

Electrolytic Reduction of Organic Compounds

VI. Aminophenols from Nitrocompounds¹

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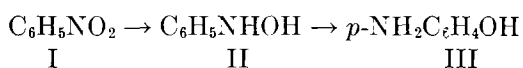
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ABSTRACT

The influence of various factors on the material yield of the aminophenol from 2-chloro-6-nitrotoluene has been investigated. The most significant increase resulted from efficient agitation best attained by high speed rotation of a disk cathode. Under these conditions current efficiency, already high, increased to virtually 100%. The effect of agitation shows that the slowest step in the process is diffusion controlled. Cathodes of monel and copper were tried. Amalgamation of the surface raised material yield of aminophenol from 21 to 58 per cent with a stationary cathode and 37 to 71 per cent with a rotating copper cathode. Increase both of temperature and of acid strength also raised material yield of aminophenol by an effect, it is believed, on rate of rearrangement of intermediate hydroxylamine. Increase in the ratio of nitrocompound to acid electrolyte reduced yield³ of aminophenol because of the formation of tarry products. Yield of amine, the only other simple chemical product, remained constant showing that the tarry products resulted by reaction of intermediate hydroxylamine with nitrocompound. Current density was increased from 0.4 to 4 amp/dm² using a rotating cathode without seriously affecting yield. This contrasts strongly with the effect of a similar change with a stationary electrode which causes yield to drop almost by half. Using preferred conditions (20 per cent acid, rotating amalgamated monel cathode, 90°C, 2.7 amp/dm²) the following nitrocompounds were reduced to give aminophenols in the material yields indicated: 4-chloro-2-nitrotoluene (82), *o*-nitrotoluene (74), *o*-chloronitrobenzene (76), 2,5-dichloronitrobenzene (72), and nitrobenzene (72).

INTRODUCTION

Gattermann's original method (1) for converting nitrobenzene (I) into *p*-aminophenol (III) by rearrangement of intermediate phenylhydroxylamine (II) made use of



strong sulfuric acid at ordinary temperatures and a platinum cathode. Instead of platinum, copper gauze (2) or carbon (3) cathodes have also been used with strong acid but the yields are all very low due primarily to the difficulty of operating in strong acid media. Nevertheless, the manufacture of *p*-aminophenol by electrolysis in 90% acid at a platinum cathode reported by McDaniel, Schneider, and Bal-

lard⁴ (1) was a commercial success as an emergency measure at the time of the first World War; although the current yield was only of the order of 25 per cent, the high purity of the product was suitable for exacting photographic applications.

Use of 80 per cent acid and platinum cathode (4) or 50 per cent acid and nickel (5) did not improve matters much and it was not until Dey and his collaborators (6) made quite new departures that the electrochemical method for aminophenols began to look interesting as a preparative method. These authors used much weaker (20–30 per cent) sulfuric acid at elevated (80–90°C) temperatures and a copper or monel cathode together with a mercury "catalyst." The yields of aminophenols from a variety of nitrocompounds ranged from 53 to 61 per cent. The present paper is essentially an extension of these findings. The effect of various factors on aminophenol formation has been determined and increased yields have been obtained using a high speed rotating cathode.

EXPERIMENTAL

Materials.—2-chloro-6-nitrotoluene, obtained from General Aniline and Film Corporation, was recrystal-

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³ Yield is used synonymously with *material yield* in this paper to indicate the percentage of theory calculated from the stoichiometric chemical equation. *Efficiency* or *current efficiency* are used in the conventional sense for percentage of current going to products other than gaseous hydrogen.

⁴ The authors thank one of the referees of this paper for this historical touch.

lized before use. It had mp 37–38°C. The other reagents were of analytical purity.

Cathodes.—Ten circular copper disks, 5 cm in diameter and 0.1 cm thick were mounted at the end of a copper rod, 0.6 cm in diameter and 35 cm long, and separated from each other by copper spacing collars, 0.5 cm long and 0.9 cm outside diameter. The whole assembly was held by tightening a nut on the threaded end of the rod. The surface area was 4.08 dm² for ten disks.

