

## Study of Anodic Dimerization of Anthracene in Nonaqueous Solvent

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### ABSTRACT

An efficient and ecocentric electrocatalyzed dimerization of anthracene is reported here. The electrooxidative dimerization of anthracene was carried out in an undivided cell. During controlled potential electrolysis, anthracenium radical cation generated by the electrochemical oxidation of anthracene, the radical cation intermediate are rapidly dimerized itself by loss of one another electron and a proton to give related dimer via an electrochemical mechanism pathway. This transformation was achieved by the transfer of electrons between the polynuclear aromatic and electrodes in the presence of non-aqueous solvent and a supporting electrolyte. At constant potential, the mechanism and role of solvents were discussed. This electrocatalyzed dimerization of anthracene was achieved at room temperature and without the use of hazardous reagent. It is simple, atom economic and ecofriendly technique hence it is a part of green chemistry.

**Keywords:** Anthracene, polynuclear, Electrocatalyzed, Green Chemistry

### 1. INTRODUCTION

Anthracene is an organic semiconductor and used as a scintillator for detectors of electrons and alpha particles. However, only a few publications concerned the electrochemical reaction of poly aromatic hydrocarbons and its derivatives.<sup>1, 2, 3</sup> We know that during organic synthesis, energy is required for the beginning of reaction which involves the activation of electrons present in organic molecule to accomplish the transformation of raw materials. This activation has generally been performed by the use of thermal energy or photo energy. Traditional techniques involve use of different time taking various steps requiring high heating and the reagents which may be expensive and hazardous that generates large amounts of toxic waste. Not only the handling of these apparatus and reagents is so difficult and dangerous but also hazardous to the environment. High precautions are needed during the synthesis from the first step to the last step of the reaction including the extraction and purification of the products. In view of environmental mandate, it is necessary to make a global effort to replace the conventional methods by eco-friendly methods for avoiding hazardous reagents and byproducts. Electrochemistry can be considered a green methodology in organic synthesis, due to its non-polluting reagent, the electron.<sup>4</sup> These electron-transfer-driven reactions involve a chemical reaction in which reagents and conditions for each of these reactions need to be designed to give a good yield and a pure product, with as little work as possible.<sup>5</sup> This is the main reason that why electroorganic

synthesis must compete with more traditional and emerging methods. Extensive reviews and research works of electroorganic synthesis are available<sup>6, 7, 8</sup>. At constant potential, a variety of electrochemical transformation takes place when a solution containing an electroactive species i.e. reacting molecule is oxidized or reduced which depend on the structure of reacting molecules and the environment viz. nature of solvent, value of electrode potential and supporting electrolytes.<sup>9,10,11</sup> One or other electrochemical processes can be make favorable by adjusting experimental parameters.<sup>12</sup> Direct electrochemical oxidations or reductions of substrates utilize practically mass-free electrons as the only reagent.<sup>13</sup> Electroorganic synthesis involves application of a potential in the presence of active electrode surfaces and the resulting flow of current drives the oxidation or reduction and subsequent recombination of reactants<sup>14</sup>. After some preliminary discussion it is clear that one or other electrochemical processes can be make favorable by adjusting experimental parameters<sup>15</sup>.

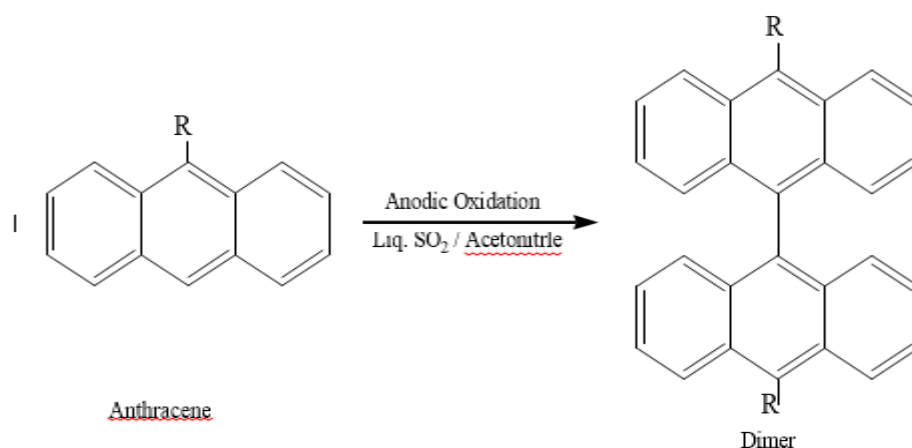


Figure 1: Anthracene to Dimer Conversion

In the present communication we are reporting the result of our comparative study on the electrocatalyzed reaction of polynuclear aromatic compounds. Among the commonly known polynuclear aromatic compounds, anthracene has a relatively low ionization potential<sup>16</sup> and acts as a good  $\pi$ -electron donor in the formation of charge transfer complexes,<sup>17</sup> since it can be readily converted to the corresponding cationic species.<sup>18</sup>

