6 amps/sq. decm.

Catholyte- 15 gm. o-nitrodiphenyl
120 ml. concentrated hydrochloric acid
90 ml. concentrated sulfuric acid
10 gm. zinc sulfate

Results- Four grams of violet colored crystals containing the chloride ion and behaving like an amine salt.

Experiment X

Anode- Lead

Anolyte- 10% sulfuric acid

Cathode- Monel metal

Current Density- 3.17 amps/sq. decm.

Catholyte- 15 gm. O-nitrodiphenyl
300 ml. 95% ethyl alcohol
25 ml. concentrated sulfuric acid
50 ml. of distilled water

Results- Steam distillation yielded unreacted o-nitrodiphenyl plus a mixture of grayish blue crystals. (Approximately 0.5 gm.)

Experiment XI

Anode- Lead

Anolyte- 10% sulfuric acid

Cathode- Zinc

Current Density- 2.02 amps/sq. decm.

Catholyte- 300 ml. 95% ethyl alcohol
15 gm. o-nitrodiphenyl
25 ml. concentrated sulfuric acid
50 ml. distilled water

Results- Unreduced 6-nitrodiphenyl recovered.

Experiment XII

Anode- Lead

Anolyte- 10% sulfuric acid

Cathode- Monel metal gauze

Catholyte- 300 ml. concentrated sulfuric acid
25 gm. o-nitrodiphenyl

Results- Fifty ml. of liquid mixture boiling from 58-76°C.

DISCUSSION:

PART I

The reduction of o-nitrodiphenyl in neutral and alkaline medium was divided into three parts. From the series of runs listed in Table I it was found that the results were easily reproduced. The concentration of o-nitrodiphenyl in the reduction mass could be stepped up to twenty-five grams per two hundred fifty milliliters of solution providing the solution was warmed to 40-50°C. before reducing.

The carbon anode while satisfactory had a tendency to flake. Hence a new anode material was sought.

In these neutral runs, the cell had a rather high resistance and it took time for the current to reach a desired value. To overcome this, the cell was warmed up to 50-60°C. for an interval of approximately five minutes.

The temperature did not have any noticeable effect on the reduction. It was found that a temperature below the boiling point of alcohol was desired so as to minimize the loss of solvent due to evaporation.

Temperature control was easily maintained. The cell warmed up with the passage of current through

The solution. The proper temperature was obtained by means of a water bath.

In the second series of runs shown by TableII the alkalinity and current density were varied and a new anode used. A lead anode was found satisfactory. It was found that increase in current density with increasing alkalinity- up to fifty milliliters of ten per cent sodium hydroxide- gave better yields. After the amount of alkali exceeded fifty milliliters of sodium hydroxide, the crystals of o-azoxybiphenyl were oily and unreacted o-nitrodiphenyl was recovered from the reduction mass.

When more than fifty milliliters of ten per cent sodium hydroxide solution was added the yields were correspondingly decreased. A decrease in yield was accompanied by a corresponding increase in the oiliness and a darkening of the crude product.

It was found that the poorest yield of o-azoxybiphenyl was obtained when two hundred milliliters of forty per cent sodium hydroxide were added to the catholyte. If more than this amount were added the catholyte solution separated into two layers.

In the third series of runs the alkalinity was held constant and the current density was varied. It was found that the best results were obtained at current densities of 3.28 amperes per square decimeters and 5.48 amperes per square decimeter.

The crude product could be recrystallized from the following solvents and mixture of solvents; acetone, a mixture of equal parts by volume of chloroform and ethyl alcohol, and a mixture of ninty per cent carbon tetrachloride and ten per cent ethyl alcochol. Acetone and the mixture of carbon tetrachloride and ethyl alcohol were the best solvents for recrystallization. Recrystallization of equal weights of the crude product from each of the solvents gave better yields in the case of acetone.

PART II

The reduction in the acid solution gave less satisfactory results. Difficulty was first encountered when the o-nitrodiphenyl tended to form a skin on the cathode and thus end the process of reduction. This was overcome by increasing the concentration of the acid in the catholyte and increasing the rate of stirring of the catholyte.

The next difficulty is the fact that the nature of the compound is such that only a small fraction of the o-nitrodiphenyl reduced under the conditions of research work. It was always possible to recover more than fifty percent of the unreacted o-nitrodiphenyl by steam distillation. There is also evidence that the compound is decomposed some what during the reduction. This is shown by the oils that form and the charring of the solution after reduction. It is also evidenced by the fact that in some instances aromatic compounds or mixtures were recovered which gave no positive test for nitrogen.

The third difficulty is the separation of the reaction mass after reduction. This had been accomplished thus; the reduction mass is made alkaline and the unreacted o-nitrodiphenyl steam distilled off; next, the solution is acidified and the phenolic compounds, if any, are distilled off. The mixtures of organic compounds obtained have been too small to permit extensive identification work.

- Experiment nine in the acid runs has produced fair results, and is furnishing the basis for further work.

SUMMARY

It has been shown that o-nitrodiphenyl can be easily reduced in alkaline medium to produce quantitatively o-azoxybiphenyl of a high grade of purity. This reduction is possible with good results at two current densities; 2.28 amperes per square decimeter and 5.48 amperes per square decimeter.

It is also possible to reduce o-nitrodiphenyl in acid solution. Here there are many difficulties to be overcome, the chief one being the separation of the reduction mass. Simplification of this problem will make it possible to reduce the compound to 2 amino 5 hydroxydiphenyl, and whatever other intermediates are possible.

It is also probable that o-nitrodiphenyl may be reduced in a manner similar to nitrobenzene in acid solution. However, since the compound, o-nitrodiphenyl is nitrobenzene with a phenyl group in the ortho position, this phenyl group may alter the nature of the compound so as to account for some of the difficulties encountered to date in this work.

If it is possible to obtain a reduced compound in acid solution, conditions can then be regulated to possibly obtain a series of compounds or "intermediates".

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