A similar monel cathode was also fabricated. In this case electrical contact was made by a brush bearing on a copper collar fastened toward the end of the monel rod remote from the disks. This contact was augmented through the bearings of the motor rotating the cathode.

Cell.—The anode was a sheet of lead 11 by 30 cm in the form of a cylinder around the cathode chamber. This was an unglazed porcelain cylinder, 21 cm long and 9 cm in diameter (Coors Porcelain Company). It was treated overnight with fuming nitric acid and then thoroughly washed with water.

Technique.—The porous pot forming the cathode chamber contained 350 cc sulfuric acid electrolyte and was surrounded by the lead anode and the whole placed in a beaker (1 liter). The beaker was placed on a hot plate connected to a variable transformer. The cathode shaft was held in the chuck of a variable speed motor and passed through a hard asbestos board lid on the porous cup. The inner surface of the porous cell carried a glass strip to act as a baffle to prevent the swirling catholyte from rising up the wall and uncovering the cathode.

When necessary the cathode was amalgamated by electrolyzing an acid solution of mercuric sulfate (0.2 g).

Reduction, using a stationary cathode, was carried out using an auxiliary glass stirrer. A thermometer also passed through the asbestos cover.

Products.—The catholyte was transferred to a two-liter flask and any unchanged nitrocompound steam distilled. If any suspended resinous matter remained it was then filtered off. The catholyte was neutralized with ammonium carbonate and steam-distilled to remove amine. The distillate was extracted with ether (25 cc) three or four times and the extract dried and evaporated. The aminophenol separated from the residue from the neutral steam distillation on cooling to 0°C. It was filtered off, washed with a little ice water, and dried in a vacuum desiccator. From 2-chloro-6-nitrotoluene the product had mp 163–164°C. The melting points of the other aminophenols agreed with the figures recorded in the literature.

All the operations with aminophenols were best conducted after addition of a little sodium bisulfite to the solution. This helped to prevent oxidation.

(2-Methyl-3-chlorophenyl)-hydroxylamine.—This compound was made for reference purposes and rearrangement to the aminophenol. 2-Chloro-6-nitrotoluene (80 g) was dissolved in ethanol (150 cc, 95 per cent) and water (100 cc) in a three-necked flask fitted with stirrer and condenser. Powdered calcium chloride (6 g, anhydrous) was added and the mixture heated to reflux while zinc dust (75 g) was added slowly during 15–20 min. After 15 min more the reaction mass was filtered, the residue washed once with ethanol (50 cc) and the alcohol evaporated under reduced pressure in the presence of nitrogen. The residue (63 g) weighed 35 g after washing with petroleum ether (100 cc, bp 30–60°C) and had mp 63°C. *Analysis:* Calc. for C₇H₈NOCl: N, 8.9.

Found: N, 9.13, 9.0 per cent.

The hydroxylamine (5 g) was dissolved in ethanol (15 cc) and benzaldehyde (3.5 g) added. After 12 hr the precipitated product (5.1 g) was collected and crystallized from alcohol, mp 123–4°C.

Analysis: Calc. for C₁₄H₁₂NOCl: N, 5.7.

Found: N, 5.8, 5.81 per cent.

The hydroxylamine (5 g) was dissolved in cold sulfuric acid (100 cc, 40 per cent) and stirred for two hours under nitrogen. Azoxycompound was filtered off and the filtrate neutralized with ammonium carbonate as above. The precipitated aminophenol had mp 163–4°C after washing with water and drying.

Analysis: Calc. for C₇H₈NOCl: N, 8.9.

Found: N, 8.91, 8.88 per cent.

