

Electrochemical Synthesis of Tris(9-crown-3)triphylene using Cyclic Voltammetry

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For the first time, electrochemical trimerization of benzo-9-crown-3 ether, in dry acetonitrile, solutions has been carried out using repeated potential cycling at a Pt electrode. This method constitutes a new alternative and efficient route for the synthesis of tris(9-crown-3)triphylene. The trimer was formed during the anodic potential scanning (in a potential range 0 to 1200 mV vs. saturated calomel electrode, SCE). During the process, the formed trimer separated from the electrode surface precipitated at bottom of the cell. Here, mechanism of the process and influence of the experimental parameters on the rate of the trimerization (or reaction yield) were investigated. It was found that the rate of the process was impressed by the concentration of the monomer, the supporting electrolyte and scan rate. The maximum reaction yield was 89%.

Keywords: Cyclic Voltammetry, Electrosynthesis, Tris(9-crown-3)triphylene

1. INTRODUCTION

Anodic electrochemical oxidation can provide a powerful technique for synthesizing and modifying aromatic molecules [1]. The main advantages of this technique lie in its utility for selectivity oxidizing functional groups, generating highly reactive intermediates and reversing the polarity of the nucleophiles. Good examples for such reactions are electrochemical oxidation of some aromatic ethers, where under a certain condition that lead to dimerization/trimerization or polymerization of the compound [2].

It is believed that the anodic oxidation reactions of aromatic ethers on a Pt electrode mostly result to formation intermediate cation radicals [3]. These radicals are very reactive transients and can react with possible existing nucleophiles in the solution (e.g. water). When aromatic ether compound

contains an electron donating ortho-substitute the electrochemical oxidation of the ether (in absence of water or other nucleophiles) leads to dimerization or trimerization of aromatic ethers [3].

A typical example of such electrochemical process was described by Bechgaard and Parker [4], where under a extreme condition, 1,2-dimethoxybenzene electrochemically was oxidized into hexamethoxy-triphenylene. Because of their liquid-crystal properties of these class of compounds (with a long side chain) [5] synthesizing of such compounds have attracted attention of many researcher, where a number of chemical and electrochemical synthesizing methods have been introduced. For instants, recently, tris(9-crown-3)triphylene was chemically produced by Buchanan's group [6]. Nevertheless, the electrochemical methods can be considered the most moderate way for synthesizing these compounds [7].

In the present study, we present a new electrochemical method for synthesizing the trimer of benzo-9-crown-3 ether by using cyclic voltammetry technique. This method is of interest owing to its mild conditions, which allows the synthesis of such trimer for the first time. Here, also, an investigation was conducted to find dependencies of rate of the process on the experimental parameters.

Benzo-9-crown-3 ether derivatives are good sensing material for Be^{2+} ions in construction of ion selective sensors [8-14].

