Electrolytic Process for the Preparation of Dianisidine Using Rotating Cathode Cell for the Reduction of o-Nitroanisole to Hydrazoanisole

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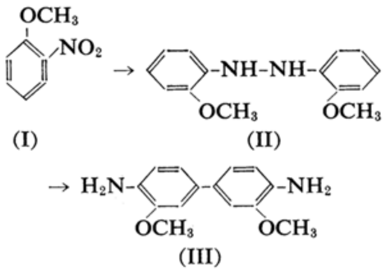
Dianisidine is largely employed as a dye intermediate in the production of direct cotton colors and the same to the extent of 573 Cwts. was imported into this country in 1959. An electrochemical method for the process would therefore be of interest to meet the immediate requirements of the country. Hydrazoanisole (II) is generally prepared[1] by the reduction of *o*-nitroanisole (I) with zinc and sodium hydroxide in alcoholic or benzene solution. The hydrazoanisole thus obtained is rearranged to dianisidine (III) by reaction with acids.



Chemical Methods of Reduction.—Pellegrini[2] studied the reduction of *o*-nitroanisole by means of sodium amalgam and found that hydrazoanisole is formed when solvents like alcohol and pyridine are used without which the nitro group is reduced to the amine. In this reduction he concluded that the initial concentration of sodium hydroxide is of great importance, the formation of primary amines as a by-product being greater, the smaller the amount of alkali present initially. Gandry and Keirstead[3] have used dextrose and sodium arsenite as a reducing agent for the reduction. Reduced nickel prepared from nickel nitrate mixed with a compound containing sulfur or chlorine as a reducing agent for the reduction has been suggested by Rikagaku[4]. Recently Iida and Konishi[5] have studied the reduction by using a ferrosilicon alloy and found that the best condition for the reduction are obtained by using 10 g. of *o*-nitroanisole with 6∼9 g. of ferrosilicon (Si content 15%) in 15∼30 g. of 13∼18% sodium hydroxide solution containing 7.9 g. of calcium hydroxide at 100°C for 2∼6 hr.

Electrolytic Methods of Reduction.—The first electrolytic reduction of *o*-nitroanisole has been reported by Haussermann[6] by reducing *o*-nitroanisole in alcoholic solution. Elbs[7] and Brand[8] have also reported the electrolytic reduction of *o*-nitroanisole. McKee and Gerapostolou[9] have extensively studied the reduction of *o*-nitroanisole in concentrated solution mixtures of sodium and potassium xylene sulfonates at different pH and reported that hydrazo compounds are formed only under alkaline pH. Dey and co-workers[10] have also studied the electrolytic reduction of an alkaline emulsion of *o*-nitroanisole, employing stationary cathode and low current densities of the order of 2 amp./dm^2 to obtain an yield of 67.7% of hydrazoanisole.

The use of rotating cathode technique in the reduction of nitro compounds in acid medium was reported from this laboratory earlier[13,14]. The reduction of nitrobenzene and *o*-chloronitrobenzene in alkaline emulsion using the same technique was reported in subsequent studies by the authors[11,12] and the application of this technique in the reduction of other substituted nitro compounds has led us to the present investigation.

Experimental

Electrolytic Cell.—The cell (Fig. 1) consisted of a 600 cc. Pyrex beaker (A) without spout, and

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[1] V. O. Lukashevich, *J. Gen. Chem.* (*U. S. S. R.*), **5**, 103 (1935); *Chem. Abstr.*, **29**, 4745 (1935).

[2] G. Pellegrini, *Giorn. chim. ind. applicata*, **8**, 175 (1926); *Chem. Abstr.*, **21**, 376 (1927).

[3] R. Gandry and K. F. Keirstead: *Can. J. Research*, **27B**, 890 (1949); *Chem. Abstr.*, **44**, 3927 (1950).

[4] K. Yoshikawa and B. Kubota, Japanese Pat. 101254 (1933).

[5] H. Iida, T. Shibano and K. Konishi, *J. Chem. Soc. Japan, Ind. Chem. Soc.* (*Kogyo Kagaku Zassi*), **57**, 830 (1954); *Chem. Abstr.*, **49**, 10873 (1955).

[6] C. Haussermann, *Chem. Ztg.*, **17**, 209 (1893).

[7] K. Elbs, *Z. Elektrochem.*, **5**, 108 (1898); **7**, 145 (1900).

[8] K. Brand, *J. prakt. Chem.*, [2] **67**, 156 (1903).

[9] R. H. McKee and B. G. Gerapostolou, *Trans. Electrochem. Soc.*, **68**, 329 (1935).

[10] B. B. Dey, T. R. Govindachari and S. C. Rajagopalan, *J. Sci. Ind. Research* (*India*), **4**, 642 (1946).

[11] K. S. Udupa, G. S. Subramanian and H. V. K. Udupa, *J. Electrochem. Soc.*, **108**, 373 (1961).

