

Studies on the Electrosynthesis of Organic Compounds

II. Reducibility of some Schiff's bases on lead and copper cathodes

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The electrochemical reducibility of some Schiff's bases was studied on copper and lead cathodes. The effects of different substituents and the nature of the cathode material on the reduction efficiency of these compounds were investigated. The products of reduction were found to catalyse the reduction process itself leading to an increase of reducibility (reduction efficiency) with time.

1. Introduction

The electrolytic reduction and hydrogenation of double bonds has been the subject of numerous investigations for quite a long time.¹ The C=N is known to be reduced by alkali-metal amalgams.² Recently, a few works have appeared discussing the electrolytic reduction of some Schiff's bases to the corresponding secondary amines,³ yet the mechanism and kinetics of such reduction processes were not sufficiently investigated.

In the present work, we have studied the reducibility of arylidineanthranilic acid, arylidine-*p*-aminobenzoic acid and cyclohexylidineanthranilic acid on lead and copper cathodes in aqueous ethanol containing sulphuric acid. The object of this investigation is to clarify the role of the different substituents in the arylidine moiety on the reduction efficiency using two different types of cathodes, namely lead possessing high hydrogen overvoltage and copper with its low hydrogen overvoltage.

2. Experimental technique

The electrolytic cell used for reduction of the compounds concerned consisted of two separate compartments, separated by a porous diaphragm of sintered glass. The anode consisted of a platinum sheet of suitable surface area. The copper and lead cathodes were made of sheets of 2.5 cm² surface area.

The electrolyte used was aqueous ethanol (50:50) containing 10 ml conc. sulphuric acid/litre. Each cathode was pretreated chemically before every experiment and then kept in the solution studied for about 15 min without the polarising current.

The hydrogen gas evolved over the copper or lead cathode was collected and compared to that evolved in a hydrogen coulometer, containing the ethanol-water solvent and H₂SO₄, in series with the electrolytic cell. The difference between both is considered to be the quantity of electricity consumed in the reduction processes of the C=N compounds. The temperature during electrolysis was kept constant at 25°C.

3. Results and discussion

In the present work, the current efficiency of reduction (η) was taken as a measure for the ease of reduction of the C=N bond:

$$\eta = \frac{V_H - V_H'}{V_H} 100$$

where V_H is the corrected volume of hydrogen evolved in the hydrogen coulometer connected in series with the electrolytic cell and V_H' is the corrected volume of hydrogen evolved over the copper or lead cathode.

The results of efficiency measurements are plotted in Figures 1, 2, 3 and 4. From these figures it is obvious that the behaviour of efficiency on increasing the current is nearly the same for all the compounds studied. Upon increasing the applied current, the reduction efficiency decreases and at higher current values it tends to have a more or less constant value.

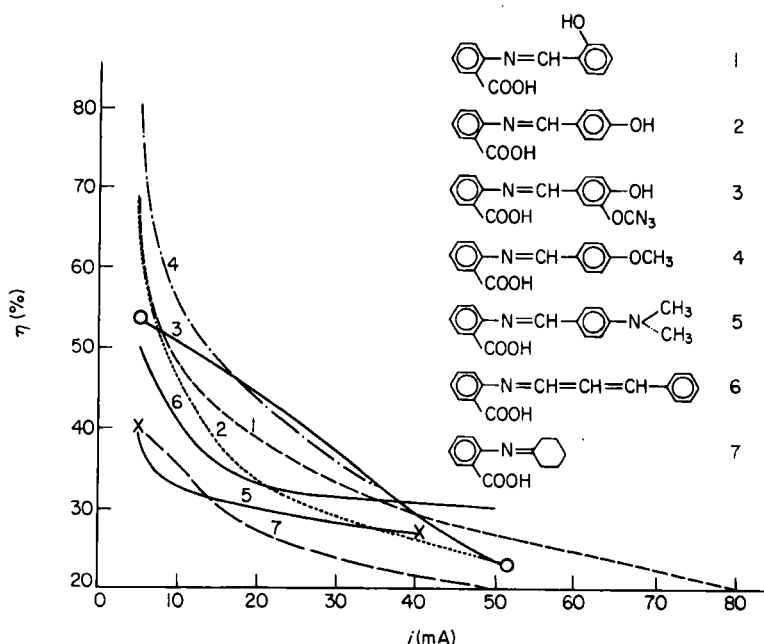


Figure 1. Efficiency of reduction on lead catalyst. Concentration = 10^{-2} M. ---, 1; ·····, 2; ○—○, 3; —·—·, 4; ×—×, 5; —, 6; — — —, 7.

It is noticed that, generally, the reducibility (reduction efficiency) of the $C=N$ double bond is higher on a lead than on a copper cathode at the same current. This phenomenon is explained on the basis of different hydrogen overvoltages on the two metals. In acid media, Tafel's constants of hydrogen evolution on lead and copper are as follows:

$$\phi = a + b \ln i$$

(a for lead and copper is 1.56 V and 0.80 V, respectively; b for lead and copper is 0.11 V and 0.15 V, respectively). As hydrogen evolution on lead is more difficult than on copper, this must lead to higher reduction efficiencies on lead than on copper.

