Journal of Electroanalytical Chemistry 648 (2010) 1–7

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

The electrochemical reduction of trinitrotoluene on a platinum wire modified by chemisorbed acetonitrile

V. Marinović [a,*], S. Marinović [b], M. Jovanović [c], J. Jovanović [c], S. Štrbac [b]

[a] Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Knez Mihajlova 35, 11000 Belgrade, Serbia
[b] Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia
[c] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

ARTICLE INFO

Article history:
Received 14 May 2010
Received in revised form 5 July 2010
Accepted 9 July 2010
Available online 15 July 2010

Keywords:
Trinitrotoluene
Electrochemical reduction
Platinum
Acetonitrile

ABSTRACT

The electrochemical reduction of 2,4,6-trinitrotoluene (TNT) was investigated by cyclic voltammetry on a platinum electrode in aqueous sodium chloride solutions with acetonitrile containing different concentrations of TNT. The obtained cyclic voltammograms showed three distinct reduction peaks in the potential range of −0.45 to −0.8 V (*vs.* an Ag/AgCl (3 M KCl) reference electrode), which refer to the multi-step process of TNT reduction. The calibration curves of the dependence of the first peak current on the TNT concentration were linear in the ranges 4.4–638.4 μM and 0.11–4.40 μM for two different scan rates, 200 mV s^{-1} and 20 mV s^{-1}, respectively. The detection limit was 0.11 μM. Acetonitrile chemisorption on Pt surface took place and caused thus modified platinum electrode to exhibit an electrochemically stabile behaviour. Hence, a very high reproducibility over a prolonged time and voltammetric cycling was provided for using a Pt wire that is easy to handle as a suitable material for TNT sensing. Additionally, it was confirmed by testing the acetonitrile modified Pt wire for TNT detection in river water.

1. Introduction

The extensive use of trinitrotoluene (TNT) for military and industrial applications has led to environmental contamination, which imparts a highly toxic, mutagenic and potentially carcinogenic substance on human beings [1]. In order to assess the extent of explosive contamination in soil and water, it is necessary to detect and identify the explosives and their degradation products in suspected areas. Hence, the detection of trinitrotoluene [2–7] has attracted considerable research attention in recent years due to urgent needs in public security and environmental protection. The structure and reactivity of trinitrotoluene within its environmental context were also investigated [8].

Trinitrotoluene, as a nitroaromatic compound, is known to exhibit well-defined redox behaviour and can be reduced electrochemically due to the fact that the nitro-groups are excellent electron acceptors. The reduction of TNT occurs in three steps in accordance with the three nitro-groups in the aromatic molecule. The nitro groups of TNT and other nitroaromatics were reported to undergo reduction to hydroxylamine, followed by conversion to amine [9]. Electrochemical sensors of nitroaromatic compounds are based on the ready electrochemical reduction of their electron-deficient nitro-group(s). Electrochemical procedures involving potentiometric methods, such as cyclic voltammetry (CV) [10,15] and square-wave voltammetry (SWV) [9–14,16], were developed for the detection of TNT in water [12–14], soil [15,16], and the gaseous phase [17]. Cyclic voltammograms and square-wave voltammograms were recorded to determine the potentials corresponding to the peaks currents, which were found to be directly proportional to the TNT concentration [10,12,14,18]. The sensitivity and selectivity of the electrochemical sensors are mainly dependent on the sensor material.

Various electrodes have been used for the electrochemical reduction of TNT, such as: glassy carbon [10], carbon-fiber [9,14, 16], carbon nanotube-modified glassy carbon [18], tin-carbon [15], gold [17], gold modified with self-assembled monolayers [11], boron doped diamond [12], polycrystalline Pt [19], and copolypeptide-doped polyaniline nanofibers [20]. The state-of-the-art in electrochemical sensing of explosives has recently been reviewed [21].