[12] K. S. Udupa, G. S. Subramanian and H. V. K. Udupa, *Bull. acad. polon. sci.*, IX, 419 (1961).

[13] G. S. Krishnamurthi, H. V. K. Udupa and B. B. Dey, *J. Sci. Ind. Research* (*India*), **15B**, 47 (1956).

[14] G. S. Subramanian, H. V. K. Udupa and B. B. Dey, Proc. of the Symp. "Electrolytic-cells" CECRI, Karaikudi-3, S. Rly (1962), p. 188.

was fitted with a cement asbestos sheet cover having the necessary openings for the introduction of cathode (B), diaphragm (D), condenser (F) and thermometer (T). The cathode (B) was of a mild steel disk type each disk being 2.5 cm. diameter and with a spacing of 1.25 cm. There are 5 such disks and the cathode is rotated at about 1800 r. p. m. by means of a fractional H. P. motor. The catholyte was 200 cc. of 10% soduim hydroxide (Commercial grade) containing 2 g. of commercial grade litharge (yellow) PbO. The anolyte was 25% sodium hydroxide. *o*-Nitroanisole (L. R. grade B. D. H.) was used in the ratio of 1 : 4 (1 g. of nitro compound per 4 cc. of the catholyte). The diaphragm was of asbestos cloth wound on a nickel plated mild steel cage – 2.5 cm. diameter ×12.5 cm. height – and the anode was a strip of stainless steel plate (C) – 1.25 cm. breadth ×15 cm. height ×0.16 mm. thick. A cathode current density of 30 amp./dm^2 was employed.

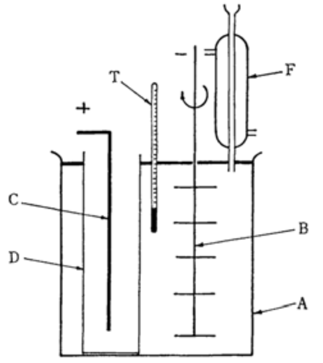

Fig. 1. Cell diagram using a rotating disk-type cathode.
A, Cell container; B, Rotating cathode; C, Anode; D, Diaphragm; T, Thermometer; F, Condenser

Procedure.—After the lead had been deposited on the rotating cathode by pre-electrolysis, with a current of 8 amp., 50 g. of *o*-nitroanisole was added to the hot electrolyte (85°C) and theoretical current for reduction to hydrazoanisole passed from a selenium rectifier. After 90% of the current was passed, xylene (50 ml.) was added into catholyte to keep the solid hydrazoanisole in solution and to favor further reduction of azoanisole and any nitroanisole trapped in the solid.

Conversion to Dianisidine and Isolation of the Product.—The xylene layer from the electrolyte was separated and poured into a mixture of ice and 19 cc. of sulfuric acid (specific gravity 1.84) and stirred for 5 hr. in the cold condition after which the temperature was raised to 90°C. The dianisidine free base was liberated by basifying the crude sulfate and the ansidine is separated by steam distillation and dianisidine was then filtered after cooling and estimated as free base. The xylene layer was steam-distilled and the *o*-azoanisole remaining in the still was cooled, filtered, dried and weighed.

Results

The results of the investigation are given in Table I. It may be seen that *o*-azoanisole is a fairly poor depolarizer, because by passing nearly 10% excess current, the dianisidine yield could be increased only by about 2%.

Cathode Potential Studies.—The measurement of cathode potentials was carried out with a view to study the nature of the reduction process. For this purpose, a cylindrical iron cathode was used and the potential measured

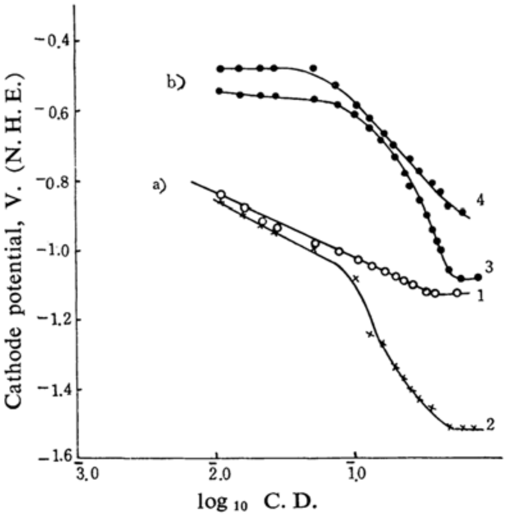

Fig. 2. Plot of cathode potential vs. log C. D. (amp./dm^2).
a) Without addition of *o*-nitroanisole
1, Stationary cathode
2, Rotating cathode
b) With addition of *o*-nitroanisole
3, Stationary cathode
4, Rotating cathode

TABLE I. RESULTS OF ELECTROLYTIC REDUCTION OF *o*-NITROANISOLE

Conditions: Catholyte, 200 cc. of 10% NaOH; Anolyte, 50 cc. of 25% NaOH; PbO, 2 g; Temperature, 85±2°C; Weight of *o*-nitroanisole taken, 50 g.; Cell voltage, 3.5 to 4.5 V.

