CROATICA CHEMICA ACTA CCACAA **64** (2) 281–287 (1991)

YU ISSN 0011-1643
UDC 546.811/.814
CCA-2000

Original Scientific Paper

Use of a Tin Cathode at Very Negative Potential

Z. Vajtner

Pliva Research Department, 41000 Zagreb, Croatia, Yugoslavia

Received June 15, 1990

The effect of some parameters, such as the charge, current density and the kind of cathode material, on the amount of the »cathodic corrosion« of tin was investigated. Preparative electroreductions of cyclohexanone, a »difficult to reduce« organic compound, were carried out as the test reaction to study the above mentioned effects on the possibility to realize preparative electroreductions, as well as for a comparison of the results with those obtained using Hg and Pb cathodes.

INTRODUCTION

Recent reports on the properties and the use of metal cathodes show that at very negative potentials neither the tetraalkylammonium (TAA) cation nor some metal cathodes are inert.[1-7] They form TAA metals at the electrode surface, species that may act as mediators in many organic reductions according to a simplified mechanism:

$$\text{TAA}^+ \xrightarrow[e-]{\text{M cath.}} \text{TAA–metal} \qquad (1)$$

$$\text{O} \xrightarrow{\text{TAA–metal}} R \qquad (2)$$

The coloured TAA-metals, observed so far at Hg, Pb, Sn, Sb and Bi cathodes, act as reducing agents, where regeneration of TAA$^+$ and metal takes place as a result of the oxidation of TAA-metal. The most extensively studied TAA metals are those generated at Hg cathodes and, recently, at Pb cathodes. In the literature cited above, the term »cathodic corrosion« is commonly used for reaction (1), but the system may be called, for example, a »consumable cathode«. It can be also noted that the term »indirect reduction using TAA metal« seems more appropriate than »electrocatalytic« because the rate of the used metal is higher than »catalytic«.

In our previous paper[7], we compared the ability of a mercury and a lead cathode for preparative electroreductions of »difficult to reduce« organic compounds at very negative potentials. We pointed to some advantages of practical work with a lead cathode in spite of its lower activity. On the basis of the results mentioned above it is obvious that a Sn cathode may also play an important role in the electroreduction of »difficult to reduce« organic compounds. The present work intends to investigate some possibilities of using a tin cathode for preparative electroreductions and to compare the results with those obtained using Hg and Pb cathodes. Also, the goal of the paper is to elucidate the effect of some parameters on the use of a tin cathode. Therefore, like in the previous work, first the effect of some factors on the amount of the »cathodic corrosion« of tin was investigated: the charge, current density and the kind of cathode material. Then, the electroreduction of cyclohexanone, a »difficult to reduce« organic substance, whose electroreduction at a mercury cathode[8] and a lead cathode[7] was described, was carried out as the test reaction to study the effects of the above mentioned parameters on the results of preparative electroreductions.

EXPERIMENTAL

Materials. The cathodes were: a Sn foil (Aldrich, 99.999%), an alloy (TOP, 60% Sn, 40% Pb) or a Pb foil (Merck, p.a. grade). Tetrabutylammonium tetrafluoroborate TBA BF_4 and *N,N*-dimethylformamide (DMF) (HPLC grade) were used as purchased from Aldrich. Cyclohexanone was Merck, p.a. grade.

Cyclic voltammetry. Measurements were performed using an Amel 563 Multifunction Unit with Function generator 564, Potentiostat 551 and X-Y Recorder 862/D. The working electrodes (0.126 cm^2) were a Sn foil purchased from Aldrich (99.99%) or an alloy plate (TOP, 60% Sn, 40% Pb), prepared as described earlier.[9] These electrodes were pretreated by scanning the potential up to –3.0 V *vs.* SCE before each measurement. The reference electrode was a SCE[10], the counter electrode was an Ingold Pt 805 NS and the cell was an Amel-Model 494 Universal cell (50 ml). The electrolyte solution consisted of 0.1 M TBA BF_4 in DMF with 0.001 cyclohexanone.

