[Contribution from the Chemical Laboratory of the University of California]

DEVELOPMENT OF THE METHOD FOR PREPARATION OF p-BENZOQUINONES FROM AROMATIC NITRO COMPOUNDS VIA ELECTROLYTIC REDUCTION TO AMINOPHENOLS

ROBERT E. HARMAN[1] AND JAMES CASON

In a previous paper (1) from this laboratory there was reported a study of the preparation of 3-chlorotoluquinone from 6-chloro-2-nitrotoluene by way of electrolytic reduction of this nitro compound to 2-chloro-4-amino-*m*-cresol. Since conditions were found under which rather good over-all yields could be obtained in this conversion and no other simple high-yield procedure is available (1) for conversion of aromatic nitro compounds to quinones, the method has now been extended. The present paper reports a more extensive investigation of several variables in this procedure and the development of a method which is generally applicable for the convenient preparation of *p*-benzoquinones.

Results of the present, more extensive study necessitate modification or correction of two features of the earlier report (1). The first of these is the previous statement that the reduction of a nitro compound to the aminophenol could not be accomplished when a copper cathode was used. Excellent results have now been obtained with a copper cathode, and it has been found that the previous failures should be ascribed, not to the material of which the cathode was constructed, but rather to the geometry of its design coupled with the use of 50% sulfuric acid as catholyte. When the depolarizer (the nitro compound, in this instance) is highly insoluble in the catholyte, the design of cathode (2) previously used permits the insoluble material to remain, in major amount, as a pool on the surface of the catholyte. Thus, the concentration of depolarizer at the cathode surface is not sufficient to prevent accumulation of electrons at the cathode and a sufficient build-up of the cathode potential to allow occurrence of undesired reductions. These difficulties may be avoided by use of a modified design of cathode, as described in the experimental part, or by use of a catholyte containing a sufficient concentration of acetic acid to dissolve most nitro compounds.

It was also indicated in the previous report (1) that yields are lowered by use of current densities greater than one ampere per sq. dec., but this effect, also, was probably caused by an inadequate supply of depolarizer to the cathode surface. With a stirred, homogeneous catholyte, there may be used, with no adverse effect, current densities (about 3 amp. per sq. dec.) as high as convenient without adopting special procedures for dissipation of heat generated in the cell.

The best of the presently described procedures, which is probably near the optimum, permits over-all yields of 60–80% in most conversions of nitro compounds to quinones. Its general application will be described in the next paper of this series (3).

RESULTS AND CONCLUSIONS

In each of the series of experiments summarized in Table I, the results recorded have been compiled from the data obtained in at least four runs. Series A and B each involved a large number of experiments.

The procedure described earlier (1) for the preparation of 3-chlorotoluquinone was carried out several times in orientation experiments, and the results (55–70% yields) agreed reasonably well with those reported. Attempted extension of this procedure for the preparation of chloroquinone was not satisfactory. Since *o*-chloronitrobenzene proved to be subject to more erratic behavior in this reduction than was the 6-chloro-2-nitrotoluene, attention was concentrated during

TABLE I

DATA ON PREPARATION OF CHLOROQUINONE

SERIES NO.	CATHODE[a]	CIRCUIT[b]	PROCEDURE[a] FOR		YIELDS, %	
			Reduction	Oxidation	Nitro Compound	Quinone[c] (Aminophenol)
A	a, b, c	Bat. ch.	1	I	0–45	24–65
B	a	Bat. ch.	2	—	0–37′	(26–55)[d]
C	d	Bat.	2	—	0	(25–62)[d]
D	e	Bat.	2	—	12–20	(15–36)[d]
E	f, g	Bat.	1	II	0	57–65
F	h	Bat.	3	II	0	8–35[e]
G	h	Bat.	3	II	0	40–45
H	f	Bat.	4	II	0	58–65
J	f, g	Bat. ch.	4	II	0	58–65

[a] See Experimental for cathode designs and procedures. [b] "Bat. ch." refers to the circuit using the battery charger alone, Fig. 2; "bat." refers to the circuit using the battery, Fig. 3. [c] Quinone was isolated by Procedure A in all runs except Series F (Procedure B) and Series G (Procedure C). Isolation procedures are described in the Experimental section. [d] In Series B and C, 15–42% yields of *o*-chloroaniline were obtained; in Series D, 50–70%. [e] Aminophenol could be isolated (Reduction Procedure 2) in 67–73% yields.

this developmental study on the former compound. During several of these series of experiments, however, the procedures were applied to *o*-nitrotoluene and 6-chloro-2-nitrotoluene; the results in every instance were parallel to those observed in the chloroquinone preparation, with the exception of the aminophenol isolation. By the procedure described, only the chloroaminophenol could be obtained in a pure state; the other two aminophenols were much less stable.