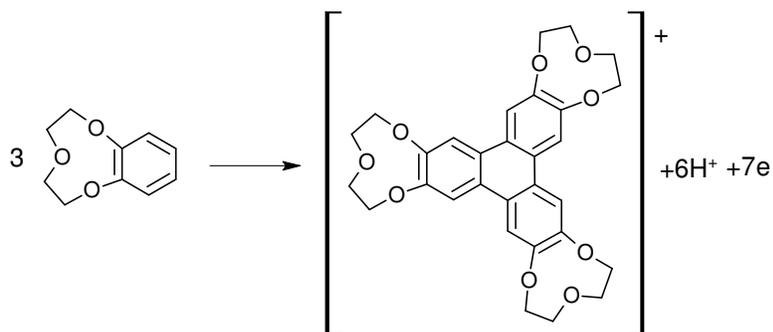
2. EXPERIMENTAL PART

The monomer, benzo-9-crown-3 ether, was prepared in our lab by a conventional synthetic method [15]. All other chemicals were prepared from Merck Co. All the experiments were run in anhydrous acetonitrile prepared as described elsewhere [3]. The supporting electrolyte was Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4). The electrochemical process was performed in a three-electrode cell (total volume: 100 ml), which was equipped with a disk Pt (0.4 mm in diameter) as the working electrode, an auxiliary electrode (Pt) and a calomel reference electrode (SCE). The reference electrode was separated from the solution by a bridge equipped with a double sintered glass junction to avoid water leakage. All solutions were degassed by bubbling argon through the solutions prior to the experiments. They were maintained under an argon atmosphere during the experiments. Cyclic voltammetric experiments were performed with a Metrohm instrument, model 746 Trace Analyzer. The obtained electrochemical data by the instrument for analysis was transferred to a computer (PC Pentium II 233 MHz). Preparative of the trimer carried out on a large Pt coil electrode (4 cm^2 , geometric surface area) in a solution of Bu_4NBF_4 0.05 M and 0.50 M of the monomer (in dry acetonitrile). The potential of the working electrode was cycled from 0 to 1200 mV, until the anodic current reaches to 0.1 μA . It must be mentioned that after each cycle the potential of the electrode was held at -100 mV for 0.5 s. The formed trimer was insoluble, which precipitated at the bottom of the electrochemical cell. The trimer separation and preparation for NMR were done according to published procedure [5]. Analysis data of the trimer were: $M/z=534.5$; M.P. 266 $^\circ\text{C}$; ^1H NMR (500MHz) CDCl_3 δ ppm; 7.8 (s,6H), 5.9 (s,12H); ^{13}C NMR (400MHz) CDCl_3 δ ppm; 71.1, 72.9, 115.8, 126.9, 157.2.

Elemental analysis, on a pureed sample, Analytical Calculated for C₂₁ H₂₀ N₂ S₆: C, 51.19; H, 4.09; O, 5.68; found: C, 51.05; H, 4.10; O, 5.83.

3. RESULTS AND DISCUSSION

Figure 1 illustrates cyclic voltammogram of a solution of acetonitrile containing 0.2 M benzo-9-crown-3 ether and 0.05 M Bu₄NBF₄, was obtained at a platinum electrode. Beside the calculation of the charge under the anodic peak shows that the process accompanies with seven electrons. From those results, one can suggest that the large anodic peak at potential 1.157 V, results of formation of salt of tris(9-crown-3)triphylyene (TCTP)⁺, as follows:



Scheme 1. Formation of salt of tris(9-crown-3)triphylyene (TCTP)⁺

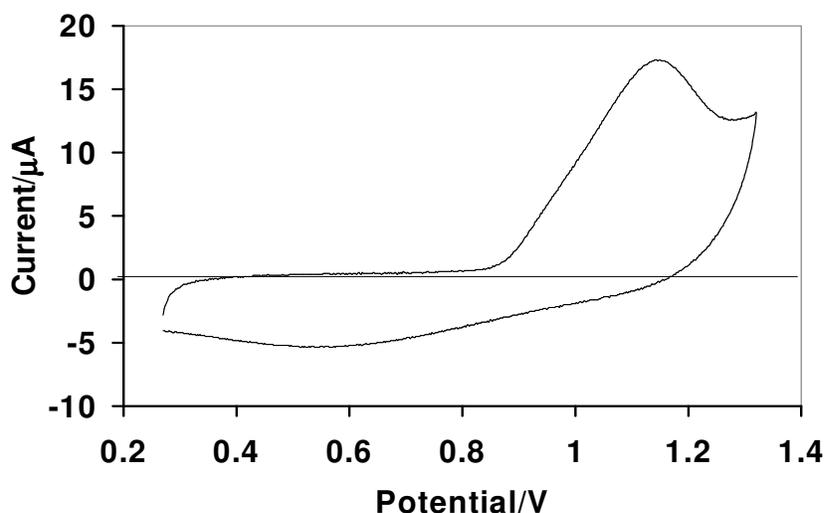


Figure 1. Cyclic voltammogram of 0.2 M benzo-9-crown-3 ether in acetonitrile containing 0.05 M Bu₄NBF₄ 0.05 M at a Pt electrode (0.4 mm in diameter), scan rate 200 mV/s

Our basic path for finding a mechanism for the process was established based on previous works. In fact, this voltammogram is very similar to the reported voltammograms by Simonet et. al. [6] for trimerization of orthodipropoxybenzene derivatives. Simonet et. al. [16], reported that the electrochemical trimerizations of phenol ethers take place in two steps electron transfer; first,

formation of a trimer and then oxidation of the product. Accordingly, here, the trimerization process at the electrode surface can be written as follows:



The obtained experimental results are in agreement with this mechanism. The variations of the anodic peak current (i_a) and potential (E_a) at the voltammogram with scan rate (ν) are shown in Figure 2.

