

Study on Electrochemical Transformations of Trichloromethylated Organic Compounds Catalyzed by Vitamin B₁₂ Derivative

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論 文 名 : Study on Electrochemical Transformations of Trichloromethylated Organic Compounds Catalyzed by Vitamin B₁₂ Derivative (ビタミン B₁₂ 誘導体が触媒するトリクロロメチル有機化合物の電気化学的変換に関する研究)

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論 文 内 容 の 要 旨

The ability of electrochemistry to generate highly reactive radical and radical ion intermediates in a controlled manner under mild conditions has enabled challenging transformations in organic chemistry. More importantly, indirect electrolysis with a redox mediator can facilitate the redox process of a substrate in more milder conditions with lower applied potential as well as high reactivity and selectivity by avoiding overoxidation/reduction. In this context, vitamin B₁₂ derivatives and its model complex were widely used as a redox mediator for several molecular transformations. The vitamin B₁₂ model complex heptamethyl cobyrinate perchlorate (**C1**, **Scheme 1**) has excellent features such as high solubility in synthetically useful organic solvents. Additionally, slightly solvent dependent redox properties of Co(II)/Co(I) couple appeared at a relatively positive potential around -0.4 V to -0.6 V *vs.* Ag/AgCl and low oxidation state of central cobalt atom stabilized by the monoanionic corrin ring. Generally, electrochemically reduced Co(I) species show supernucleophilicity toward electron deficient centre and initiate redox reaction either by forming alkylated complex or transferring electron which facilitates the reactive radical generation and initiate further reaction sequences. Therefore, we focused on the electrochemical transformation of trichloromethylated organic compounds to value-added chemical mediated by **C1**.

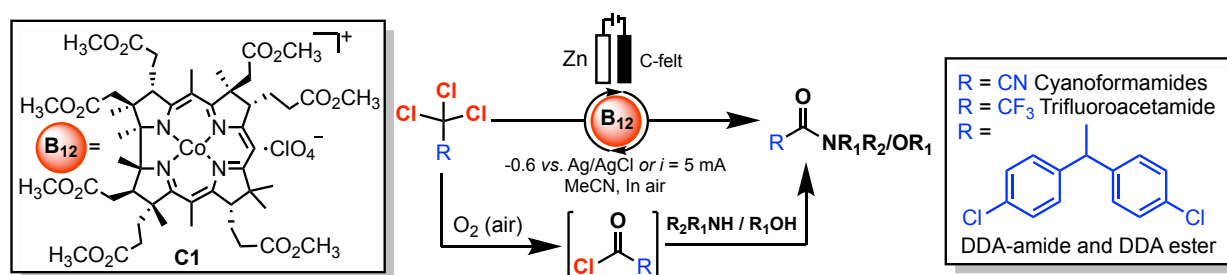
In **chapter 1**, the catalytic efficiency of vitamin B₁₂ derivatives and their model complexes in organic synthetic chemistry has been described briefly.

In **Chapter 2** the first electrochemical synthesis of cyanoformamides from trichloroacetonitrile (CCl₃CN) and secondary amines mediated by the B₁₂ derivative was depicted. Cyanoformamides are a class of compounds widely used as the key building blocks for several classes of compounds, and acts as a natural product. Generally, the available methods for the cyanoformamides synthesis need prefuntionlization of starting materials, multistep procedure, harsh reaction conditions, and toxic reagents as the cyanides source. Therefore, we developed straight forward one pot synthesis of cyanoformamides in air at room temperature in which CCl₃CN converted to cyanoformamides in presence of amines just after 1.5 h electrolysis at -0.6 V *vs.* Ag/AgCl in an undivided cell comprised with C-felt as the cathode, Zn-plate as the anode and **C1** as the redox mediator (**Scheme 1**). The DFT calculation and detail mechanistic studies revealed that homogeneous single electron transfer from the mediator **C1** to CCl₃CN

produce radical intermediate $\text{CCl}_3\text{CN}^\bullet$ which led carbon centered radical. Combined with atmospheric oxygen, the carbon centered radical initiate the reactive cyanoformyl chloride as the intermediate product which reacts with amines to produce cyanoformamides. This method was demonstrated with 41 electronically diverse examples of cyanoformamides with 21 new compounds.

In **chapter 3** Electrochemical approach to trifluoroacetamides synthesis from 1,1,1-trichloro-2,2,2-trifluoroethane (CFC-113a) catalyzed by B_{12} derivative (**C1**) was disclosed. Conventional organic methodologies for trifluoroacetamides synthesis are suffering from limited substrate scope, corrosive reagents etc. Hence, we developed one pot synthesis of trifluoroacetamides using CFC-113a in presence of amines in an undivided cell equipped with C-felt as the cathode, Zn-plate as the anode and by the catalysis of **C1** at -0.6 V vs. Ag/AgCl (**Scheme 1**). Mechanistic studies revealed that the formation of Co-C with the substrate CFC-113a initiated the reaction. Cleavage of Co-C bond could be generated carbon centered radical which led the intermediate product acyl chloride in presence of atmospheric oxygen and nucleophilic attract by amine on acyl chloride produce trifluoroacetamides. This first electrochemical synthesis of trifluoroacetamides was demonstrated with a broad range of products.

In **Chapter 4** electrochemical transform of DDT into amides and esters mediated by B_{12} derivative (**C1**) under air was reported. 1,1,1-trichloro-2,2-bis(4-chlorophenyl) DDT is still allowed in research as well as an effective means for controlling vector-borne diseases. Consequently, it is found at a significant concentration in water or soil due to its persistency towards environment degradation and linked to several health problems of human and wildlife. Although some organometallic complexes were developed for the electrocatalytic dechlorination of DDT under inert conditions in a divided electrolytic cell which needs extra leverage to handle experimental set-up and more importantly the major product derivatives are still toxic such as DDD, DDE, DDMU etc. Here, we demonstrated the facile transformation of DDT into amide and esters in air (**Scheme 1**). Generation of carbon center radical from DDT was initiated by constant electrolysis at $i = 5 \text{ mA/cm}^2$. Incorporation of atmospheric oxygen with the carbon center radical led oxygen center radical, which then led acyl chloride intermediate. Finally, the acyl chloride reacts with amine or alcohol to give amides and esters respectively.



In **Chapter 5** the summary and perspective of this study were described.