Preparative electrolysis. Experiments were made at a constant current using a Fisher Electroanalyzer with a coulometer. During several experiments, the potential was also determined only at the start and at the end of electrolysis using a SCE.[10] The cathodes (4 cm^2) were a Pb foil, a Sn foil or an alloy plate (60% Sn, 40% Pb) at the bottom of the cell and the counter electrode was a Pb foil (4 cm^2) enclosed in an alundum cup (Fisher) as the anode compartment. The temperature was kept constant using a thermostat (VEB, Type NBE) or an ice bath and nitrogen was bubbled through the catholyte for 10 min prior and during the experiment.

To determine the extent of the »cathodic corrosion« electrolyses were carried out without cyclohexanone using 20 ml of the electrolyte solution and the anolyte (10 ml) consisted of the same electrolyte solution. Cathodes were washed with water and acetone, dried and weighed before and after electrolysis.

In a typical experiment of preparative electrolysis, 0.20 ml of cyclohexanone was dissolved in 20 ml of the electrolyte solution. Samples were taken at various times after starting and analyzed by means of GC with *n*-octane as the internal standard. GC analyses were performed with a column (3% Carbowax 20M + 3% OV-210 on Supelcoport 80/100) and using a Perkin-Elmer GC-900 gas chromatograph with a flame ionization detector. Cyclohexanol, the main product of preparative electrolysis of cyclohexanone, was isolated by extraction with diethylether after completion of the electrolysis and was identified by the IR and ^{1}H NMR spectra.

RESULTS AND DISCUSSION

To investigate the effect of several possible factors, such as the charge and the current density, on the »cathodic corrosion« we first performed electrolyses without any

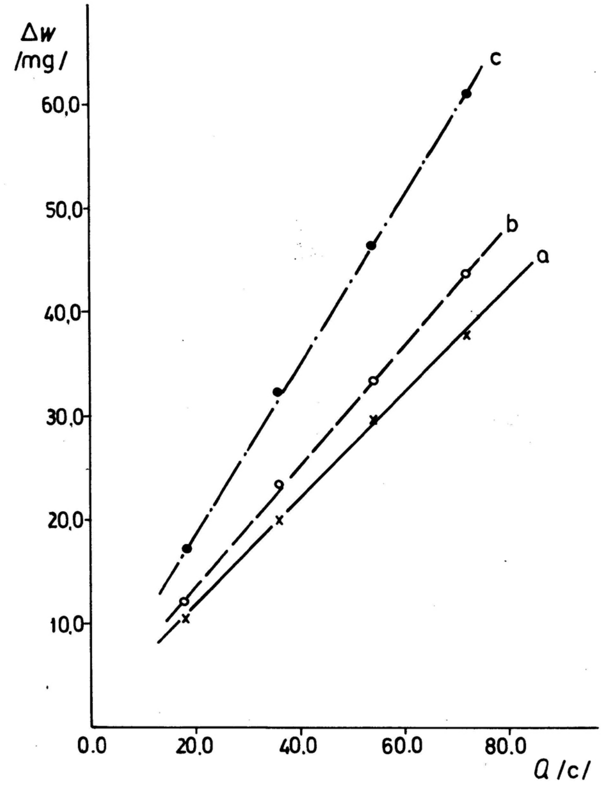


Figure 1. The plot of »cathodic corrosion«-charge, 0.1 M $(C_4H_9)_4$ NBF_4 in DMF, 20 °C, 5 mA cm^{-2}; (a) tin cathode; (b) lead cathode; (c) Sn(60%)-Pb(40%) alloy cathode.