In the numerous experiments of Series A, it was found that varying amounts of nitro compound remained unreduced even though as much as twice the theoretical amount of current was passed through the cell. Often the chloroquinone was of very poor quality and almost impossible to obtain in a pure state. Workup of the reduction mixture for amine and aminophenol (Series B) showed that the yields of these two products also varied between wide limits in successive runs. Brief investigation of the effect of varying the current (0.5–2.5 amperes), with the same variable results, indicated that the system was not operating at a

borderline current value such that small changes in the current would have a large effect on the cathode potential and hence the electrode reaction (*Cf.* Discussion). Experiments described below substantiate this conclusion.

Two unsuccessful modifications in the design of the cathode are recorded in Series A. Observations of the predominantly vertical flow in the stirred catholyte led to the modification of the cathode design which was successful in promoting complete reduction of the nitro compound. Openings were cut in the cathode at the surface of the catholyte so that uninterrupted vertical flow was possible. It was found that with this modified cathode, 1.2–1.3 equivalents of current ensured complete reduction of the nitro compounds (Series C).

With the assistance of Prof. C. T. O'Konski of this laboratory, the output of the battery charger was subjected to investigation with an oscilloscope. During a normal run, with the ammeter reading 0.6 amperes, the current varied between 0 and 1.7 amperes. To ensure that this current ripple was not responsible for the unsatisfactory operation of the system, a battery-powered circuit was set up (*Cf.* Experimental, Fig. 3). From the results in Series C, however, it will be noted that, even with the improved cathode design and the stable battery circuit, product yields were still subject to large variation.

At this point the investigation of the nickel electrode was discontinued, for it was concluded that the variable surface of the nickel electrode, visibly unstable to the electrolyte, was probably responsible for the erratic results obtained in these studies. It should be noted that the nickel-nickel ion potential has not been directly measured, as have most metal-metal ion potentials, apparently because reproducible values cannot be established (4).

Series D records the results of a brief investigation of the performance of a lead cathode, reported in the literature (5) to favor formation of aromatic amine. This observation was confirmed. The amine arises from reduction of the hydroxylamine, rather than the aminophenol, for the stability of the aminophenol to the reducing conditions in this cell was demonstrated by an attempt to reduce the chloroaminophenol at the lead cathode. No amine could be isolated from the reaction mixture, and there was recovered 92% of the aminophenol used. Thus, rearrangement of the hydroxylamine competes with its reduction when the cathode potential is sufficiently high to reduce hydroxylamine. These results make it clear why use of excess current does not adversely affect the yield of aminophenol. They further suggest one reason why excellent yields of aminophenol may be obtained at a copper or platinum cathode, with formation of only small amounts of amine, even though the cathode potential is not controlled by reduction of applied E.M.F. near the end of the run. To obtain good yields of aminophenol, it is necessary, of course, to use a cathode at which the reduction potential for hydroxylamine is significantly higher than that for nitrobenzene (*Cf.* Discussion).

Accumulation of a quantity of the chloroaminophenol permitted investigation of the oxidation conditions. It was found that the temperature previously maintained in this step had been too low; this allowed the accumulation of intermediate species which interacted to form tarry material. Comparative experi-

ments showed that room temperature, rather than 0°, gives a higher yield of cleaner product. Oxidations in Series E–J were carried out under the more favorable conditions.

Series E records the consistent results obtained when experiments were carried out with a copper cathode of the modified design; the 75% sulfuric acid catholyte was used. The contrast with Series A–C demonstrates the undesirability of the nickel cathode.

