

Acceleration of Diels-Alder Reaction in Aqueous Fluorinated Micelles and Droplets: An Application for Electrolytic Cycloadditions

Kohsuke Nishimoto, Shokaku Kim, Yoshikazu Kitano,
Masahiro Tada and Kazuhiro Chiba

Laboratory of Bio-organic Chemistry,
Tokyo University of Agriculture and Technology,
3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan

During the last two decades, organic reactions in aqueous media have been attracting increasing attention. Furthermore, It has been established that some Diels-Alder reaction dramatically accelerated in aqueous media. These have been alternatively ascribed to hydrophobic association of the reacting partners, micellar catalysis, solvophobicity, high internal solvent pressure, cohesive energy density, solvent polarity and hydrogen bonding. Previously, we found a moderate acceleration property of some Diels-Alder reactions in aqueous SDS dispersion even in the absence of Lewis acids.¹⁾ On the other hand, it has proven that fluorocarbon solvents showed poor miscibility and lower solvating power than normally associated with non-polar organic liquids (“fluorophobic effect”), and these highly fluorinated solvents showed solvophobic properties of other liquids lead to rate enhancements similar to those observed in water. In these exclusive solvents, however, most of Diels-Alder partners unescapably show very low solubility to limit the reaction efficiency and productivity.

We hypothesized that the solvophobic effects for such reactions having large negative volumes of activation could be effectively introduced by exposing both of the reaction partners to the solvents of low solvating power. It was further expected that the construction of widely spread interface of fluoruous phase in an aqueous media might effectively adsorb the substrates to accelerate the intermolecular reaction by a possible reciprocal repellency from both side of the fluoruous and the aqueous phase. Based on assumptions, we initially found the marked acceleration of a Diels-Alder reaction in the fluoruous micelles²⁾ and microdroplets formed fluorinated liquid and detergent in water as substrate-exclusive bi-phase reaction fields (Figure 1).

The mixture of fluoruous micelles and liquid formed a fine droplet in water, which showed marked acceleration property of Diels-Alder reaction. At the interface of droplets in water, most of Diels-Alder partners must have adsorbed at the interface to complete the cycloaddition reaction by the highly exclusive property from both phases. Furthermore, it showed rate enhancement of Diels-Alder reactions involved electrochemically-generated quinones in this media (Figure 2).

References

- 1) Chiba K.; Jinno M.; Nozaki A.; Tada M.; *Chem. Commun.*, 1403-4, **1997**
- 2) Chiba, K.; Kono, Y.; Kitayama, M.; Uchiyama, R.; Kim, S.; Kitano, Y.; Tada, M.; *Electrochemistry Communications*, **2001** 3(2), 63-66.

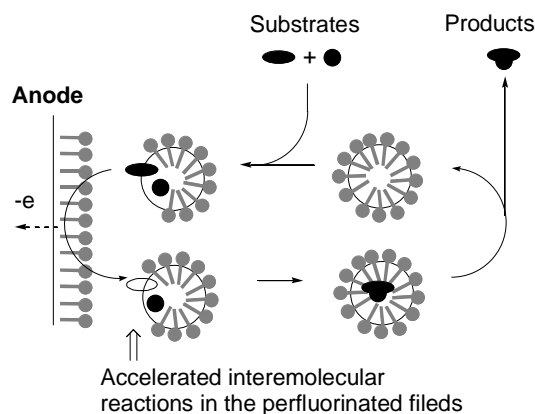


Figure 1. Electrolytic Activation and Reaction in the Aqueous Perfluorinated Micellar and Droplet Fields.

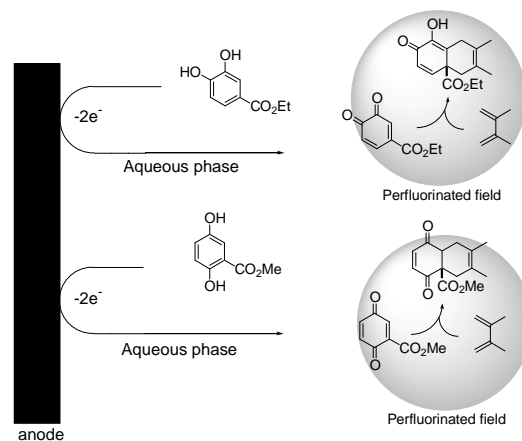


Figure 2. A Proposed Mechanism of Electrochemical Diels-Alder Reactions in the Fluorinated Reaction Field.