organic substrate. The experiments were made at 20 °C using the same cell as for preparative electrolyses. The results (the average values of min. three experiments using each time a new cathode) with a Sn cathode, an alloy cathode as well as a Pb cathode (for the comparison) are presented in Figures 1–2. Figure 1 plotted the values of the »weight loss« (Δw) against the charge for different cathode materials at the same current density. Figure 2 shows a Δw – charge dependence for two different current densities using a Sn cathode. During all the experiments, the formation of a »dark rust powder« was evident in catholyte when using the Sn and Sn alloy cathodes. This points to »cathodic corrosion« of Sn and the formation of TBA-tin (solid). The plot of the values of the »weight loss« (Δw) as a measure of »cathodic corrosion« against the charge show a linear dependence for all investigated cathodes. The Δw values for Sn cathode (Figure 1, (curve a) are somewhat smaller than the corresponding values for Pb cathode (curve b) but, surprisingly, the values for Sn-Pb alloy are significantly higher than those for both Sn and Pb cathodes (curve c). It could be concluded that the extent of the »corrosion« depends not only on the kind of the metal but also on the kind of the metal electrode structure. With increasing the current density, the »cathodic corrosion« of Sn cathode also increased, but this amount is only about 20% for the double increase of the current density from 2.5 to 5.0 mA cm^{-2} (Figure 2, curve b).

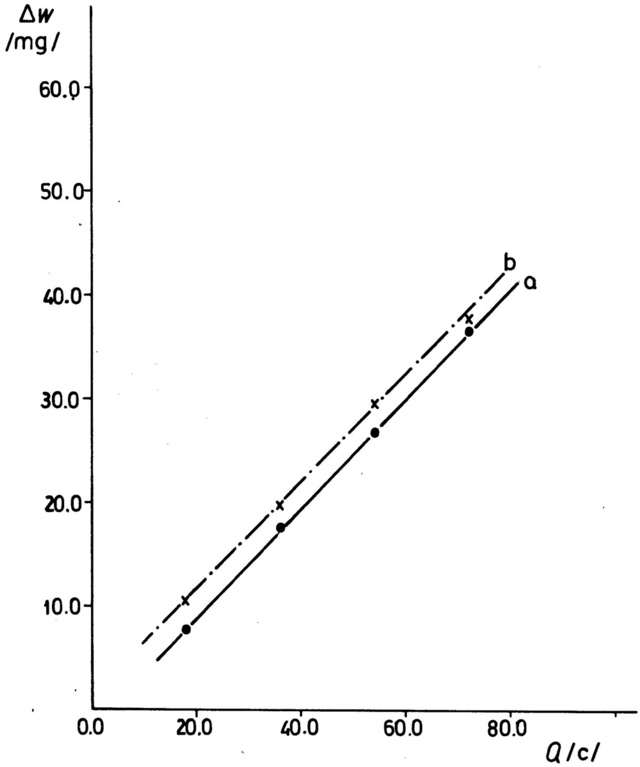


Figure 2. The plot of »cathodic corrosion«-charge, tin cathode, 0.1 M $(C_4H_9)_4$ NBF_4 in DMF, 20 °C; (a) 2.5 mA cm^{-2}; (b) 5.0 mA cm^{-2}.

Cyclic voltammograms of the electrolyte solution (0.1 M TBA BF_4 in DMF), presented in Figure 3, show the formation of tetrabutylammonium tin starting at approx. –2.6 V *vs* SCE (curve a). Using an alloy (60 % Sn – 40 % Pb) electrode, the formation of TBA metal started at approx. –2.7 V *vs* SCE (curve b) and cyclohexanone (0.001 M added in the same electrolyte solution) exhibits only a shoulder on the rising background current (curve c). These results of CV measurements indicated a possibility of preparative reduction of cyclohexanone on Sn and Sn alloy cathodes by indirect reduction using tetraalkylammonium metal in competition with direct electron transfer reduction.