In view of the importance of establishing a high concentration of depolarizer at the cathode surface (*Cf.* Discussion), it was considered desirable to examine the catholyte first used by Elbs (6). This consists of 75% by volume sulfuric acid diluted with about two volumes of acetic acid, and is an excellent solvent for the nitro compound. Low and variable yields of quinone were obtained in the first runs (Series F) by this procedure, but this was traced to instability of chloroquinone to sodium bicarbonate, which was used to remove acetic acid after oxidation (*Cf.* Experimental, Quinone Isolation, Procedure B). When the aminophenol was isolated in Series F, consistent yields of 67–73% were obtained. In order to avoid use of bicarbonate, removal of acetic acid from the aqueous phase during extraction of the quinone was minimized by substitution of pentane for ether in the extraction process. This gave improved and consistent yields (Series G), but best results are obtained (Series H and J) when acetic acid is removed from the catholyte prior to oxidation.

Series J shows that the battery charger circuit is just as satisfactory for the reduction step as is the battery. On the basis of evidence available thus far, the preceding statement should not be generalized for other electrolytic reductions. The procedure used in Series J is considered the most suitable for use as a general preparative method. It represents about 80% conversion of nitro compound to aminophenol, and nearly 80% in the oxidation step. The use of aqueous sulfuric acid as catholyte (Series E) gives the same yields, with somewhat less labor; however, the necessity for very careful set-up of the apparatus and the limit on current density imposed by the low water solubility of the nitro compound are disadvantages of the use of the aqueous electrolyte.

DISCUSSION[2]

Haber (7) and Russ (8) came to the conclusion many years ago that the reaction occurring at the cathode, in a system in which there are several possible reduction stages, is controlled by the cathode potential. Nevertheless, much of the electrochemical literature since 1900 contains statements to the effect that the isolation of intermediate reduction products is made possible by the use of low cathodic current densities and electrodes having low hydrogen overvoltages (9). Lingane and co-workers (10) have described the fallacies inherent in statements of this sort and observed that the variables mentioned are of significance only in so far as they influence the cathode potential.

No relationship, to our knowledge, has been established between the cathode

potential in a given system (a function of the depolarizer, the electrolyte, the cathode material, and the rate of supply of depolarizer to the cathode) and current density or overvoltage. Indeed, the latter appears to be a rather nebulous quantity, both theoretically and practically.

To account in part for the successful operation, in the present study, of the copper cathode in contrast, for example, to that of lead in the same electrolyte, it is desirable to define briefly the current–cathode potential (E_c) relationship existing in a multi-stage system of the type studied in this investigation. A, C, and D in Figure 1 (probably somewhat idealized) are intended to represent,
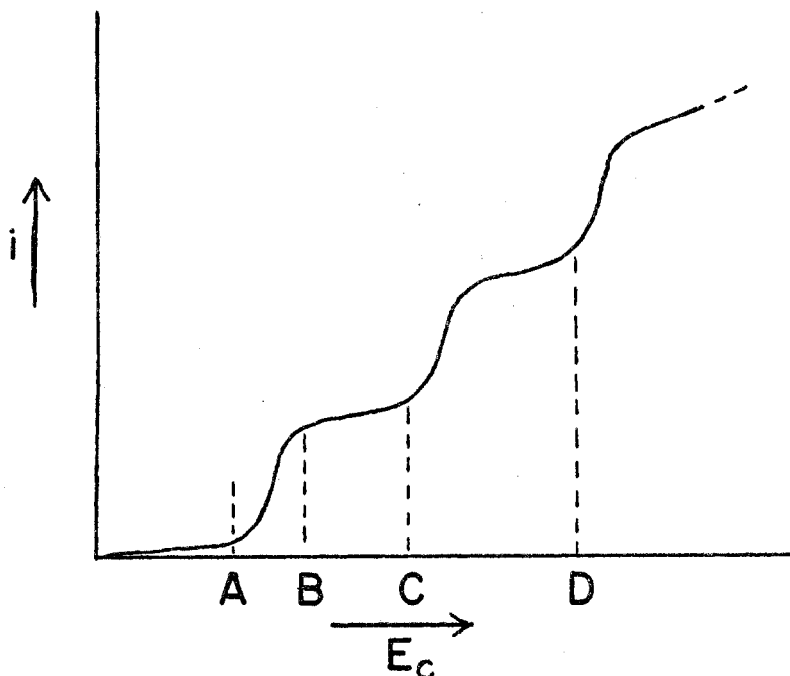

FIGURE 1. RELATIONSHIP OF CURRENT TO CATHODE POTENTIAL IN AN ELECTROLYTIC CELL

respectively, the lowest potentials at which nitrobenzene, phenylhydroxylamine, and hydrogen ion are reducible. The nitroso compound, undoubtedly a transient intermediate, has never been isolated from this reduction so its potential must lie close to or below that of nitrobenzene.