The reduction efficiency of the $C=N$ compounds, containing different substituents, on copper and lead differs widely depending on the nature of the substituent and its position. It is known that different substituents on the organic molecule polarise the reducible functional group in a different manner. Thus, adsorbability and correspondingly, the reducibility, is affected by the different substituents. Of particular interest is the reducibility of *p*-dimethylaminobenzylideneanthranilic acid, 5 (cf Figures 1 and 2) and *p*-dimethylaminobenzylidene-*p*-aminobenzoic acid, 4 (cf Figures 3 and 4). The reducibility of these two compounds contrasts the general trend observed in the reduction of the other compounds in that it is lower on lead than on copper. This may be attributed to quaternisation of the amino group in the acidic medium to form ammonium ion. This reduces the polarity of

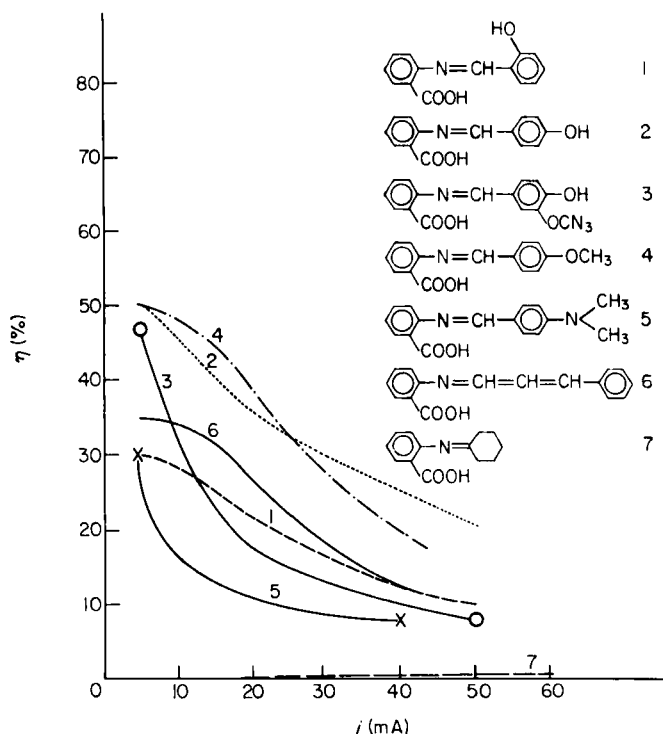


Figure 2. Efficiency of reduction on copper catalyst. Concentration = 10^{-2} M. ---, 1; ·····, 2; ○—○, 3; —·—·, 4; ×—×, 5; —, 6; — — —, 7.

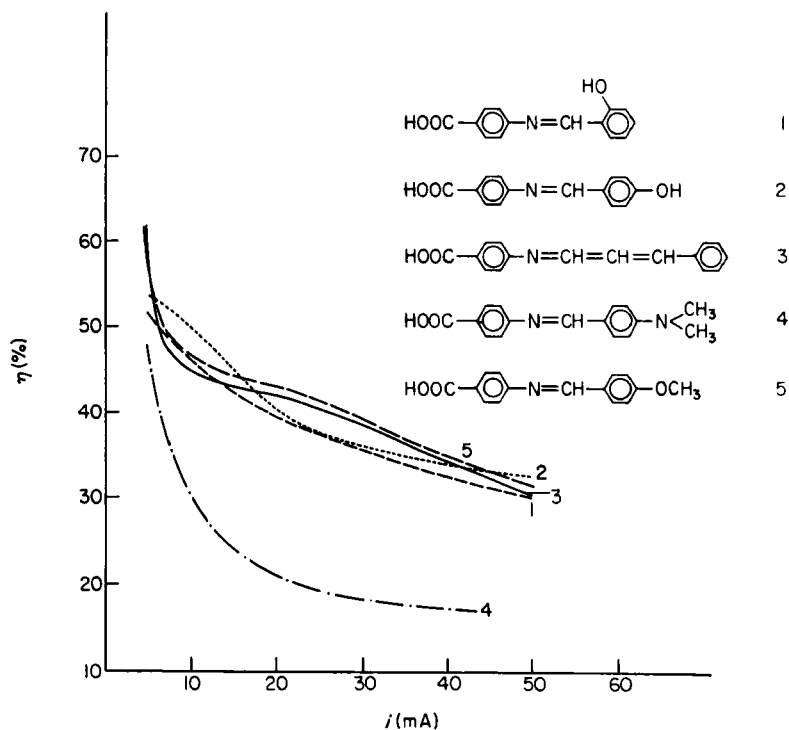


Figure 3. Efficiency of reduction on lead catalyst. Concentration = 10^{-2} M. ---, 1; ·····, 2; —, 3; —·—·, 4; — — —, 5.