Expt. No.	Current passed (amp.·hr.)	Current density (amp./dm^2)	Per cent yield		
			Dianisidine	*o*-Azoanisole	Anisidine
1	44	30	70.2	19.7	7.8
2	44	30	74.5	20.5	5.8
3	48.4 (10% excess)	30	76.5	17.1	4.9

Energy consumption: 9.0 kwh./kg.

against Hg/HgO/N NaOH reference electrode and a calibrated Heathkit vacuum tube voltmeter.

The influence of current density on the cathode potential was studied for the cathode that was plated rotating as well as that plated stationary. Graphs 1 and 2 in Fig. 2 show the polarization under stationary and rotating conditions of the respective cathodes plated under stationary and rotating conditions. It is necessary to indicate here that the lead deposit is spongy and not adherent when deposited on a stationary cathode and hence cannot be rotated after deposition without dropping out the deposit. Hence only the cathode on which lead was deposited while rotating can alone be used in the reduction of nitroanisole with rotation. These results clearly indicate the advantages of rotation of the cathode while depositing lead. The deposit though somewhat spongy, is quite adherent, and does not peel off during the reduction of nitroanisole so that the cathode can be used several times without having to redeposit lead. The rotating cathode is polarized to a greater extent because the deposit is less spongy. The cathode potential was also measured at different current densities after adding *o*-nitroanisole. Graphs 3 and 4 in Fig. 2 show considerable lowering of the cathode polarization on addition of *o*-nitroanisole.

A study of the cathode polarization curves shows that *o*-nitroanisole is a good depolarizer. A maximum displacement of 0.39 V. in the case of stationary cathode and of 0.64 V. in the case of rotating cathode in the positive direction was observed. This displacement is observed at a particular depolarizer ratio of 1 : 4 and at a temperature of 80~85°C. The maximum displacement in the cathode polarization occured at a current density of 7.8 amp./dm^2 in the case of stationary and at 23.4 amp./dm^2 for the rotating cathodes respectively. Figure 3 shows the change of cathodic polarization during the actual course of reduction of *o*-nitroanisole in alkaline emulsion at a rotating cathode with a deposit of lead at a current density of 25 amp./dm^2. The curve indicates the combined effects of the depolarizing action of different compounds which are likely to be formed at various periods during the course of reduction of the nitro compound. The first steep fall (A to B) is probably due to the depolarization of *o*-nitroanisole and the portion (B to C) represents the reduction to the nitroso stage and the fairly steady state (C to D) is probably due to the combined action of reduction of the nitro and nitroso to the azoxy stage. The steep fall (D to E) points to the reduction to the azo and/or hydrazo stage and thereafter the steady portion E to F probably represents the reduction of azo to hydrazo only and the potential slowly approaches the hydrogen evolution potential.

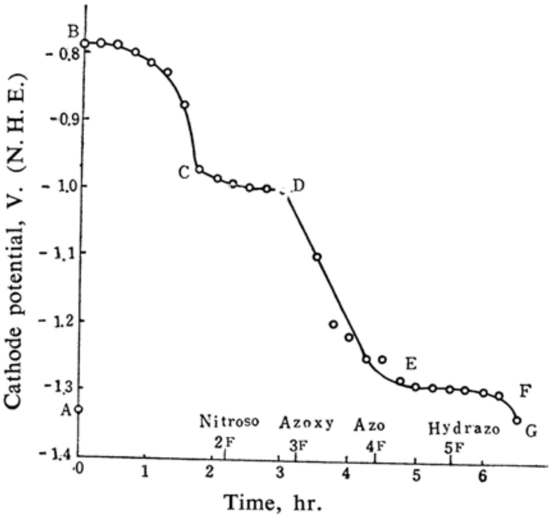

Fig. 3. Plot of cathode potential vs. duration on electrolysis using rotating cathode.

Summary

The technique of using rotating cathodes for electrolytic reduction of nitro compounds developed in this Institute earlier has now been extended to the study of the reduction of *o*-nitroanisole in an alkaline emulsion to obtain hydrazoanisole, which is subsequently converted to dianisidine by reaction with acid. The various chemical methods of obtaining hydrazoanisole as well as the previous attempts for obtaining the same by electrolytic reduction of *o*-nitroanisole are briefly reviewed.

The experimental technique adopted, the isolation of the product and the subsequent conversion of the hydrazoanisole to dianisidine are described.

Cathode potential has been measured at different current densities using lead deposited iron cathode under stationary and rotating condition of the cathode without the addition of nitro compound. The effect of the nitro compound addition on the cathode potential at different current densities has also been studied. The potential of a rotating cathode measured during the course of an experiment is graphically presented and the results discussed.

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