In operation of a given cell with a large cathode, the E_c may not be readily selected by the operator so long as the concentration of depolarizer is relatively high. In order to raise E_c above the value at which the first step of the reduction occurs, the rate of supply of electrons to the cathode must exceed the rate of supply of fresh depolarizer. The E_c is not proportional to the current flowing. As shown in Figure 1, the E_c increases rapidly from zero, with very little current flowing, as the applied E.M.F. is increased, until E_c reaches A, at which poten-

tial the depolarizer can accept electrons and become reduced. As the applied E.M.F. is raised further, the current increases rapidly but the E_c suffers little increase until the value B is reached, for the electrons do not accumulate on the electrode but react instead with the depolarizer. Above $E_c = B$, the rate of supply of electrons to the electrode surface is greater than the rate of supply of the reducible material; thus, there is an accumulation of electrons at the electrode and the E_c increases until that value is attained at which the next stage in the reduction becomes possible. Only in this manner can the E_c be raised above the value, A. As the concentration of depolarizer decreases, it follows that the E_c may be raised correspondingly more easily.

If the electrolytic cell be operated so that the E_c remains between A and B, there will be clean reduction of nitrobenzene to the hydroxylamine. If the potential be between B and C, there will be reduction of both nitro compound and hydroxylamine. In acid, of course, rearrangement of the hydroxylamine is a competing reaction. It appears probable that, on the lead cathode, the separation between the potentials required for the two stages of the reduction is very small, whereas on the copper cathode there is a clean separation between these two potentials. There appears to be, however, no reason for saying that the two potentials lie closer together on the lead cathode because its hydrogen overvoltage is higher. It is probably safe to generalize, as have Lingane and co-workers (10), that in a two-stage reduction system, the item of fundamental importance is the separation between the potentials required for the two stages. If this is sufficient, clean reduction to the intermediate stage is possible. This separation, for a given process, is a function of the cathode material and the electrolyte, and *if the geometry of the cell is satisfactory* these are the variables which should be studied in development of a procedure for electrolytic reduction.

A technique that has been reported recently (11) for preparation of aminophenols involves the use of amalgamated copper and Monel electrodes in 30% sulfuric acid in the presence of copper sulfate. The yields reported were 46% of 4-amino-*m*-cresol, 55% of 4-amino-*o*-cresol, and 30% of 3-chloro-4-aminophenol. The yields of the corresponding quinones obtained in our studies (3) were 80%, 80%, and 60%, while the 3-chloro-4-aminophenol was isolated in 70% yield. It is difficult to see the advantages of the rather complex systems used by Dey and co-workers (11), and it would appear that such reports tend to obscure the simplicity of the principles involved in selecting proper conditions for an electrolytic reduction.

EXPERIMENTAL

APPARATUS

Cathodes. a. This type of cathode was constructed of *nickel* in a manner similar to that described by Lukens (2). A sheet of pure nickel (25 gauge) was cut to $3\frac{3}{4}''$ by $6''$. A line was drawn $2\frac{1}{2}''$ from one of the short sides (the bottom) and parallel to it. This $2\frac{1}{2}''$ space was divided into ten $\frac{1}{4}''$-strips by lines drawn parallel to the bottom. Along both sides of the parallel-ruled section $\frac{1}{4}''$ strips were marked off; these two strips and the $\frac{1}{4}''$ strip at the bottom were left clear. The rest of the section was marked off into alternate $\frac{1}{4}''$ and $\frac{1}{2}''$ vertical strips, starting with a $\frac{1}{4}''$ strip nearest the side. Five vertical $\frac{1}{4}''$ strips resulted from this

procedure, each pair separated by a $\frac{1}{2}''$ strip. Every alternate $\frac{1}{4}''$ square in the bottom row was cut along the top and bottom and one side, forming a row of tabs. In the next higher row, tabs were cut similarly, but displaced laterally $\frac{1}{2}''$ from the tabs in the first row. This procedure was continued throughout the $2\frac{1}{2}''$ section, producing finally 9 rows of tabs, the free ends of which were all on the same side.

