JOURNAL OF APPLIED ELECTROCHEMISTRY **16** (1986) 907–912

Electrochemical synthesis of tetra-alkylthiuram disulphides in emulsions

Z. IBRIŠAGIĆ, V. MIŠOVIĆ, I. TABAKOVIĆ, I. ŠANTIĆ*

Faculty of Chemical Engineering, The 'Djuro Pucar Stari' University, 78000 Banja Luka, Yugoslavia

Received 4 October 1984; revised 2 January 1986

Sodium dimethyldithiocarbamate, NaDTC, was electrochemically oxidized to tetramethylthiuram disulphide, TMT, in an univided electrolytic cell using a couple of rhutenized titanium electrodes; in earlier work the electrodes were platinum. The reaction was carried out in an emulsion formed by mixing saturated aqueous sodium chloride solution containing the substrate with a suitable organic solvent at constant current density. The product was obtained with a high yield and high degree of purity after the passage of the theoretical amount of charge. It was found that at a high current density and a high reactant concentration the product solubility in the organic solvent used determines the success of the electrochemical reaction. Possible reaction mechanisms are also discussed.

1. Introduction

Tetra-alkylthiuram disulphides are industrially important chemicals: they are used as vulcanization accelerators, fungicides and seed treating agents. The usual industrial method for the production of tetra-alkylthiuram disulphides is the chemical oxidation of dialkyldithiocarbamates by chlorine [1]. Since this procedure cannot avoid further oxidation of the reaction product, the yield does not exceed 88% [2]. Direct electrolytic oxidation can overcome this problem, giving excellent yields of high purity products [2–4]. One reported method uses expensive platinum anodes in a divided cell in a slurry electrolytic process [2], while another which involves constant potential electrolysis in a two-phase system, again using platinum anodes, gives a high yield of tetra-alkylthiuram disulphides with a high degree of purity [4]. It was, however, reported [4] that the electrosynthesis of 0.36 g tetramethylthiuram disulphide (TMT) had been taking place for 23 h.

The process described here [5] combines several features which are very attractive for an industrial purpose, i.e. ruthenized titanium electrodes, constant current electrolysis, an undivided cell, high concentration of reactants, a low energy consumption and simple separation of the very pure product.

2. Experimental details

Cyclic voltammograms were recorded for 1–3.2 × 10^{-3} kmol m^{-3} sodium dimethyldithiocarbamate (NaDTC) in 0.1 kmol m^{-3} Et_4NClO_4–acetonitrile and in 0.1 kmol m^{-3} aqueous NaCl using a HI-TEK potentiostat (type DT2101), a HI-TEK PPR1 waveform generator and a Philips PM8120 X-Y recorder. The measurements were performed in a 25 cm^3 conical cell fitted with a platinum disc electrode, 1 mm in diameter, a platinum gauze as a counter electrode and a saturated calomel electrode (SCE).

Electrolyses were carried out on $Ti/TiO_2 + RuO_2$ electrode plates at a constant current density, at room temperature and in an undivided cell equipped with a water cooled condenser. The $Ti/TiO_2 + RuO_2$ electrode plates were 5 × 5 cm each and the interelectrode gap was 4–10 mm. The cell was filled with an equal amount (150 cm^3) of an aqueous phase and an

---

* *Present address*: Unis, Ro Sintevit, Vitez, Yugoslavia.

0021–891X/86 $03.00 + .12

appropriate immiscible organic solvent, i.e. chloroform, methylene chloride or benzene. The aqueous phase was always saturated with NaCl and contained various concentrations of NaDTC. Electrodes were simply dipped in the emulsion, which was formed with a rapidly rotating magnetic stirrer within the cell, hence producing a fine emulsion without visually separate droplets of dispersed organic phase. It was seen that the presence of undissolved sodium chloride stabilizes the emulsions formed.