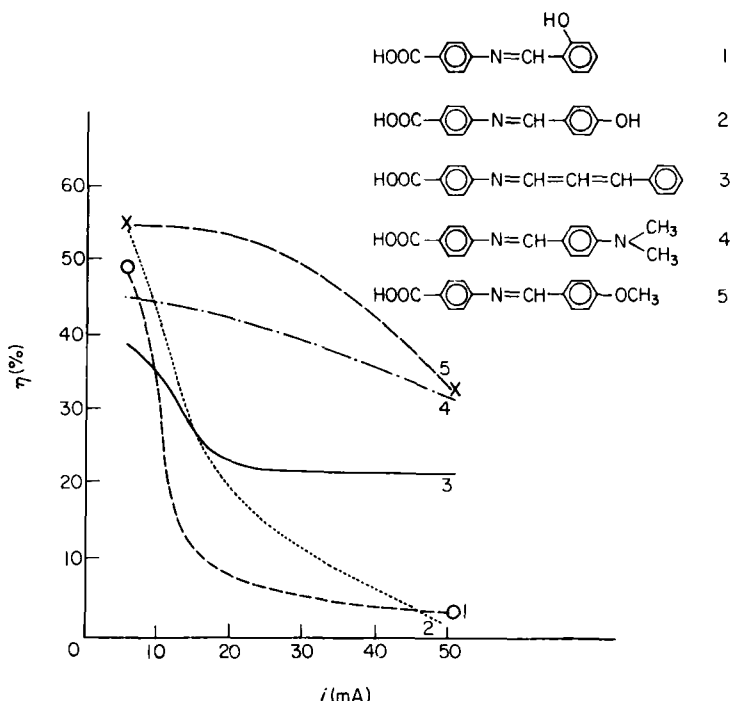
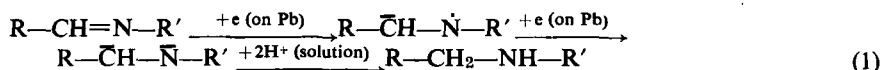


Figure 4. Efficiency of reduction on copper catalyst. Concentration = 10^{-2} M. \bigcirc — \bigcirc , 1; \cdots , 2; —, 3; —·—·—, 4; \times — \times , 5.

the C=N bond which leads to a decrease in the adsorbability of the compound on the lead electrode and hence the reducibility decreases on this electrode. Moreover, the quaternary ammonium salts exert a greater catalytic effect on copper than on lead (see later).

It is suggested that the reduction of organic compounds on metals with high hydrogen overvoltage takes place through an electronic mechanism before protonation. That is why the adsorbability of organic compounds plays a very important role in their reduction.⁴ This was later supported by evidence from polarographic studies and a mechanistic scheme involving two one-electron stages of reduction was postulated:⁵



The reduction of the Schiff's bases under investigation on a lead cathode is in accordance with this mechanism (equation (1)). That the secondary amine is the product of this reduction was confirmed by a preparative run in which benzylideneaniline was reduced on a lead cathode to give benzyaniline (identical in all respects with an authentic sample) in 85% yield. A compound, most probably a dimeric product, was also obtained in about 10% yield.

It is of interest to note that the reduction efficiency of compounds containing a *p*-carboxylic acid group is generally higher than that for the same compounds containing an *o*-carboxylic group. This may be attributed to the hydrogen bonding between the nitrogen atom and the carboxylic group *ortho* to it, i.e. the nitrogen atom of the reducible C=N is partially linked by its lone pair of electrons with the carboxyl group. This would lead to lower reducibility of the C=N on the cathodes.

The consecutive repetition of efficiency measurements for one and the same compound on copper cathode confirmed the increase of reducibility with time. This may indicate the existence of an auto-catalytic effect, which may be attributed to the adsorption of the reduction products (secondary

amines) on the cathode.^a Secondary amines are known to form quaternary ammonium salts in acidic media. These salts accelerate the cathodic reduction processes when occurring in the range of their adsorption.⁶ This explains the higher catalytic effect on copper than on lead electrodes as illustrated by Figure 5.

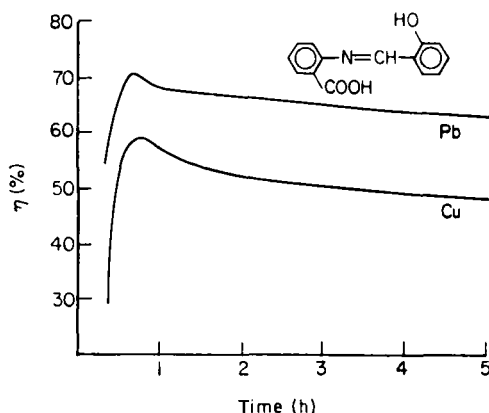


Figure 5. Efficiency of reduction vs time on lead and copper catalysts. Concentration = 10^{-2} M.

4. Conclusions

- a. The Schiff's bases are more easily reduced on lead than on copper cathodes; cyclohexylideneanthranilic acid is not reducible on copper, but on lead the reduction efficiency of this compound is appreciable.
- b. The reducibility of the different azomethine compounds depends on the nature and position of the substituents present.
- c. The secondary amines produced during the reduction processes are converted to quaternary ammonium salts which catalyse the hydrogenation of the compounds studied.
- d. The catalytic effect on copper cathodes is higher than on lead cathodes.

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^a Further studies on the catalytic effect are being carried out at the present time on the azomethine compounds.