The sheet so prepared was shaped into a cylinder around a wooden dowel, and the tabs pushed in at a small angle from outside the cathode. The metal is sufficiently rigid that no positive union between the two ends of the sheet is required; a simple butt-joint is satisfactory. A binding post was fixed to the top of the cathode.

b. A *nickel* cylinder was constructed, of the same size and shape as type "*a*", but with the lower three inches cut vertically into $\frac{1}{4}''$ strips which were twisted at about 15° from the direction of rotation of the stirrer.

c. A *nickel* cylinder $1\frac{1}{4}''$ in diameter and $2\frac{1}{2}''$ long was pierced with about 400 holes of 1-mm. diameter. A $\frac{1}{2}''$ strip of nickel 6″ long, bent lengthwise into a "V" shape for rigidity, was riveted to it with short lengths of the same metal; this strip was used to support the cathode in position totally immersed in the electrolyte. It also carried at its top end the binding post.
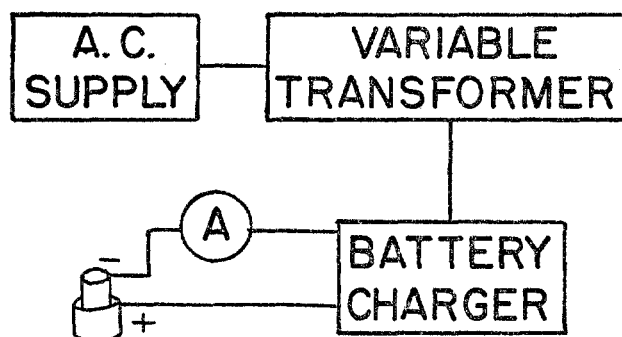

FIGURE 2. CIRCUIT USING A BATTERY CHARGER AS POWER SUPPLY

d. The type "*a*" cathode (*nickel*) was modified as follows: seven evenly spaced vertical slots $\frac{1}{4}''$ wide and $1\frac{1}{4}''$ long were cut in the cylinder above the tabbed area, leaving for rigidity a quarter-inch length of the cathode between the tabs and the slots. In proper operation, a smooth flood of catholyte flowed over the lower edges of these slots. This required adjustment of the catholyte volume so that its surface was about even with the bottom of the slots.

e. A *lead* cathode of the same construction as "*d*" was made from a sheet about 1 mm. thick. For rigidity, a 1″ cylinder of nickel carrying the binding post was soldered to the top of the cathode about 1″ above the level of the catholyte.

f. This was a cathode of type "*d*" constructed from 25 gauge sheet *copper* (99.98% Cu).

g. A cylinder of sheet *copper* (25 gauge) of the same dimensions as "*a*" was constructed, provided with only the vertical slots as described for type "*d*". The part of the cathode below the slots was not pierced at all.

h. This was a *platinum* cathode of a type commonly used in certain inorganic metal ion determinations, a cylinder one inch in diameter and two inches long pierced with several hundred 1-mm. holes. A 6″ platinum wire (heavy gauge) served as the electrical lead and also as a means of support.

Electrical circuits. 1. The circuit powered by the battery charger[3] was set up as shown

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[3] A "Battery Booster", Type 6-AC-4, manufactured by P. R. Mallory and Co., Inc., Indianapolis, Ind.

in Figure 2. Wire capable of carrying 6 amperes and a 0–3 ampere range ammeter were used. Investigation of the characteristics of the charger output with an oscilloscope showed a deep ripple in the current; at an ammeter reading of 0.6 amperes, the actual current varied with time from 0 to 1.7 amperes.

2. A battery circuit, containing a charging circuit, was set up as shown in Figure 3. To confine the ripple in the charger output to the charging circuit, it was necessary to construct that part of the wiring common to both the charging and reduction circuits from heavy copper rod (5 gauge), as indicated by the heavy lines in the figure.

