（様式５）

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学位（博士）論文要旨
(Doctoral thesis abstract)

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論文題目 Title	光/電気エネルギーを用いた有機電子移動反応 Photo-/Electrocatalytic Chemistry: Electron Transfer in Synthetic Organic Reaction

The photo-/electrocatalytic chemistry field has been developed and focused on as sustainable chemical reactions, since light energy is directly and electrical energy is indirectly gained from sunlight. Their reactions are commonly promoted by electron transfer, which is mainly carried out by photocatalysts or electrodes. Metal complex photocatalysts or organophotocatalysts have been widely studied in synthetic organic chemistry; however, semiconductors, which are represented by TiO_2 photocatalysts and widely used in the materials field, are still a few reported. TiO_2 photocatalysis is categorized within interfacial electron transfer, namely, the gap of reactivity between it and electrocatalysis should be verified.

The purpose of this research was development of TiO_2 photocatalytic and electrocatalytic electron transfer chemistry modeling the radical cation Diels-Alder reaction.

In chapter 2, radical cation Diels-Alder reaction of β-methylstyrenes by TiO_2 photocatalysis have been demonstrated. Optimization of controls and scope of dienes were examined using *trans*-anethole as a model, suggesting that TiO_2 photocatalysis promoted cycloadditions and steric hindrance of diene have effect for the reaction. Isomerization using *cis*-anethole showed that mechanism was stepwise and there were two ways that isomers were produced before or after trapping of diene. It was found that a non-protected alcohol introduced at the β-position of styrenes gave cycloadducts in good yields. Significantly, the corresponding cyclohexene of *trans*-β-methylstyrene was obtained in acceptable yield by TiO_2 photocatalysis, which was impossible to synthesize by Ruthenium photocatalysis and electrodes electrocatalysis. The reaction mechanism was proposed that it is mainly SET-oxidation and SET-reduction by TiO_2 photocatalysis.

In chapter 3, the reaction mechanism of the Photo-/Electrocatalytic Radical Cation Diels-Alder reaction described in Chapter 2 was analyzed by CV measurements and supported by DFT calculations. The EC-backward-E process, which SET-redox was occurred on single electrode, was successfully observed using CV analysis for β-methylstyrenes which was found to be reacted with diene. The reasonable radical cation intermediates were designed from the HOMO and spin density plots using DFT calculations. In case of 2,4-dimethyl *trans*-β-methylstyrene and diene, spin density plots were on its cyclohexene double bond, suggesting that this intermediate was unstable and had to receive reductive-SET immediately for cycloaddition. Therefore, TiO_2 photoredox had an advantage for this reaction.

In chapter 4, radical cation Diels-Alder reaction of arylidene cycloalkanes by interfacial electron transfer catalysis has been demonstrated. The cycloaddition of 4-methoxyβ-dimethylstyrene and diene was obtained less than using *trans*-anethole under TiO_2 photocatalytic and electrodes electrocatalytic conditions, suggesting that the additional methyl group at the β-position of styrene caused steric hindrance and interrupted the reaction. The 4-methoxy, 2,4-dimethyl and non-substituted β-cycloalkane styrenes were prepared to examine the effect of tying up two methyl groups; unexpectedly, the arylidene cyclobutane was found to give spiro ring in acceptable yield, and 4-methoxy β-cycloalkane styrenes were reacted with diene by more electrocatalytic condition than photocatalytic condition. It was suggested that TiO_2 photocatalytic reductive-SET seems to decrease the reactivity of intermediates in case of 4-methoxy β-disubstituted styrenes.

This research will support to use of TiO_2 photocatalyst in synthetic organic chemistry and understand the interfacial electron transfer catalysts. I hope that this study will promote the sustainable synthetic chemistry field and lead to a breakthrough in the various energy problems facing us today.

（英訳）※和文要旨の場合(300 words)

If the abstract is written in Japanese, needed to translate into English.(300 words)