It seems that in this scan range the kinetic of the electron transfer is quasi-reversible. So that it can be speculated that the trimer formation process is controlled by the rate of the electron transfer with $\alpha = 0.67$ as determined from the slope ($30/n\alpha = 7.6$ per decade) of the anodic peak shift with scan rate.

Moreover, the inset plot in the figure shows that the value $i_a/\nu^{1/2}$ increases slightly with an increase in the scan rate. The existence of a cathodic peak in the reverse scan indicates that the oxidation and reduction of the trimer is reversible. This was concluded from the inset graph in Figure 2. The graph shows $i_c/\nu^{1/2}$ is independent to ν , which is characterization of a reversible reaction [17]. As conclusion, such behavior is adopted as indicative of an EE mechanism for the trimerization process. However, considering the voltammograms in Figures 1 and 2, the absent of second anodic peak for the oxidation of the trimer, similar to electrochemical oxidation of orthodipropoxybenzene derivatives [6], it can be come out that reaction 4 takes place at potential lower than the trimerization potential.

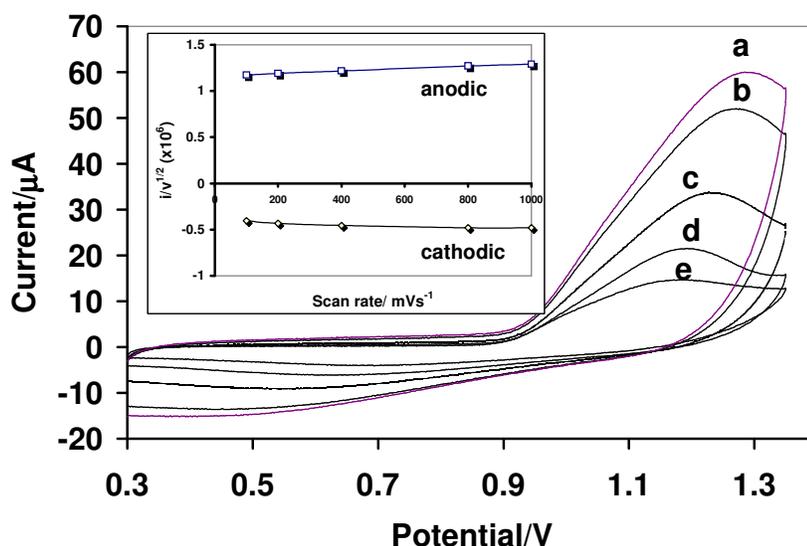


Figure 2. Cyclic voltammograms of 0.2 M benzo-9-crown-3 ether in acetonitrile containing 0.05 M Bu_4NBF_4 0.05 M at a Pt electrode (0.4 mm in diameter), scan rate, a) 1000, b) 800, c) 400, d) 200, e) 100: Inset variation of the peak current function ($i_a/\nu^{1/2}$) vs. Scan rate; $T=25\pm 1$ °C

The above mechanism suggests that under electrolysis condition, the trimerization reaction lead to formation of a trimer cation radical. Therefore, in order to obtain free trimer the electrode potential must be set to potentials in which the trimer cation radical is reduced. Practically, this was accomplished by reversing the potential scan between 1200 to 0 mV. However, the experimental results showed that holding the potential at negative value (e.g. -100 mV) increase the rate of the process. The rate increase may be due to a better condition for migration of the generated $TCTP^+$ toward the electrode surface.

Figure 3 illustrates the recorded cyclic voltammograms at various concentrations of the monomer. Considering for reactions 3 and 4, it is expected that the overall trimerization reaction (where three molecules of the monomer involve in the process) to be third order respect to the monomer concentration.