In operation, the rheostat was adjusted to supply the desired current (A_2) to the cell, then the input to the charger was regulated so that no current flowed (A_1) across the battery. The knife switch across the ammeter was then closed. Investigation with an oscilloscope showed that there was negligible ripple in the current in the reduction circuit.
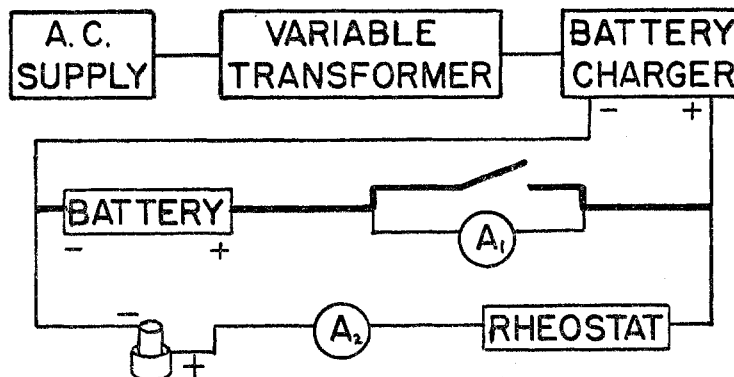

FIGURE 3. CIRCUIT SUPPLYING A CONSTANT POTENTIAL

Electrolytic cell assembly. The reductions were carried out in a divided cell made up in an ordinary 400-ml. beaker. The anode, a cylinder of $\frac{1}{8}''$ sheet lead 3″ in height and $2\frac{1}{4}''$ in diameter and provided with a binding post, rested on the bottom of the beaker. Clamped inside the anode and extending almost to the bottom of the beaker was the catholyte chamber, a porous cup[4] of reduced pososity 5″ deep and $1\frac{3}{4}''$ in diameter. Clamped securely inside the cup was the cylindrical sheet metal cathode. A mechanically-driven two-bladed propeller-type stirrer, both blades set deep in the catholyte, was mounted on ball bearings to run inside the cathode. The blades were pitched to drive the electrolyte down.

PROCEDURES

Reduction. 1. The stirrer was positioned carefully inside the cathode which was clamped in place by its top end. The porous cup, previously impregnated with the electrolyte, was charged with 11.4 g. (0.073 mole) of o-chloronitrobenzene and about 80 ml. of 75% (by wt.) sulfuric acid warmed to about 50°. The cup was then clamped securely in position with its bottom about $\frac{1}{4}''$ below the cathode. The beaker containing the anode was supported in position just clear of the bottom of the porous cup and filled with the same warm acid to the same level as the liquid inside the cup. A hot plate was adjusted under the cell to maintain a temperature of 50–60° in the cell during the reduction. The stirrer was started at high

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[4] A "Norton" dense grade alundum extraction thimble was used. In order to reduce the porosity of the alundum, the cups were soaked in 20% water glass for about an hour, then in 20% sulfuric acid for about three hours. Finally they were stored immersed in the electrolyte.

speed, the current turned on, and the system observed for a few minutes until the current had become stable at 0.6 amperes.

During the experiments of Series A, up to two equivalents of current were used. No advantage or disadvantage could be discovered in the use of this excess of current, and the rest of the runs in the aqueous acid were conducted with 1.3–1.5 equivalents.

After the desired amount of current had been passed through the cell, the system was disassembled. The contents of the porous cup were poured into a flask, and the stirrer, cathode, and cup were rinsed with hot water into the same flask. The volume was made up to 500 ml. with water and the diluted catholyte cooled in an ice-bath. The unreduced nitro compound was separated by filtration, and the filtrate containing the aminophenol reserved for oxidation (see below).

2. The reduction was carried out as in procedure "1". The raw catholyte, at the original volume plus a minimum rinse, was steam-distilled to recover unreduced nitro compound, made alkaline cautiously with 40% sodium hydroxide, and again steam-distilled to remove the *o*-chloroaniline. The residual alkaline solution of the aminophenol was brought to *p*H 7 with 6 *N* sulfuric acid and extracted with ether in a continuous-type liquid-liquid extractor. The ether solution was filtered through anhydrous sodium sulfate and the ether was distilled. The light amber granular aminophenol was dried in a vacuum desiccator over calcium chloride.

3. The reduction was carried out as detailed in procedure "1", except that the catholyte first used by Elbs (6) was used. It consisted of 70% (by volume) of glacial acetic acid, 22% concentrated sulfuric acid, and 8% water. The nitro compound was very soluble in this electrolyte so heating the cell was not necessary. Temperatures up to 42° were attained spontaneously during reductions carried out at currents up to 1.3 amperes, which current strength was used during most of the experiments. With higher current strengths and the resultant higher temperatures, loss of acetic acid became troublesome.

Slow evaporation of the electrolyte during a reduction necessitated the occasional addition of a few ml. of 90% acetic acid to maintain the catholyte surface at the desired level, *i.e.* near the lower edges of the slots in the cathodes. In these experiments, 1.2 equivalents of current were used; no nitro compound has been isolated from reductions carried out under these conditions in the acetic acid catholyte.