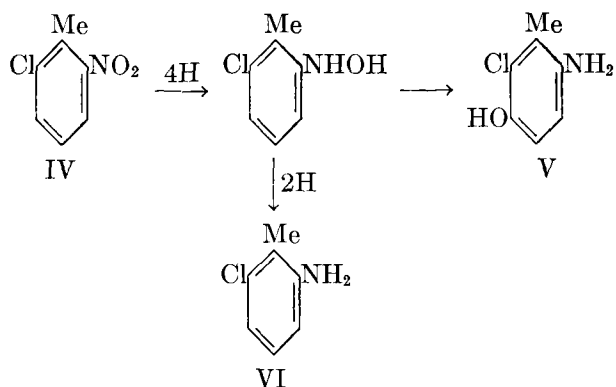
The Schiff base from 2-chloro-3-methyl-4-aminophenol and benzaldehyde was obtained in quantitative yield and had mp 95–96°C after crystallization from ethanol.

Analysis: Calc. for C₁₄H₁₂NOCl: N, 5.70.

Found: N, 5.85, 5.86 per cent.

DISCUSSION OF RESULTS

Most of the present experiments on the effect of conditions on products were carried out using 2-chloro-6-nitrotoluene (IV). This compound has been reduced before (7) in strong sulfuric acid to give a very small yield of aminophenol and considerable sulfonated material. In the present experiments the



only significant products were the aminophenol (V) and the amine (VI). Some tarry material resulted if the amount of nitrocompound was high.

Effect of amalgamation of cathode.—In dilute sulfuric acid at 80–90°C, in agreement with the findings of Dey and collaborators (6) the addition of mercury salts raised considerably the yield of aminophenol using a brass, nickel, monel, or copper cathode. With the last this was from 21 to 58 per cent. This experience along with other data for the reduction of compounds such as acetone, cinnamic acid, crotonic acid, sorbic acid, etc., suggests that the behavior of such surface-amalgamated cathodes resembles very nearly what is obtained at pure mercury. Copper seems to be the best since, apparently, the mercury forms a more continuous surface layer. It is considered that the effect of amalgamation is due to the conversion of the metal surface into something akin to mercury rather than a "catalytic" influence of added salts as envisaged by the Indian authors (6).

Surface amalgamation of a medium or low over-voltage cathode such as copper must have the effect of raising cathode potential. The role of overpotential in reduction has been envisioned (8) as attracting polar molecules to the metal surface. For nitrocompounds any increase in overpotential will result in attraction for the more polar nitrocompound rather than the less polar hydroxylamine intermediate. Since the metal surface is well covered in efficient reductions such as these, the result of added electrostatic attraction will be to displace hydroxylamine by nitrocompound. The hydroxylamine thus loses opportunity to be reduced and undergoes rearrangement instead. It will be realized that reduction only proceeds in the neighborhood of the cathode surface whereas rearrangement, which is acid catalyzed, takes place throughout the solution.

Agitation. Rotation of the cathode.—Effective stirring has frequently been recommended in electrolytic reduction to increase current efficiency. When this happens it is evident that the process is controlled by diffusion which is speeded up by agitation. Law (8) appreciated this long ago. Since most of the depolarizer deficiency arises in the so-called diffusion layer, which may be as much as 0.05 cm thick, the most effective way to speed up diffusion, and with it, efficiency, is to rotate a circular cathode so that maximum shear occurs nearest the metal-liquid interface. This was done by Plump and Hammett (9) in their studies with ethyl iodide and by McKee and Gerapostolou (10) in the reduction of nitrobenzene. Moreover, as speed of rotation increases, efficiency should also increase until a limit is attained beyond which further increase in speed has no further effect. This is known to be true for the reduction of azobenzene (11).

The effect of rotation of the cathode was studied in the present investigation. Current efficiency was already at least 90 per cent with a stationary cathode, and rotation caused it to rise to virtually 100 per cent. Rotation (2500 rpm), however, caused an unexpected rise in the yield of aminophenol and a corresponding drop in that of the amine. With copper, for example, aminophenol rose from 21 to 37 per cent; when amalgamated, the corresponding figures were 58 (auxiliary glass stirrer) and 73 per cent. As the speed of rotation increased, yield rose at first rapidly but then remained sensibly steady at 64 per cent between 1000 and 2000 rpm. A further rise occurred up to 2500 rpm. This relationship is shown in Fig. 1. In the remainder of the present experiments with a rotating