In this study, a further investigation of the electrochemical reduction of trinitrotoluene by cyclic voltammetry in aqueous sodium chloride solutions with acetonitrile (AcN) was undertaken. The goal was to detect and quantitatively determine trinitrotoluene as simple as possible with respect to both the technique and the electrode used. A simple Pt wire electrode that is easy to handle was used as the working electrode. It was shown earlier [22] that a platinum electrode was deactivated by repeated reductions of nitroaromatic compounds in solution of phosphate buffer with methanol. In the present investigation an electrolyte was used which contained acetonitrile (as a solvent for TNT) which was

---

* Corresponding author. Tel.: +381 11 2636 994; fax: +381 11 2185 263.
E-mail address: vedrana@tmf.bg.ac.rs (V. Marinović).

1572-6657/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jelechem.2010.07.008

reductively chemisorbed at Pt surface [23–27]. It was expected that such a "chemically modified Pt electrode" would exhibit electrochemically stabile behaviour for the TNT reduction process. This supposition was confirmed in this study.

2. Experimental

The electrochemical reduction of TNT was investigated by cyclic voltammetry using a sweep generator (PAR M175) driving a potentiostat (PAR M173). The electrochemical measurements were performed in a standard glass cell with a Pt wire of 0.32 cm^2 surface area (2 cm long; 0.5 mm diameter) embedded into the glass holder as the working electrode, a spiral Pt wire (10 cm long; 0.5 mm diameter) as the counter electrode and a standard Ag/AgCl (3 M KCl) electrode as the reference.

All solutions were made with analytical grade chemicals and Milli-pure water. In all the experiments the supporting electrolyte was 0.5 M sodium chloride solution. Due to the limited solubility of TNT in water [28], sample solutions (50 m L) of between 0.1 μM and 638.4 μM TNT were prepared by adding an appropriate amount of previously prepared 1000 mg L^{-1} or 3000 mg L^{-1} solution of TNT dissolved in acetonitrile (HPLC grade) into the supporting electrolyte maintaining an approximately constant concentration of 5 vol.% of acetonitrile throughout the experiments. Additionally, water from the river Sava was used for testing the method in natural media. River water was prepared by filtering and without any other purification step. pH of the river water was 7.8 ± 0.2, which was close to pH 7.0 ± 0.2 of a supporting electrolyte.

Before the experiments, the cell with electrodes were cleaned in acetone and washed in distilled water. Cyclic voltammetry in 0.5 M H_2SO_4 was applied to electrochemically polish the Pt electrode and to check the state of the electrode surface until a voltammogram with hydrogen adsorption and desorption peaks characteristic for a Pt electrode in H_2SO_4 was obtained. The potential was cycled from −0.2 to 1.0 V using a 200 mV s^{-1} scan rate.

In order to investigate the effect of the basic electrolyte (0.5 M NaCl with acetonitrile) on the platinum electrode, cyclic voltammetry experiments were performed and results were compared to the cyclic voltammograms obtained in pure 0.5 M NaCl. The concentration of acetonitrile in the supporting electrolyte varied from 0.02–5.00 vol.%. Before each cyclic voltammetry experiment in electrolytes without and with TNT, the electrode was held at the open circuit potential for 30 min.

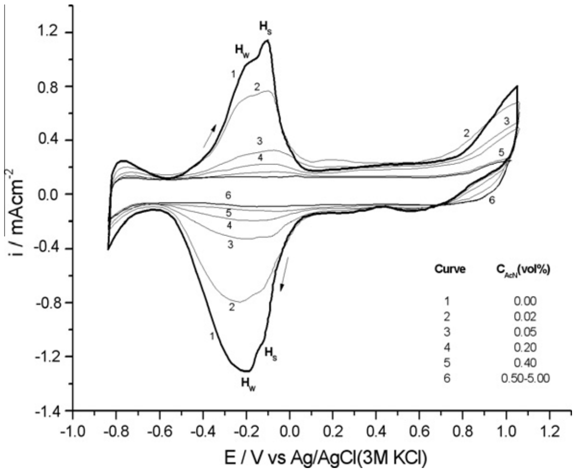

Fig. 1. CVs for a Pt electrode recorded in oxygen free 0.5 M NaCl solution without (Curve 1) and with the addition of 0.02–5 vol.% of acetonitrile (Curves 2–6). Potential scan rate was 200 mV s^{-1}.

