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ON THE ELECTROLYTIC REDUCTION OF OXIMES AND SEMICARBAZONES IN ALKALINE SOLUTION

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Some years ago it was suggested (1) that the electrolytic reduction in acid solution of azomethine compounds of the type RR'C=N—Y—R" depended on the nature of Y. When Y was equal to C or H, a two-electron reduction to an amine could be expected, whereas a four-electron reaction would be expected to occur, when Y was equal to O or N. In the latter case the following general reduction path was suggested (1).

$$\mathrm{RR'C{=}N{-}Y{-}R''} + \mathrm{H^+} \rightleftarrows [\mathrm{RR'C{=}N{-}Y{-}R''}]\mathrm{H^+} \qquad (A)$$

$$[\mathrm{RR'C{=}N{-}Y{-}R''}]\mathrm{H^+} + 2e + 2\mathrm{H^+} \rightarrow \mathrm{RR'C{=}\overset{+}{N}H_2} + \mathrm{H{-}Y{-}R''} \qquad (B)$$

$$\mathrm{RR'C{=}\overset{+}{N}H_2} + 2e + 2\mathrm{H^+} \rightarrow \mathrm{RR'CH\overset{+}{N}H_3} \qquad (C)$$

Most evidence accumulated later have supported the proposed reaction sequence (2,3,4,5); a notable exception has, however, been found in the electrolytic reduction of 1(2H)-phthalazinones to 3,4-dihydro-1(2H)-phthalazinones (6). The applicability of the reduction schème to the reduction of semicarbazones (7) and azines (8) has been questioned.

In slightly acid to slightly alkaline solution a simultaneous four- and two-electron reduction have been found to take place (1,4); thus benzophenone semicarbazone yields in acetate buffer some benzhydrylsemicarbazide together with benzhydrylamine (1) and similar results were obtained in the reduction of Girard hydrazones (4). At pH 11 the two-electron reduction of the Girard hydrazone to the hydrazine was the main reaction (4). A similar electrolytic reduction of oximes to hydroxylamines would be of synthetic interest, but no such reduction has been reported.

The reduction of benzaldehyde oxime was investigated at different pH-values. In Table 1 is presented the yield of benzylhydroxylamine, determined by anodic polarography and corrected for a small (0-12 %) concentration of unreduced oxime, obtained by controlled potential reductions of syn-benzaldoxime under various conditions. The electrolysis was performed in a 0.5 m buffer solution and pH was kept within a small range by suitable addition of hydrochloric acid.

TABLE 1

Buffer	Borate	Borate	Phosphate	Phosphate	Phosphate
pH-interval	9.2-9.5	10.1-10.3	12.25-12.45	12.25-12.45	12.6-12.8
E(SCE)	-1.75	-1.75	-1.80	-1.80	-1.80
Temperature	25°	25°	25°	5°	25°
% benzylhydroxylamine	6	8	27	42	28

The mechanism of the benzylhydroxylamine formation is not clear. K_A of syn-benzaldoxime is $2.1 \cdot 10^{-11}$ (11) and very special conditions should prevail at the electrode surface if the formation of a mixture of benzylamine and benzylhydroxylamine should be explained by a competition between the reduction of the protonated and the neutral oxime. Another possibility could be that the oxime anion which would be the dominant species in the bulk of the solution at high pH could pick up a proton at the electrode surface and this neutral species was reduced immediately. The oxime anion can pick up a proton in three different ways with the formation of the following tautomeric species:

$$C_6H_5CH{=}NOH,\ C_6H_5CH{=}\overset{+}{N}H{-}O^-,\ \text{and}\ C_6H_5CH_2{-}NO,$$

and these might be reduced differently. The nitroso derivative would, if formed, probably yield the hydroxylamine, but the lack of exchange (12) of hydrogen bound to carbon with tritium in alkaline solution of benzaldoxime makes the formation of the nitroso compound a less likely explanation.

A further possibility is that a branching in the reduction exists as a competition between a protonation and an electron transfer, and that the protonation is slower at high pH and low temperature. The first step is an electron uptake, but the next one could either be a proton or an electron uptake, thus a competition between e,H^+, e,H^+, and e,e,H^+, H^+; alternatively the branching could occur after the uptake of an electron and a proton, and the reaction mixture could be the result of a competition between the reaction sequences e,H^+, H^+, e and e,H^+, e,H^+. The latter alternative seems most likely, but further investigations are needed to throw light on the problem.

The electrolytic reduction of benzaldehyde semicarbazone was reinvestigated. In glycine buffer (pH 2, E = -1.0 V (SCE)) benzylamine was formed in a four-electron reduction. In alkaline solution benzaldehyde semicarbazone shows a polarographic wave [pH 9, $E_{\frac{1}{2}}$ = -1.85 V (SCE); pH 13, $E_{\frac{1}{2}}$ = -1.87 (SCE)] with a wave height half of that in acid solution and corresponding to a two-electron reduction. Controlled potential reduction of benzaldehyde semicarbazone [0.2 m KOH, 50 % aqueous alcohol, E = -1.88 V (SCE)] produced 1-benzylsemicarbazide (m.p. 155°) in an isolated yield of 87 %.

1-Benzylsemicarbazide was investigated polarographically; it gave no cathodic wave in the investigated pH-interval (pH 0-14), but an anodic wave in alkaline solution [pH 13, $E_{\frac{1}{2}}$ = -0.27 V (SCE)]. Controlled potential oxidation [50 % alcohol, pH 13, E = -0.20 v (SCE)] yielded benzaldehyde semicarbazone.

A reinvestigation of the reduction of benzalazine in an acetate buffer pH 4,5 confirmed the previous results (1) in that the over-all six-electron reduction in acid solution was either a two-electron reduction to benzaldehyde benzylhydrazone followed by a four-electron reduction to benzylamine or a two-electron hydrogenation of the nitrogen-nitrogen bond followed by reduction of the benzaldimine. No N,N'-dibenzylhydrazine could be detected by anodic polarography; the suggestion (8) that this is formed at pH 4 can thus not be substantiated.

The results obtained confirm that the protonated substituted hydrazones and oximes do not have the hydrazines or hydroxylamines as intermediates, but rather follow the reduction route (1) → (2) → (3). In alkaline solution, however, a reduction to a hydrazine or hydroxylamine may be found.

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