After the reduction was complete the catholyte was poured into a flask, the apparatus was rinsed with hot water into the same flask, and the concentration of acid was adjusted to about 4 *N* in preparation for the oxidation.

4. The reduction was carried out as detailed in "3" above. The raw catholyte was extracted with ether in the continuous extractor in order to remove most of the acetic acid. The extraction was continued arbitrarily for about a half-hour after there was no longer any visible decrease in volume of the aqueous phase. Examination of the ether extract showed that it contained only negligible amounts of the aminophenol. The aqueous acid solution of chloroaminophenol was made up to 4 *N* in sulfuric acid in preparation for the oxidation.

Oxidation. I. Before the oxidation of the 3-chloro-4-aminophenol had been investigated to determine the optimum conditions, all the oxidations were carried out by cooling the aminophenol solutions to 0° and adding dropwise, at 0–5°, a solution of 11.4 g. (1.5 equivalents) of sodium dichromate dihydrate in 20 ml. of water. The reaction mixtures were then stored overnight in the refrigerator. This procedure was found to give only 65% conversion of aminophenol to quinone.

II. The oxidant was added in one portion to the aminophenol solution at 25° and the reaction mixture allowed to stand at room temperature for two hours. The oxidation was exothermic and the temperature was moderated only if it tended to rise above 35°. At higher temperatures, the quinone was of poorer quality. Conversion of aminophenol to quinone was about 80%.

Quinone isolation. A. Supercel (3 g.) was added to the oxidation mixture which was then filtered with suction. The aqueous quinone solution was extracted with ether in 30–40-ml.

portions until the ether remained nearly colorless. Each extract in turn was used to extract the filter cake, with the addition of a few grams of clean sand as an "extender" if the material was of a tarry consistency. The deep red extracts were combined, the ether was removed by distillation, and the dark tarry residue was steam-distilled. About 50 ml. of distillate was collected after solid quinone no longer appeared in the condenser.

The suspension of chloroquinone in water was extracted with several portions of ether, the ether solution was dried by filtration through anhydrous sodium sulfate, and the ether was distilled carefully. After it had been air-dried for ½ hour, the crude quinone was weighed. Several samples of the crude material so obtained were stored in a vacuum desiccator over calcium chloride; they showed negligible loss in weight.

B. Ether extraction of the oxidation mixture was carried out in the continuous extractor. The ether solution then contained most of the acetic acid as well as the quinone. Successive water and sodium bicarbonate solution washes were used to remove the acetic acid. A Kies "cascade extraction apparatus" (12) was found convenient; in it, the ether solution was allowed to percolate *via* sintered glass thimbles through two water washes, two half-saturated bicarbonate washes, and a final water wash. Each of the wash solutions was of about 120 ml. in volume. A countercurrent effect was provided by following the quinone solution through the extractor with about 200 ml. of ether. The ether solution of the quinone was then worked up as described in isolation procedure "A".

C. The oxidation mixture was extracted with *n*-pentane in the continuous extractor. The pentane was distilled from the dark red solution and the tarry residual quinone was steam-distilled as in procedure "A".

SUMMARY

1. It has been shown that a satisfactory yield of chloroquinone may be obtained by oxidation of the aminophenol prepared by electrolytic reduction of *o*-chloronitrobenzene. The recommended electrolyte consists of 75% by volume sulfuric acid diluted with 2.5 volumes of acetic acid. There is described a useful design of copper cathode.

2. Investigation of several variables in the electrolytic reduction is described.

3. No adverse effect has been observed when the reduction was accomplished at current densities up to 3 amperes per sq. dec.

4. Conditions could not be found under which reproducible results could be achieved with a nickel cathode. This appears due to alteration of the surface of the nickel by attack of the acidic catholyte.

5. Lead is not a satisfactory cathode for reduction of a *nitro* compound to the aminophenol, for further reduction of the intermediate hydroxylamine appears to occur at about the same cathode potential as does the first stage of the reduction.

6. A critical discussion of some of the principles of electrolytic reduction has been presented, in which it has been mentioned that in a multi-stage reduction the separation between the potentials required for the several stages is of importance rather than the potentials themselves, the current density, or the cathode overvoltage.

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