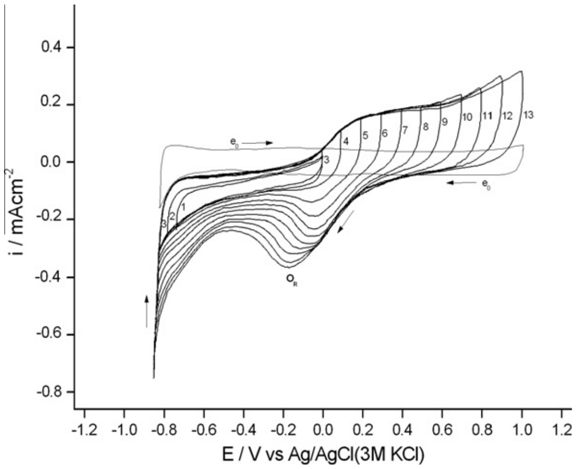

Fig. 2. CVs for a Pt electrode in a solution of 0.5 M NaCl containing acetonitrile obtained without purging of electrolyte, as a function of the negative and positive potential limits (Curves 1–13). CV of acetonitrile modified Pt electrode obtained in the oxygen free electrolyte is presented by Curve e_0. Potential scan rate was 200 mV s^{-1}.

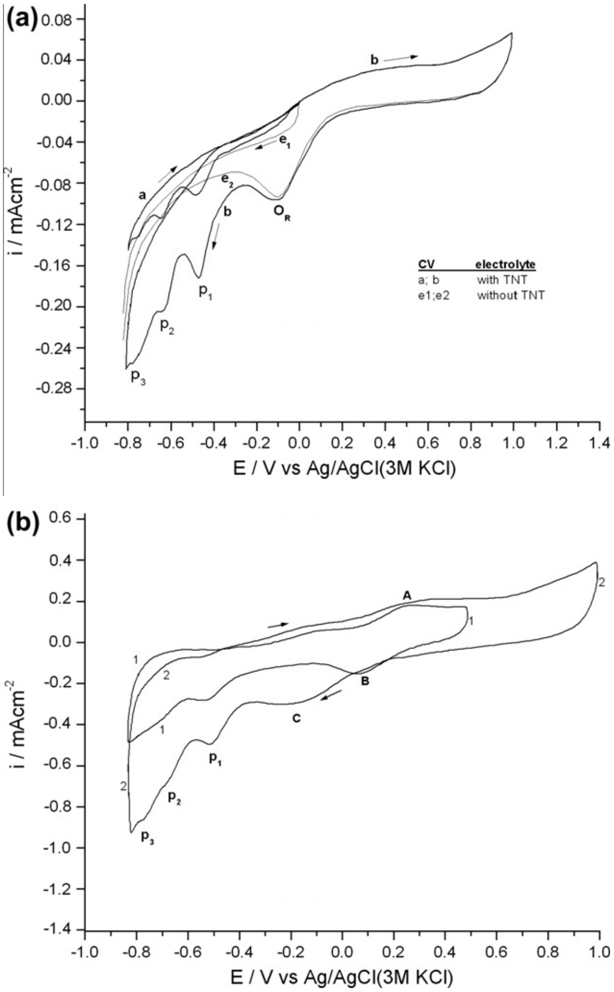

Fig. 3. CVs of TNT reduction on the Pt electrode in a solution of 0.5 M NaCl with acetonitrile containing 220 μM L^{-1} TNT as a function of the anodic potential limits at a potential scan rate of: (a) 20 mV s^{-1}; (b) 200 mV s^{-1}.