

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

The Nature of Electrode Reactions. I. Factors Affecting the Electrochemical Reduction of N-Nitrosomethylaniline¹

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Alpha methylphenylhydrazine was first prepared electrochemically by Backer² through the reduction of phenylmethylnitramine and later³ from the corresponding methylphenylnitrosamine. Tinned copper cathodes were used in both instances but no detailed study of the reaction was made.

The present work consists of the investigation of the influence of the following factors on the electrochemical reduction of N-nitrosomethylaniline at copper, lead, cadmium, mercury and cadmium amalgam electrodes: (1) temperature, (2) current density, (3) acid concentration of the catholyte, (4) the extent to which the cathodes dissolve during the course of the reduction and the amount of chemical reduction produced thereby, (5) the magnitude of the potential drop at various current strengths resulting from the presence of the depolarizer.

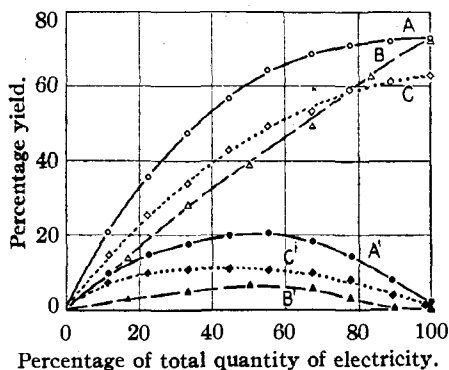


Fig. 1.—A and A', 2 amp. per $2/3$ dm.² at cadmium cathode; B and B', 3 amp. per $2/3$ dm.² at cadmium cathode; C and C', 2 amp. per $2/3$ dm.² at cadmium amalgam cathode.

The cell used was similar to that previously described.⁴ The nitrosomethylaniline was specially prepared to ensure a high degree of purity by the method of Reverdin and de la Harpe.⁵ A weighed sample of the nitrosamine was placed in the cathode compartment of the cell with 200 ml.

(1) Presented in part before the Organic Division of the American Chemical Society at the Chicago meeting, September, 1933.

(2) Backer, *Rec. trav. chim.*, **51**, 142 (1912).

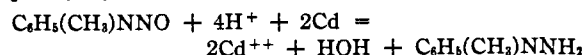
(3) Backer, *ibid.*, **32**, 39 (1913).

(4) Cook and France, *J. Phys. Chem.*, **36**, 2383 (1932).

(5) Reverdin and de la Harpe, *Ber.*, **22**, 1906 (1889).

of electrolyte of known acid concentration, a further portion of the same acid solution was added to the anode compartment and the cell placed in a thermostat. The electrolyte was rapidly stirred and a constant current was maintained until the theoretical quantity of electricity required for the reduction had passed. Throughout the course of the reduction small samples of the catholyte were removed at ten minute intervals and analyzed for cathode metal ions and hydrazine content. The hydrazine was determined by a modified method of Strache,⁶ and the metal ion content by electrotitration. The collected data are contained in the accompanying table and curves.

In Fig. 1 curves A, B and C, indicate the yield of hydrazine at various time intervals corresponding to the passage of definite percentages of the total quantity of electricity theoretically required for the reduction. A', B' and C' are plots of the concentrations of the metal ions present in the catholyte at these same intervals in terms of the chemical equivalents of methylphenylhydrazine based on the equation



These data show that during the course of the reduction the cadmium at first dissolves but later redeposits on the cathode and at the higher current densities the dissolution of the electrode is diminished and the final yield of the hydrazine is increased. The curves in Fig. 2 in which the percentage yield is plotted against the current density show that the maximum yield for each electrode occurs at some definite current density. At current densities above or below this value the yields are smaller. The decreasing order for the optimum current densities of the electrodes is lead, cadmium, cadmium amalgam, mercury and copper. The same order was observed for the decreasing values of the maximum yields at the various electrodes.

From the curves in Fig. 3 in which the yields are plotted against the temperature it is clearly evident that a decrease in the temperature of the

(6) Strache, *Monatsh.*, **12**, 526 (1891); **13**, 229 (1892).

reduction results in an increase in the yields at all electrodes. The temperature is of further importance in that it affects the velocity of the undesirable side reactions. The first and most important of these is the rearrangement of the N-nitrosomethylaniline into *p*-nitrosomethylaniline, from which the desired hydrazine cannot be obtained. At the higher temperatures at which this reaction is most rapid the yields for all electrodes were very low. The nitrosomethylaniline solidifies at a temperature of from 7–8° in 1.0 *N* hydrochloric acid, and therefore below this temperature all reductions drop to a negligible value. The maximum yields were obtained at temperatures just above the freezing point of the depolarizer.

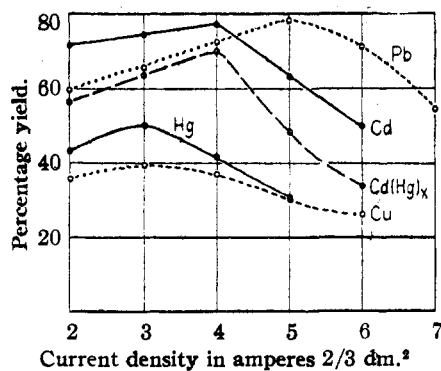


Fig. 2.