In some experimental runs the reactant, NaDTC, was prepared *in situ* in the electrolytic cell by mixing equimolar amounts of $(CH_3)_2NH$, CS_2 and NaOH in water for 2 h. Syntheses were carried out at room temperature. The initial reactant concentration in the aqueous phase was determined by titration with an $0.05\,\mathrm{kmol\,m^{-3}}$ I_2 solution. The amount of unreacted NaDTC as a function of current passed was determined by cyclic voltammetry, i.e. $1\,\mathrm{cm^3}$ samples of the aqueous phase were diluted to $1\text{–}7 \times 10^{-3}\,\mathrm{kmol\,m^{-3}}$ NaDTC solutions with $0.1\,\mathrm{kmol\,m^{-3}}$ NaCl solution and cyclic voltammograms were recorded. The sweep rate was $150\,\mathrm{mV\,s^{-1}}$. Before each measurement the platinum working electrode was rinsed with acetone and polished on filter paper.

The concentration rise of TMT in the solvent phase as a function of charge consumed was followed gravimetrically, i.e. $2\,\mathrm{cm^3}$ samples of the solvent were taken at intervals during electrolyses, each thoroughly washed out with water, the solvent was removed on a rotary evaporator and residual crystals were dried off in an oven at 160° C for 2 h. The purity of TMT was checked by the melting point determination and the structure was confirmed by IR spectrum. A few experimental runs were performed using sodium acetate (50 g per $150\,\mathrm{cm^3}$) instead of sodium chloride as a supporting electrolyte, but otherwise similar conditions were used.

3. Results and discussion

The electrochemical behaviour of sodium dithiocarbamate (NaDTC) was investigated by cyclic voltammetry in non-aqueous and aqueous media.

Cyclic voltammograms obtained for NaDTC in acetonitrile–Et_4NClO_4 electrolyte show two peaks at 50 mV and around 1000 mV versus SCE (Fig. 1) characteristic of irreversible processes. Similarly, cyclic voltammograms recorded in aqueous NaDTC using sodium chloride as the electrolyte showed two peaks at 270 mV and 700 mV versus SCE, the peaks were also irreversible (Fig. 2).

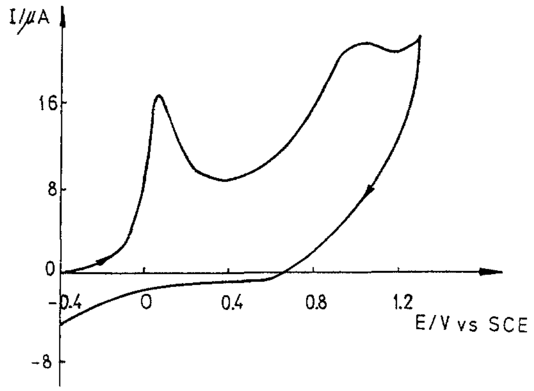


Fig. 1. Cyclic voltammogram recorded for 1×10^{-3} $\mathrm{kmol\,m^{-3}}$ NaDTC in $0.1\,\mathrm{kmol\,m^{-3}}$ Et_4NClO_4–acetonitrile.

Plots of the peak current versus the square root of the potential scan rate for the first electron transfer process gave a linear relationship for both media, showing that the first electron transfer in the aqueous as well in the non-aqueous media was mass transfer controlled.

Preparative electrolyses in acetonitrile–Et_4NClO_4 electrolyte, on a platinum electrode at 300 mV versus SCE, produced 68% yield of TMT after the passage of the theoretical amount of charge for the reaction investigated (Scheme 1). However, the experiments in the saturated aqeuous sodium chloride solution and an immiscible organic solvent (i.e. chloroform, methylene chloride) system, well mixed to the state of an emulsion, gave an almost quantitative yield after the passage of the theoretical amount of charge. Electrolyses were performed in an undivided cell at constant current density ($4\text{–}20\,\mathrm{A\,dm^{-2}}$) on platinum or using a couple of $Ti/TiO_2 + RuO_2$ electrodes.