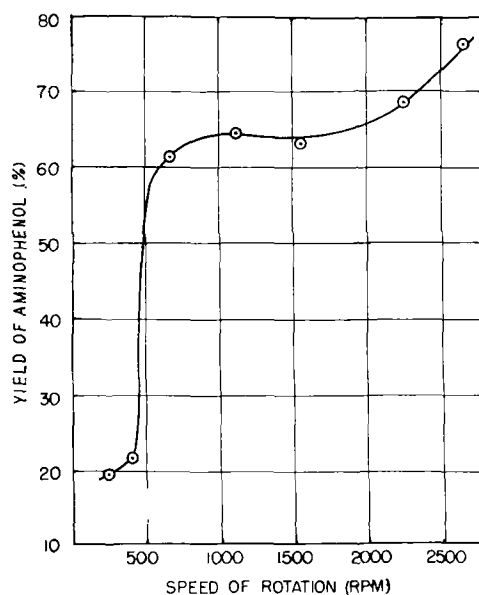


FIG. 1. Influence of speed of rotation of amalgamated copper cathode on yield of aminophenol from 2-chloro-6-nitrotoluene (10 g nitrocompound in 350 ml 20% sulfuric acid, cathode area 4.08 dm², current 11 amp, 60°C).

cathode the speed was arbitrarily set at 2500 rpm. It was impossible with the present apparatus to study higher speeds and keep liquid and electrode in contact.

Since the catholyte consisted of a suspension of liquid nitrocompound in sulfuric acid the influence of rotation on both efficiency of reduction and yield of aminophenol might have been due to variations in the degree of mechanical dispersion. This was shown not to be the case by carrying out reduction in homogeneous solution when changes of degree of dispersion are not possible. In alcoholic sulfuric acid solution using amalgamated copper, rotation at 2500 rpm raised the yield of aminophenol from 17 to 33 per cent. The low yields are due to ether formation. In a medium containing sufficient acetic acid to render the mixture homogeneous, rotation raised the figure from

55 to 80 per cent. When the electrode was stationary an auxiliary stirrer was always employed since this was essential to maintain an intimate mixture of nitrocompound and electrolyte. Such auxiliary stirring does, of course, have an effect in the same direction as that obtained by rotating the cathode but of a much smaller magnitude. Thus with the most violent auxiliary stirring which could be employed, yield of aminophenol rose to 58 per cent compared with 75 per cent when the cathode was rotated.

The effect of high speed rotation on efficiency of reduction is undoubtedly due to speeding up the movement of organic molecules to and from the cathode so that their reduction becomes favored over hydrogen evolution. It should be remembered that the discharge of hydrogen ions is not, under these conditions, controlled by diffusion. The increase in the yield of aminophenol at the expense of amine caused by stirring may be explained as follows. Intermediate hydroxylamine either is reduced further or rearranges, and the ratio of products will be determined by the relative speeds of the two reactions. Rearrangement is acid catalyzed and depends on the strength of acid but is independent of the cathode. Reduction on the other hand is dependent on the cathode and since an organic molecule being reduced must attain a certain proximity to the cathode surface for an adequate period of time it follows that reduction will become less possible the shorter the time spent by the hydroxylamine in the neighborhood of the cathode. Stirring will decrease this period of time by increasing the speed of diffusion of hydroxylamine molecules away from the electrode. In effect, if surface concentration has any real meaning, rotation, like increase in potential caused by amalgamation, raises the ratio of nitrocompound to hydroxylamine on the surface.

Temperature.—Experiment showed that with both stationary and rotating cathodes, increase of temperature raised both current efficiency and yield of aminophenol by an appreciable amount. Gattermann and Kaiser (12) found also when using concentrated sulfuric acid that increase of temperature favored aminophenol. In the present experiments using a stationary amalgamated copper cathode with auxiliary stirrer, a rise of temperature from 50 to 90°C increased efficiency from 88 to 99 per cent and yield of aminophenol from 43 to 58 per cent. The effect on efficiency must undoubtedly be due to the influence of increased temperature in speeding up diffusion; the effect on yield of aminophenol has to be sought in the greater facilitation of rearrangement over further reduction of the hydroxylamine. The change with temperature was also evident with a rotating electrode. If it be assumed that under these conditions the surface concentrations are in equilibrium

with the bulk of solution, increase in yield of aminophenol may mean favored rearrangement due to either a higher energy of activation or a decreased surface concentration of hydroxylamine compared to that of nitrocompound or both. Above about 60°C yield of aminophenol did not rise much further.