On the basis of the CV measurements described above, we carried out preparative electroreductions of cyclohexanone under similar conditions and investigating the parameters mentioned above in experiments with »cathodic corrosion«. These results are given in Table I and experiments were also performed, for practical reasons, at a constant current. The electroreductions were made at 5 °C in order to minimize possible undesirable reactions of tetrabutylammonium metal. Reactions were, in general, carried out to complete conversion of the reactant, *ie.* until GC analysis indicated a minimal amount or absence of cyclolhexanone in catholyte. Cyclohexanol was obtained as the main product of all electroreductions mentioned above. Formation of the »dark rust powder« was also visible in all experiments of preparative electroreductions but

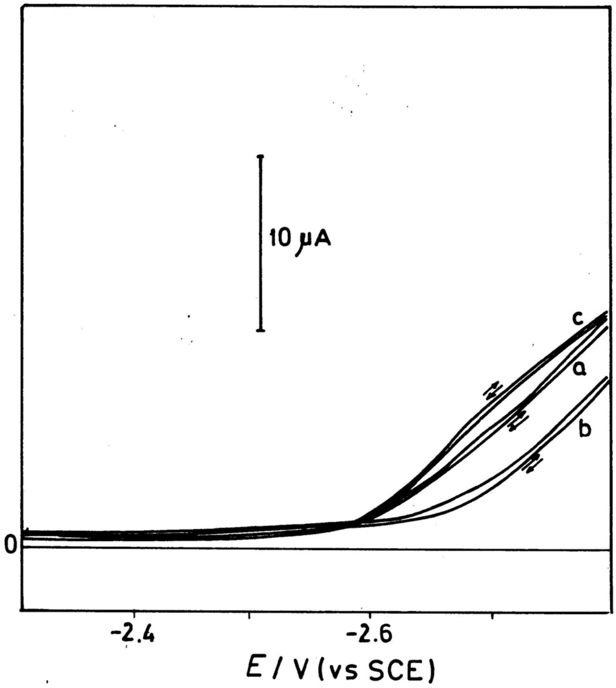


Figure 3. CV at Sn and Sn 60%– Pb 40% alloy electrodes, v = 20 mV s^{-1}, 20 °C;
(a) electrolyte solution, 0.1 M $(C_4H_9)_4$ NBF_4 in DMF, Sn electrode;
(b) electrolyte solution, Sn alloy electrode;
(c) repeated (a) after addition of 0.001 M cyclohexanone.

TABLE I

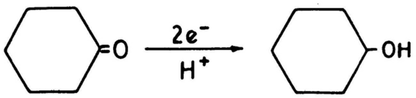
Preparative electroreductions of cyclohexanone, 0.1 M TBA BF_4 in DMF, 5 °C, 2.5 mA cm^{-2}

	Cathode	Q (F mol^{-1})	Cyclohexanone (%)	Cyclohexanol (%)
1	Pb	4.5	5	78
2	Sn	3.7	0	74
3[a]	Sn	3.9	4	80
4	Sn alloy	4.2	6	71

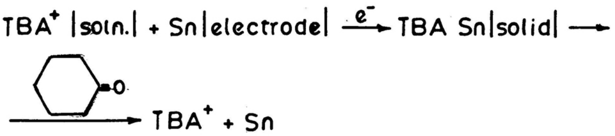
[a]Current density 5.0 mA cm^{-2}

was not so remarkable as in experiments with »cathodic corrosion«, ie. a part of the »powder« was obviously consumed. The electroreduction of cyclohexanone using a Pb cathode was repeated[7] to eliminate the influence of somewhat changed reaction conditions (Table I, entry 1). In comparison, the use of a Sn cathode using identical conditions gave better results (entry 2) due to smaller current consumption for the same quantity of cyclohexanone. The result of using a Sn alloy cathode (entry 4) is in between the results mentioned above: somewhat better than using a Pb but smaller than using pure Sn cathode. The reduction at double current density (entry 3) using a Sn cathode gave practically the same results as in entry 2.