The improvement in the yield in the emulsion electrolysis could be ascribed to the extraction of the product into the organic phase and its protection from further oxidation or reduction on the counter electrode. The use of saturated

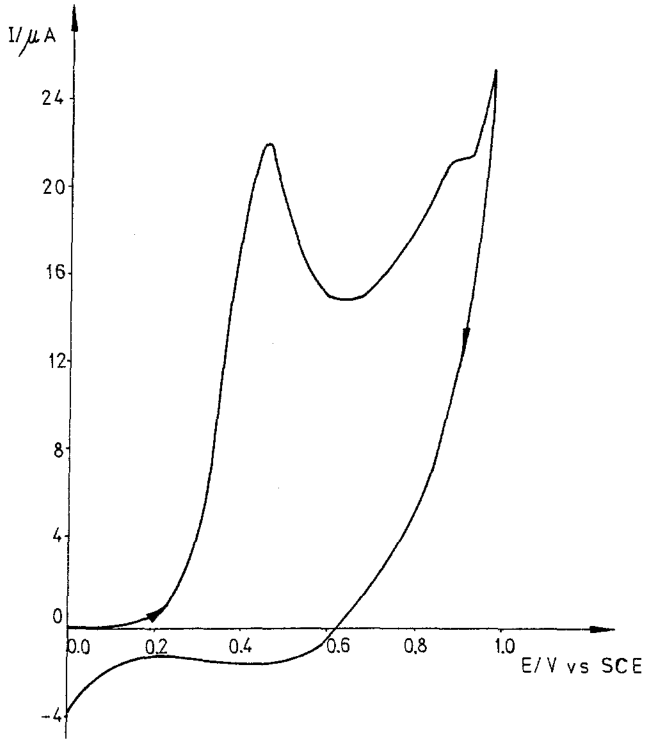
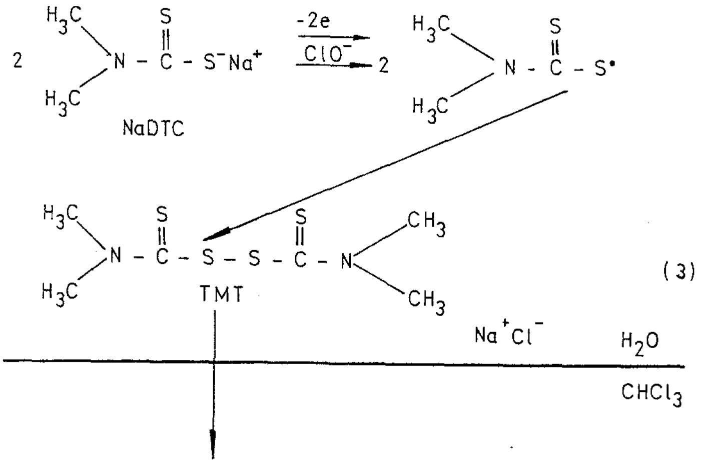


Fig. 2. Cyclic voltammogram recorded for 1.43×10^{-3} kmol m^{-3} NaDTC in 0.1 kmol m^{-3} aqueous NaCl. The scan rate was 150 mV s^{-1}.

sodium chloride solution probably also enhances the yield by salting out the product. It is possible that, in addition to the direct electrolysis on the electrode surface, an indirect oxidation occurred simultaneously, with electrogenerated hypochlorite as the oxidizing agent (Scheme 1.). The results with two $Ti/TiO_2 + RuO_2$ electrodes were as good as with the platinum anode used previously. Experiments with other electrode materials such as gold, a 70% silver–30% palladium alloy and graphite were not so successful since TMT easily adsorbs

$$2\,Cl^- \longrightarrow Cl_2 + 2e \qquad (1)$$

$$Cl_2 + 2\,OH^- \longrightarrow ClO^- + Cl^- + H_2O \qquad (2)$$



Scheme 1.

Table 1. The effect of the concentration of NaDTC on the electrochemical synthesis of TMT

NaDTC (kmol m^{-3})	*Cell voltage (V)*	*Product yield and current efficiency (%)*
0.675	2.2–2.8	80
0.762	2.2–2.6	85
1.012	2.1–2.3	91
1.350	2.1–3.0	85
1.690	2.1–2.7	80
2.030	2.2–3.8	70

Electrolysis conditions: NaDTC dissolved in 150 cm^3 saturated aqueous sodium chloride solution and 150 cm^3 of CH_2Cl_2, well mixed to the emulsion state. An undivided cell with a couple of $Ti/TiO_2 + RuO_2$ electrode plates (5 × 5 cm); electrode gap, 4 mm; current density, 8 A dm^{-2}. Electrolyses were terminated after the theoretical amount of charge.