Acid strength.—Yield of aminophenol rose with acid strength at both rotating and stationary electrodes. Thus with rotating amalgamated copper an increase of acid from 5 to 30 per cent changed yield of aminophenol from 50 to 75 per cent. Increase to 40 per cent acid did not further change aminophenol appreciably. The effect of acid is undoubtedly on rearrangement since it is unlikely that it affects reduction much. This is supported by the absence of any great dependence of electrode properties such as overvoltage on acid strength (13) although, in the polarograph, dependence of ease of reduction on pH is frequently evident.

It is of especial interest from the preparative standpoint that better results are obtained using dilute acid at elevated temperature rather than strong acid at low temperature. It must be that increase of temperature enhances the relative rate of rearrangement more than reduction of acid strength depresses it. Using weaker acid also prevents sulfonation, sometimes a serious side reaction in the earlier work.

Current density.—With a stationary amalgamated copper cathode, the yield of aminophenol rose to a maximum (58 per cent) at 1 amp/dm² and then fell progressively to 31 per cent at 4 amp/dm². Over the same range, efficiency dropped from 97 to 80 per cent. When the same cathode was rotated both yield and efficiency remained sensibly constant at 70 and 100 per cent respectively. The relationship between yield and current density is illustrated in Fig. 2. With the present equipment it was not possible to study current densities much higher than 4 amp/dm². Analogous results were obtained with an amalgamated monel cathode but, with plain copper, yield of aminophenol fell as current density was increased even when the cathode was rotated. This effect with plain copper is not easily explained nor is the initial rise of the curves in Fig. 2, but in a broad way the results are adequately interpreted as an effect of rotation in speeding up diffusion.

Surface depletion of nitrocompound means lowered reduction efficiency, an effect more noticeable at a stationary electrode and high current density. In addition, failure to remove hydroxylamine rapidly from the cathode means a greater chance of further reduction and a consequent drop in yield of aminophenol and increase in that of the amine.

With adequate rotation of an amalgamated cathode, control of the reduction process by diffusion is completely removed and rate of reduction to hy-

droxylamine is determined solely by the current. Movement of nitrocompound to, and hydroxylamine from, the surface becomes so much faster than either reduction or rearrangement that, to all intents and purposes, distribution equilibrium of these two compounds between solution and cathode surface is maintained even up to high current densities. Since rearrangement is acid catalyzed, independent of cathode and probably a first order reaction with respect to hydroxylamine, it follows that, in order to maintain the ratio of aminophenol to amine independent of current density as required by Fig. 2, the ratio of the concentrations of hydroxylamine on the surface and in the bulk of solution must remain independent of current density. This is in keeping with the existence

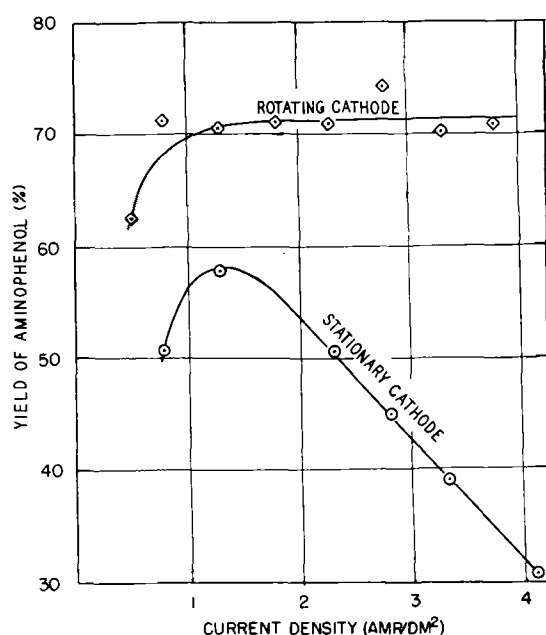


FIG. 2. Effect of current density on yield of aminophenol from 2-chloro-6-nitrotoluene at a stationary and at a rotating amalgamated copper cathode (10 g nitrocompound in 350 ml 20% sulfuric acid, cathode area 4.08 dm², 60°C).