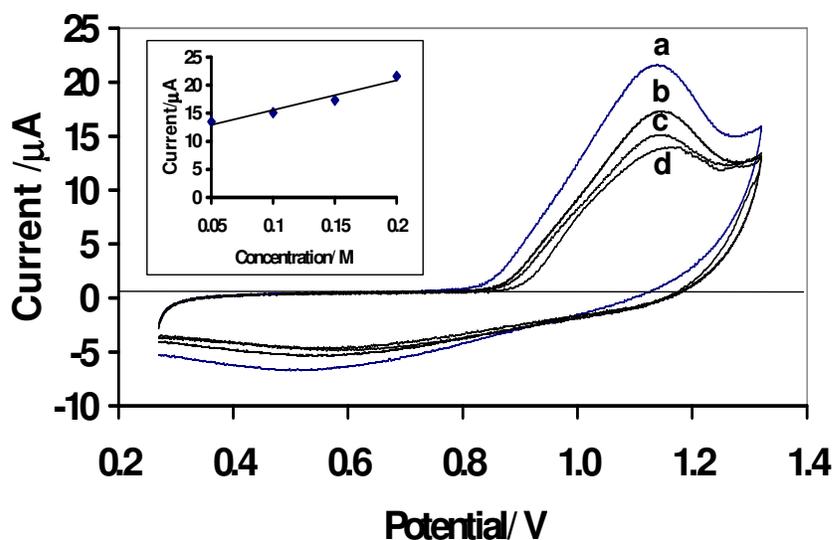


Figure 3. Cyclic voltammograms of a) 0.2, b) 0.15, c) 0.1, d) 0.05 M benzo-9-crown-3 ether in acetonitrile containing 0.05 M Bu_4NBF_4 0.05 M at a Pt electrode (0.4 mm in diameter), scan rate 200 mV/s

However, the obtained results did not show such relationship. Kinetically, it seems that the first order component introduced by the true radical cation/radical three-molecular coupling step is compensated by the reciprocal first order behavior.

Figure 4 shows the changes in the voltammogram with increase the concentration of the supporting electrolyte. It can be seen that the anodic and cathodic peaks slightly increases with increasing the concentration of BuN_4BF_4 up to 0.5 M. This may result of an enhancement in the conductivity of the solution. Due to this fact that the present of, even, small amount of water in the in the solvent or BuN_4BF_4 causes a significant decline the anodic peak. Therefore, using a high concentration of the supporting electrolyte may increase impurity of solution.

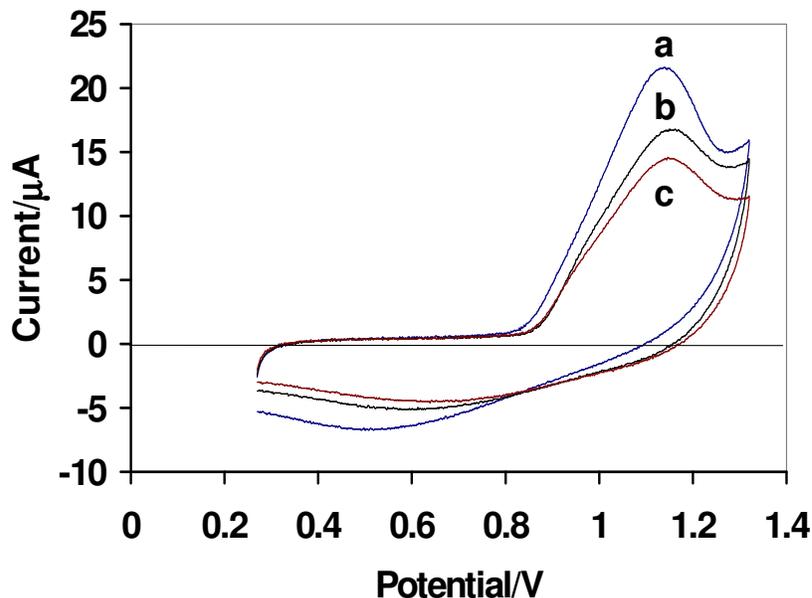


Figure 4. Voltammograms of 0.2 M benzo-9-crown-3 ether in acetonitrile containing a) 0.3, b) 0.1, c) 0.05 M Bu_4NBF_4 0.05 M at a Pt electrode, scan rate 200 mV/s

4. CONCLUSIONS

1. The present work shows that electrochemical anodic oxidation is a good alternative method for synthesizing trimer, tris(9-crown-3)triphylene.
2. However, due to this fact the formed trimer immediately is oxidized after formation, it is necessary to the cycling the potential and holding electrode potential at -100 mV (after each cycle) to increase reaction yield the process.
3. It must be noted that existence of any nucleophile such as water significantly inhibits the process; a special precaution therefore should be taken to purify the initial reagents (e.g. water).

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