Table 3. The effect of the current density on the electrochemical synthesis of TMT

Current density (A dm^{-2})	*Cell voltage (V)*	*Product yield and current efficiency (%)*
4	–	93
8	2.0–2.2	90
12	2.5–3.6	92
16	3.5–4.7	89
20	–	77

Electrolysis conditions: 1.0 kmol m^{-3} NaDTC in aqueous saturated sodium chloride solution (150 cm^3) and 150 cm^3 $CHCl_3$, well mixed to the emulsion state in an undivided cell with a couple of $Ti/TiO_2 + RuO_2$ electrode plates (5 × 5 cm). The interelectrode gap was 4 mm. Electrolyses were terminated after the theoretical amount of charge.

on most electrode materials and hence stops any further progress of the electrochemical reaction. When graphite was used, the anode surface became covered with the TMT formed and after 50% conversion the reaction stopped.

Experiments demonstrated that the electrochemical oxidation of NaDTC to TMT could proceed at a relatively high current density (Table 1) and with a high reactant concentration (Tables 2 and 3), but the success of the reaction was limited by the product solubility in the organic solvent used (Tables 2 and 3; Figs 3, 4). In fact, the product yield is better along the series benzene < methylene chloride < chloroform (Table 2). This observation correlates very well with the increased solubility of TMT in the organic solvent. Following the progress of the electrochemical reaction in water–chloroform emulsions we found a linear relationship between the amount of TMT formed and the unreacted NaDTC against the consumed charge (Fig. 3). On the other hand, when electrolyses were run in water–benzene emulsions the relation between the product formed or the reactant consumed and charge passed was non-linear (Fig. 4).

Table 2. The effect of the organic solvent on the electrochemical synthesis of TMT

Organic solvent	*Cell voltage (V)*	*Product yield, current efficiency (%)*
benzene	2.6–3.4	56
CH_2Cl_2	2.2–2.6	85
$CHCl_3$	2.0–2.9	91

Electrolysis conditions: 0.763 kmol m^{-3} NaDTC in 150 cm^3 saturated aqueous sodium chloride solution and 150 cm^3 of the organic solvent, well mixed to the emulsion state. A couple of $Ti/TiO_2 + RuO_2$ electrodes (5 × 5 cm); current density, 8 A dm^{-2}. Electrolyses were terminated after the theoretical amount of charge.

Hence, in addition to the other reaction conditions, a good product solubility in the solvent used is required to obtain a high product yield and a high current efficiency (Fig. 5). If this condition is not met, as in the experiment with benzene (Fig. 6), the product yield and the current efficiency are lower.

Experiments carried out at different current densities (Table 1), showed that a change in the current density within the range 4–16 A dm^{-2} neither affects the product yield nor the current efficiency. However, the current efficiency obtained at 20 A dm^{-2} fell slightly, most likely due to excessive oxygen evolution.

Preparative electrolyses performed in sodium acetate–water–chloroform emulsions produced ~86% product yield and current efficiency. Reactions were run at 8 A dm^{-2} on platinum or $Ti/TiO_2 + RiO_2$ electrodes while the initial reactant concentration in the aqueous phase was

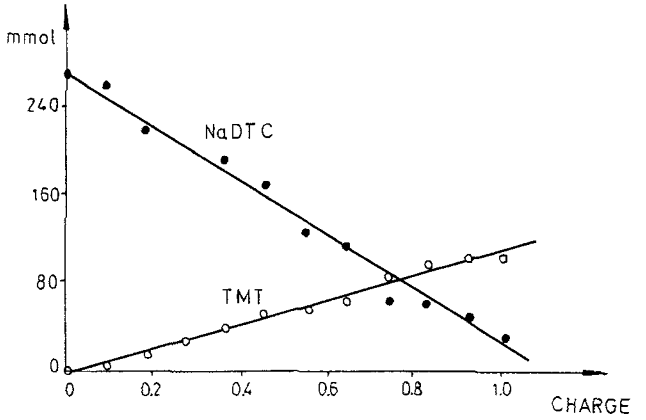


Fig. 3. Conversion of NaDTC to TMT as a function of charge passed in the laboratory stirred tank reactor. The electrolyte was 0.268 mol NaDTC in 150 cm^3 saturated aqueous sodium chloride solution and 150 cm^3 $CHCl_3$, well mixed to the emulsion state. Electrodes were 5 × 5 cm $Ti/TiO_2 + RuO_2$ electrode plates; $i = 16\,A\,dm^{-2}$.