of the equilibrium proposed above. Since efficiency remains at 100 per cent and amine and aminophenol are the only significant products, it also follows that concentrations both on the surface and in solution will bear a linear relationship with current density. It would be an interesting investigation to check this point by estimating the concentration of hydroxylamine in the bulk of solution at various current densities and nitrocompound concentrations.

Assuming that at high speeds of cathode rotation both nitrocompound and hydroxylamine are partitioned between solution and the diffusion layer in something approaching equilibrium conditions, the relative rates of reduction of the two entities need not simply be related to their relative concentration on the surface, and consequently by a factor to

their relative concentrations in solution, that factor being the ratio of partition coefficients. It is quite likely that both potential and some specific effect of the metal surface will enter the picture. In order to explain the effect of amalgamation it has already been assumed that the raised potential increases the surface concentration of nitrocompound at the expense of hydroxylamine. However, until more is known about the "specific" effects of a cathode and the effects of potential other than on surface concentrations, it is a tempting assumption to relate relative rates of reduction determined by product formation to relative surface concentrations and to imagine the electrons transferred in unit time being divided between the entities on the surface in proportion only to their surface concentrations.

Effect of changing nitrocompound concentration.—One simple corollary of what has just been said is that if nitrocompound concentration in solution were

TABLE I. Reduction of various nitrocompounds to aminophenols at a rotating amalgamated monel cathode (10 g nitrocompound in 350 cc sulfuric acid (20%). Current density 2.7 amp/dm² 90°C)

Nitrocompound	Yield of aminophenol (%)		
	Rotating cathode	Stationary cathode*	Dey <i>et al.</i> (6)
2-Chloro-6-nitrotoluene.....	72	46	—
4-Chloro-2-nitrotoluene.....	82	44	—
<i>o</i> -Nitrotoluene.....	74	56	46
<i>o</i> -Nitrochlorobenzene.....	76	50	29
2,5-Dichloronitrobenzene.....	72	44	—
Nitrobenzene.....	72	57	55-60

* Auxiliary glass stirrer.

raised, and by so doing its concentration in the diffusion layer were enhanced, then aminophenol formation would increase. Experiment showed, however, that with a rotating amalgamated copper cathode, yield of aminophenol (per cent) *decreased* as nitrocompound (g) in the electrolyte was increased, as follows—85 per cent (10 g); 79 per cent (20 g); and 72 per cent (30 g). It was also shown that amine remained sensibly constant at 8.5, 7.9, and 8.5 per cent yield, respectively, the difference being accounted for by increased tar (azo-and-azoxy-compounds) formation. These facts indicate the following explanation. Since the nitrocompound is insoluble in the catholyte no matter how much is added, its concentration in solution, and consequently on the surface, will not change. Furthermore, hydroxylamine in solution is further partitioned between solution and liquid nitrocompound acting as extraction solvent. The more nitrocompound there is, the more hydroxylamine will be present in the organic phase. Azo- and azoxy-by-products are known to result by reaction between

nitrocompound and hydroxylamine and this reaction will, therefore, be favored by large amounts of insoluble nitrocompound.

Aminophenols from other nitrocompounds.—The optimum conditions for reducing 2-chloro-6-nitrotoluene to aminophenol were applied to a series of nitrocompounds with excellent results. The data together with yields obtained by the Indian workers are collected in Table I.

It is of interest that with diffusion control, yield of aminophenol is lower with the bigger molecules. When diffusion control is absent (rotating cathode) the yields from all the nitrocompounds are approximately the same. Could this indicate that the surface-solution partition coefficient depends essentially on the nitro-group and not the rest of the molecule?

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1953 issue of the JOURNAL.

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