In order to determine which part of overall electrode reaction corresponds to an electron transfer reaction, we determined also the extent of the »cathodic corrosion« of tin during preparative electroreduction of cyclohexanone (experiment 2, Table I). The average »cathodic corrosion« was approx. 25% smaller than the result obtained for the »cathodic corrosion« without cyclohexanone for the same charge and temperature. This may be explained by taking that the difference of 25% is the electron part (reaction 3) in overall electrode reaction and the rest of 75% is the part of interaction of TBA^+ with tin followed by indirect reduction of cyclohexanone using tetrabutylammonium tin (reaction 4):



(3)



(4)

This ratio is not unexpected because the CV measurements showed formation of tetrabutylammonium tin (Figure 3, curve a) starting at the potential more positive than the starting potential of tetrabutylammonium lead under the same conditions.[7]

Therefore, it is difficult to determine exactly whether tetrabutylammonium tin is more or less active in an indirect reduction than the corresponding tetrabutylammonium lead. But, in any case, the overall electroreduction of cyclohexanone runs better using a Sn cathode. It may be also noticed that during repeated experiments of cyclohexanone reduction, using the same tin or tin alloy cathode, no significant decrease of the cyclohexanol yield was obtained in comparison with the first experiments cited in Table I. This means that a tin cathode can be reused many times.

CONCLUSION

In summary, we can say, like in our previous paper of a Pb cathode[7], that the activity of a tin cathode in an indirect reduction using tetraalkylammonium salts in a solvent like DMF is somewhat smaller than that of a mercury cathode.[1,7] But this activity seems to make it possible for a tin cathode to replace successfully a mercury cathode for preparative electroreductions of »difficult to reduce« organic compounds such as cyclohexanone. First of all, there are some advantages of working with a solid cathode: the facility of a »scale up«, the cost (possibility of using cheaper alloys, for example), etc. In general, the reaction conditions like these described in our papers are considered in recent literature as competitive with Birch's reductions of »difficult to reduce« organic compounds.

Acknowledgement – The Author wishes to thank Mr. M. Lukić for helpful GC analyses and the Research Fund of Croatia (SIZ) for financial support.

REFERENCES

1. E. Kariv-Miller, R. I. Pacut, G. K. Lehman, *Topics in Current Chem.* Vol. **148**, Springer Verlag, Berlin-Heidelberg, 1988. p. 97.
2. E. Kariv-Miller, P. B. Lawin, and Z. Vajtner, *J. Electroanal. Chem.* **195** 1985 435.
3. E. Kariv-Miller and P. B. Lawin, *ibid.* **247** (1988) 345.
4. P. B. Lawin, V. Svetličić, and E. Kariv-Miller, *ibid.* **258** (1989) 357.
5. P. B. Lawin, A. C. Hutson, and E. Kariv-Miller, *J. Org. Chem.* **54** (1989) 526.
6. D. M. Loffredo, J. E. Swartz, and E. Kariv-Miller, *ibid.* **54** (1989) 5953.
7. Z. Vajtner and M. Lukić, *Croat. Chem. Acta,* **63** (1990) 263.
8. E. Kariv-Miller and T. J. Mahachi, *J. Org. Chem.* **51** (1986) 1041.
9. Z. Vajtner and B. Lovreček, *J. Electroanal. Chem.* **213** (1986) 113.
10. E. Kariv-Miller and R. Andruzzi, *ibid.* **187** (1985) 175.

SAŽETAK

Uporaba kositrene katode pri vrlo negativnom potencijalu

Z. Vajtner

Istraživan je utjecaj parametara, kao što su veličina struje, gustoća struje i vrst katodnog materijala, na pojavu »katodne korozije« kositra. Provedena je preparativna elektroredukcija cikloheksanona, »teško reducibilnog« organskog spoja, kao test-reakcija za proučavanje utjecaja spomenutih faktora na mogućnost realizacije preparativnih elektroredukcija kao i radi usporedbe dobivenih rezultata s rezultatima na Hg i Pb katodi.