## 2. Results and Discussion

Due to the conjugative structure of polynuclear aromatic compounds, these were the choice of investigation for researchers to explore various transformations take place within them. The redox behavior of anthracene has therefore been the subject of extensive study. A number of chemical methods regarding anthracene derivatives have been reported. Many of these, such as the Gomberg reaction and the Ullman reaction, have the disadvantage that the aryl group must have a substituent that is lost during the coupling process. Biaryls can also be prepared by oxidative dehydrodimerization with various metal salts.<sup>19</sup> The second alternative i.e. electrocatalyzed dimerization also based on the activation of inert precursors through electron transfer, consists

in pulsing the potential of an electrode alternately to anodic and cathodic potentials to generate in turn an electrophile and a nucleophile.<sup>20</sup>

In any electrochemical study, the first question which must be answered is which component of the solution is actually undergoing electron transfer because the direct electrochemical oxidations or reductions of substrates utilize practically mass-free electrons as the only reagent.<sup>21</sup> Thus electrochemical method can provide a powerful means for making and modifying organic molecules. Most anodic reactions of aromatic compounds are initiated by oxidation of hydrocarbon, it is then appropriate to inquire into the nature of the oxidation step. It is generally accepted that most oxidations of aromatic hydrocarbons involve removal of one electron from the hydrocarbon to afford a radical cation. The structure of the radical cation and the environment in which it is created both influence its subsequent reactions. When the nucleophile is another reactant, it can attack the ring to afford a cationic intermediate after a second electron transfer, which most commonly will lose a proton to regenerate the aromatic ring and afford a nuclear substitution product. Electron transfer from aromatic hydrocarbons to form such reactive intermediates as arene cation radicals is playing an increasingly important role in various oxidative processes in organic chemistry.<sup>22,23</sup> The chemical method for the oxidation of anthracene in solvents of low nucleophilicity has been reported extensively in the literature. In particular, the multiplicity of pathways of cation radicals derived from anthracene and its derivatives is of unique interest.

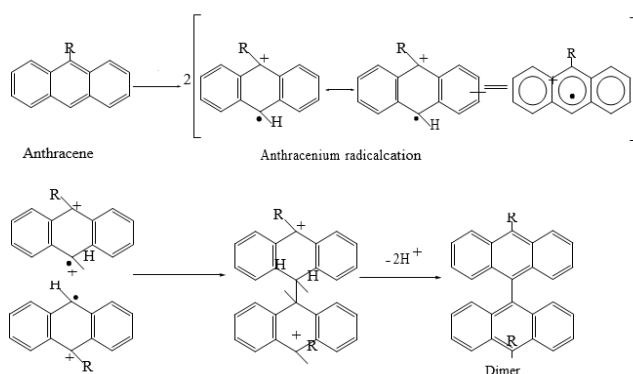


Figure 2: Scheme 1

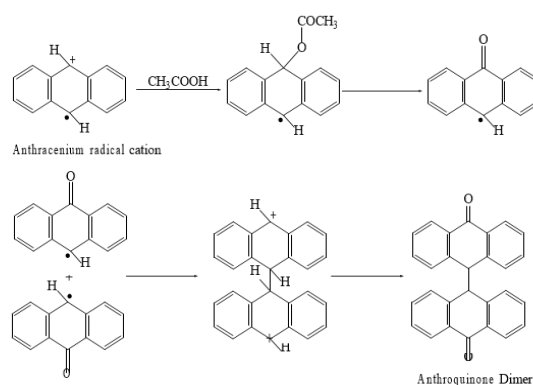


Figure 3: Scheme 2

The Electrochemical oxidation of anthracene in the chosen solvent, acetonitrile, is chemically irreversible on the normal voltammetric time scale due to a reaction between the initially formed radical cation and the solvent. Anodic oxidation of anthracene affords anthracenium radical cation at a constant potential of 1.25 volt in a nonaqueous solvent may be either acetonitrile or a mixture of liq.sulphur dioxide and acetonitrile in the presence of lithium perchlorate as a supporting electrolyte for electrolysis. The electrolysis was monitored by cyclic voltammetry. (Fig. 4) shows the cyclic voltammogram obtained for a 1.0 mM solution of anthracene in the acetonitrile as a nonaqueous solvent. Cyclic voltammetry shows one anodic peak which corresponds to the transformation of anthracene to anthracenium radical cation via one electron process and proves its irreversible nature. Electrochemical oxidation of anthracene in acetic acid affords the formation of anthroquinone dimer with 9-acetoxy anthracene and 9-acetoxy-9,10- dihydroanthracene as a side products. In acetic acid, the formed anthracenium radical cation was attacked.

