

学位 (博士) 論文要旨

(Doctoral thesis abstract)

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論文題目 Title	ラジカルカチオン環化付加反応における分子内電子移動と分子間電子移動の追跡			
<p>論文要旨 (和文要旨(2000字程度)または英文要旨(500words))</p> <p>For the development of green procedures for chemical manipulation of compounds, chemists can now utilize electrons as a traceless redox reagent. More chemical transformations which are initiated by single electron transfer reactions, are developed since they produce less waste from reagents and have unique reaction mechanisms compared to conventional methods. In the many reactions caused by single electron transfer events, radical ion chain pathways have long been recognized by synthetic organic chemists and are thought to be operative in various mechanisms. But since directly counting and identifying how electrons transferred during a reaction is not straightforward, probing electrons to investigate how electrons behave in a reaction was rather difficult. To tackle this task, electrochemistry is a powerful tool to elucidate and identify these mechanisms, since it is easier to control the number of electrons which promote the reaction as electrical current, compared to ways which utilize chemical redox agents or photoredox catalysts.</p> <p>Herein, a series of bis-(beta-methylstyrenes) were designed and synthesized as probes to investigate electron transfer events within a radical cation [4+2] cycloaddition reaction. The probes were designed to have 2 benzene rings connected by a hydrocarbon linker in varying lengths and structures. These benzene rings were equipped with a methoxy group and a conjugated alkene to the benzene ring. When a styrene unit is oxidized into its radical cation form, it can go through a radical cation [4+2] cycloaddition reaction with a diene. After the formation of the cyclohexene, a sequential electron transfer can occur with either another intramolecular styrene or another intermolecular styrene. The results of these electron transfer events will be preserved as a cyclohexene therefore, probing of electron transfer</p>				

events will be available through investigation of the yields of mono-cycloadducts and bis-cycloadducts. These probes were designed to have small molecular weights for the convenient investigation of reaction yields using the GC-MS. In similar research done prior to this using bis- (aryl vinyl ethers), the electron transfer events were seen to be affected largely by the length and structure of the hydrocarbon linkers. When dimethyl methylene structure was used as the linker in the bis- (aryl vinyl ether) case, it exhibited results where yields of mono-cycloadducts were low and bis-cycloadducts were high throughout the reaction and (sub)stoichiometric amounts of electric current was needed to complete the reaction. From these results, intramolecular electron transfer was presumed but intermolecular electron transfer seemed to be less effective.

In this investigation using the bis-(beta-methylstyrenes), it is demonstrated that even in the case where dimethyl methylene linker was used to connect the two styrene units, high mono-cycloadduct yields were obtained. From these results, intramolecular electron transfer seemed to be less effective. On the other hand, 0.03-0.05 F/mol was enough to complete the radical cation cyclo-addition reaction in every bis-styrene used in this investigation. The small amount of electricity needed for the completion of this reaction suggested a strong effect of intermolecular electron events taking place during the reaction. In both investigations, dimethyl methylene linker proved to promote the most effective electron transfer events completing the reaction in 0.03 F/mol which meant, 1 electron was able to conduct 66 cycloaddition reactions. In this investigation, by molecular design, a radical cation cycloaddition reaction was completed in a truly catalytic amount of electricity. By the utilization of bis-styrene probes, the involvement of a chain pathway was confirmed during the radical cation cycloaddition reaction.