The data presented in Fig. 1 indicate conclusively that the electrochemical reduction is accompanied by a certain amount of purely chemical reduction when cadmium and cadmium amalgam electrodes are used. In order to study further the extent of the chemical reduction the following experiments were carried out over a selected range of temperatures and acid concentrations. The cells were set up exactly as before using the same quantity of depolarizer but without any current flowing. After a period of ninety minutes; the time required for the electrochemical reduction, the catholyte solution was analyzed for hydrazine content. These results are recorded in Table I.

These data together with those of Fig. 1 show that the dissolution of the electrode is a direct function of the temperature and acid concentration and an inverse function of the current density. It is interesting to note that whereas cadmium and the cadmium from the amalgam dissolved appreciably the other electrodes of copper, lead and mercury did not. However traces of these latter

TABLE I
REDUCTION BY PURELY CHEMICAL MEANS WITH THE SAME ELECTRODES USED IN THE ELECTROCHEMICAL REDUCTIONS

Acid HCl normality	Electrode metal	Temp., °C.	Yield, %
1.0	Cd	20	66.0
0.75	Cd	20	53.3
.50	Cd	20	35.6
.10	Cd	20	8.4
1.00	Cu	20	0.0
1.00	Pb	20	.0
1.00	Hg	20	.0
0.90	Cd	23	66.7
0.90	Cd(Hg) _z	22	16.2
1.00	Cd	15	57.5
1.00	Cd	10	31.2
1.00	Cd	5	0.0

metals were usually found in the catholyte solutions. In the case of the cadmium amalgam the magnitude of the chemical reduction of the nitrosamine was diminished to a very small value. This decrease corresponded to the lowered concentration of cadmium in the amalgam relative to that of the pure metal.

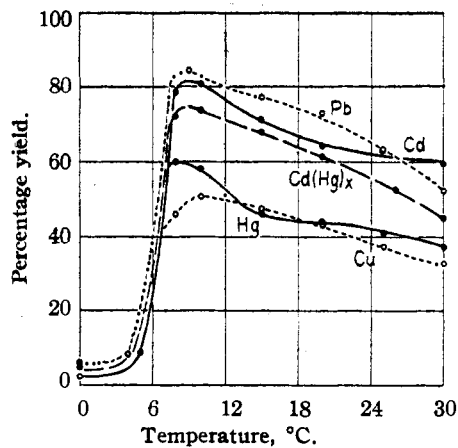


Fig. 3.

The copper cathodes appeared to be oxidized, presumably by the NO group of the nitrosamine. This fact together with the presence of the metal ions in the catholyte is strongly suggestive of the existence of a tendency on the part of the metal of the electrode to combine with the nitrosamine adsorbed on the surface of the electrode.

Liebreich considered the tendency of the metals⁷ to dissolve or corrode as being a function of their overvoltage values. He regarded the hydrogen as acting in two ways, one to reduce the metal oxide or form hydrides and two to be evolved as

(7) Liebreich, *Korrosion Metallschweis*, 3, 78-82 (1927).

gaseous hydrogen. The same conclusion was reached by Theil and Echell.⁸

The magnitude of the potential drop of the cathodes at various current strengths due to the presence of the depolarizer was determined and found to be appreciable in all cases, the decreasing order of magnitude being cadmium amalgam, lead, cadmium and copper. These results are expressed graphically in Fig. 4 in which the

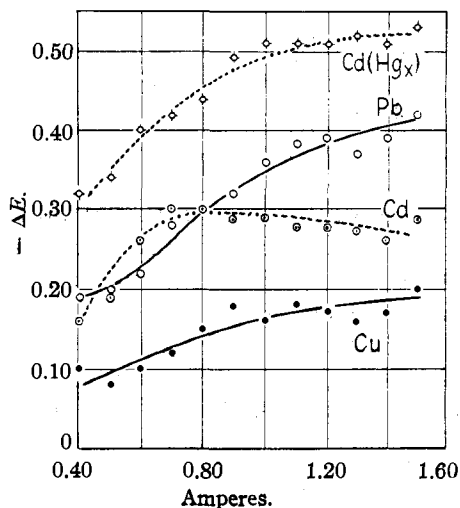


Fig. 4.

potential drop ($-\Delta E$ volts) due to the presence of the depolarizer is plotted against the corresponding current strengths (amperes) at which the electrode potentials were measured. When considered in relation to the dissolution of the cadmium amalgam electrodes, these results suggest

(8) Theil and Echell, *Korrosion Metallschutz*, **4**, 121-133 (1928).

the possibility that the loss in the overvoltage value of the electrode due to the depolarizer may be the direct cause of the dissolution. This view is given added support by the fact that at the higher current densities and hence higher overvoltage values, the concentrations of the metal ions in the catholyte solutions were lower.

Summary

The results of this investigation may be summarized as follows.

1. The electrochemical reduction of N-nitrosomethylaniline proceeds most readily at a temperature slightly above the freezing point of the depolarizer.

2. For Cd, Cd(Hg)_x, Pb, Cu and Hg the optimum current density is a specific characteristic of the electrode material.

3. In the main electrochemical reactions the acid concentration is not a major factor; however, the kind and concentration of acid and also the temperature may determine the course and extent of undesirable side reactions.

4. Purely chemical reductions and associated side reactions may occur along with the electrochemical reductions at the active electrodes employed in this investigation.

5. The dissolution of the electrodes may be the result of the drop in the cathodic overvoltage due to the presence of the depolarizer.

6. The electrochemical reduction of N-nitrosomethylaniline provides a highly satisfactory way of preparing α -methylphenylhydrazine, giving yields as high as 85%.