1 kmol m^{-3} of NaDTC. Results clearly show that the electrochemical oxidation of NaDTC in the emulsion could proceed by a direct electrochemical process in the aqueous phase while the reaction product was extracted into the organic phase resulting in a high product yield after the passage of the theoretical amount of charge required for a one-electron transfer process.

4. Conclusions

The electrochemical behaviour of dimethyldithiocarbamate in aqueous and non-aqueous media was defined by cyclic voltammetry. Additional information was obtained by preparative electrolyses in Et_4NClO_4–acetonitrile and in emulsions formed from saturated aqueous sodium chloride solution and an immiscible solvent, i.e. chloroform, methylene chloride and benzene. It was shown that the electrochemical oxidation of NaDTC in an emulsion could produce an almost quantitative yield of highly pure product in an undivided cell using two $Ti/TiO_2 + RuO_2$ electrodes and a constant current density (4–16 A dm^{-2}).

The following conclusions can be drawn from the data obtained for the electrochemical oxidation of NaDTC to TMT in an emulsion.

1. The oxidation can be visualized as a direct anodic oxidation of the substrate, probably mass transfer controlled, followed by the extraction of the reaction product into the solvent phase.
2. When saturated sodium chloride solution was used there could also be a contribution from indirect electrolysis via hypochlorite.

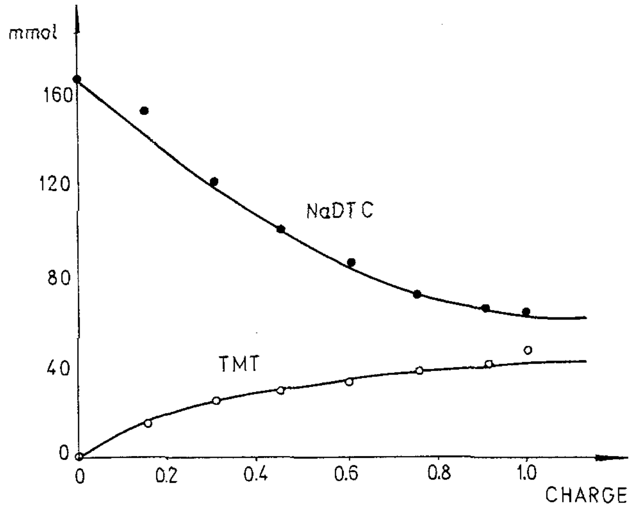


Fig. 4. Conversion of NaDTC to TMT as a function of charge passed in the laboratory stirred tank reactor. The electrolyte was 0.174 mol NaDTC in 150 cm^3 saturated aqueous sodium chloride solution and 150 cm^3 benzene, well mixed to the emulsion state. Electrodes were 5 × 5 cm $Ti/TiO_2 + RuO_2$ plates; $i = 16\,A\,dm^{-2}$.

3. The role of a solvent is to protect the reaction product from harmful reactions at the anode and cathode. Moreover, it was found that the product solubility in the solvent used determines the product yield and the current efficiency of the reaction investigated.

References

[1] G. E. P. Smith, G. Alliger, E. L. Carr and K. C. Young, *J. Org. Chem.* **14** (1949) 935.

[2] L. H. Cutler, US Patent 4032416 (1977).

[3] J. A. Gardner, US Patent 2385410 (1945).

[4] S. Torrii, H. Tanaka and K. Misima, *Bull. Chem. Soc. Japan* **51** (1978) 1575.

[5] Z. Ibrišagić, V. Mišović, I. Tabaković and I. Šantić, Yugoslav Patent No. 2528 (1982).