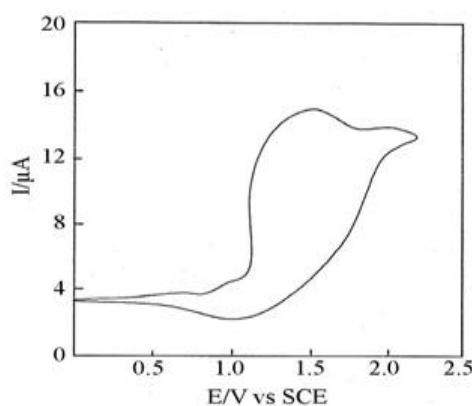


Figure 4: Cyclic voltammogram of 1 mM anthracene in acetonitrile. Scan rate:  $100 \text{ mV s}^{-1}$ ;  $t = 25 \pm 1$  °C

### 3. Experimental Section

The electronic electrochemical equipment used was of an entirely conventional nature. The electrolysis was carried out at constant potential in four necked 50 ml undivided cell. For constant potential electrolysis we have used conventional three electrode undivided cell assembly designed in our laboratory using 1cm x 0.5cm platinum electrode<sup>24</sup> as working as well as counter electrode. The platinum electrodes were surrounded from one side with glass material and saturated calomel electrode<sup>25</sup> (SCE) is used as reference electrode to determine the anode potential.

The electrocatalyzed dimerization of anthracene was carried out via two different routes. In first one, electrolysis was carried out with 0.1mM mol of aromatic substrate in 50 mL of acetonitrile. In second one, reaction mixture contains 0.1 mol of anthracene in 50 mL of nonaqueous solvent containing 20 mL of liquid sulphur dioxide and 30 mL of acetonitrile. Acetonitrile is the choice of solvent because it is resistance and unreactive with intermediate cation radical species<sup>26</sup> in electrooxidative reactions. Liquid sulphur dioxide is also a good choice of solvent for such reactions due to its low nucleophilicity. 0.1M Lithium perchlorate was used as a supporting

electrolyte for electrolysis. The working electrode potential was maintained between 1.20 and 1.40 V vs SCE. At the initial stage, the reaction mixture was transparent and colourless. As electrolysis proceeded the platinum anode surface was covered with dark yellow brownish layer of the product which continuously diffused in the bulk into the solution and the whole reaction mixture gets darkened. For the properly diffusion of product from platinum electrode surface, we used magnetic stirrer. The product obtained after electrolysis was extracted from the solution by simple extraction method using distilled water and chloroform. The product was analysed by chemical method as well as spectral technique. Mps were determined in open capillary tube using Toshniwal's melting point apparatus and are uncorrected. Compounds were purified by column chromatography.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectra were recorded on a Bruker AVANCE II-400 (400  $\text{MHz}$  FT NMR) spectrophotometer using TMS as internal standard; IR (KBr) spectra on Perkin-Elmer 1800 and Shimadzu 8201 PC (4000-350  $\text{cm}^{-1}$ ) FTIR spectrophotometer; mass spectra on Jeol D-300 (EI) and Jeol SX-102 (FAB) spectrometer.

#### 4. Conclusion

Needs for green chemistry become much important in this century. Electrochemical technique is a very useful for achieving environmentally benign organic synthesis, since electrons are a clean reagent and the organic electrochemistry proceeds efficiently under mild conditions. Because in this process, the formation of an active species i.e. anthracenium radical cation from anthracene is achieved by the transfer of electrons between substrate and the platinum electrode, there is no need the use of heating or catalysts. Only an electrochemical cell with two platinum electrodes and electrolytic solution with a supporting electrolyte is used in the anodic dimerization of anthracene, hence it is known as one pot electrochemical synthesis. This technique is very simple and convenient in easy handling, versatility, amenability to automation and less space requirement.<sup>27, 28, 29</sup> Except this, it also follows green chemistry principles; hence electro-organic synthesis is a safer and environmental benign technique and can be considered as a part of green chemistry.

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