

## Thesis Summary

Dynamic Solvent Effect on the Lifetime of Singlet Diradicals with  $\pi$ -Single Bonding  
( $\pi$ 単結合性をもつ一重項ジラジカルの寿命に及ぼす動的溶媒効果)

Name LIU QIAN (刘倩)

During the last few decades, much effort was devoted to investigating the dynamic solvent effects which is understood in terms of an increase in friction between molecules in highly viscous solvents on the thermal and light-induced isomerization reactions and the results suggest that both polarity and viscosity of solvents play pivotal roles in molecular isomerization. A typical study of dynamic solvent effects on thermal cyclization of 1-prop-2-enylidene-naphthalen-2-one derivatives discloses that high viscosities resulted in slow thermal rate process for thermal ring closure. In 2016, the dynamic solvent effect was firstly observed in ionic liquid for the thermal isomerization of 1-prop-2-enylidene-naphthalen-2-one derivatives. Furthermore, solvent viscosity served as an experimental tool to identify the moving moiety of molecules. For example, the relative mobility moiety is the ethenyl instead of the naphthalenone moiety during thermal cyclization of 1-prop-2-enylidene-naphthalen-2-one derivatives. Besides, dynamic solvent effects can also be used to explore the photochemical denitrogenation mechanism of DBH.

Regarding solvent dynamic effect on the reactivity of diradicals featuring  $\pi$ -single bonding as the important key intermediates in the process of bond homolysis, moderately linear correlation was observed between the lifetime ( $\tau_{293} = 1/k_{293}$ ) of localized singlet diradical 2,2-diethoxy-1,3-diphenylcyclopentane-1,3-diyl and solvent polarity. However, the deviation of some points from the roughly linear correlation suggested that the lifetime value cannot be explained by polarity only. In high viscous viscosity, the transition state theory cannot be applied to explain the transformation of molecular due to the slow thermal fluctuations comparing with the structure change of the reactant. High viscous solvents can be caused by high pressure. Therefore, high pressure seems to be an ideal tool to provide a convenient way of exploring the dynamic solvent effect. Recently, the dynamic solvent effects on the rates of isomerization of localized singlet diradicals having bulky aryl groups to  $\sigma$ -single-bonded isomers was investigated in our laboratory. We found an almost linear relationship between the lifetime which was determined by the isomerization of localized singlet diradicals and the solvent viscosity. Most notably, the  $\tau_{293}$  of the singlet diradical having bulky aryl group reached 2 s at room temperature in the highly viscous solvent under high-pressure conditions. In addition, the dynamic sol-

vent effects on the rate of isomerization of localized singlet diradicals having a macrocyclic structure was investigated in our laboratory. We found that comparing with parent singlet diradical lacking a macrocyclic structure, more pronounced viscosity effect for isomerization of diradical with a macrocycle structure was observed. Besides, regression analysis was performed to evaluate the impact of solvent viscosity and polarity.

In this study, the solvent polarity and viscosity effects on the lifetime ( $\tau_{293}$ ) values of the singlet diradicals **S-DR4a** (R = CH<sub>3</sub>) and **S-DR4b** (R = (CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>) which are determined by the rate constant for the isomerization of  $\pi$ -single bonding singlet diradicals to the  $\sigma$ -bonded isomers were thoroughly investigated in 18 different solvents including binary mixed systems containing ionic liquids with considerably wide range polarity  $\pi^*$  (from -0.11 to 1.00 kcal mol<sup>-1</sup>) and viscosity  $\eta$  (from 0.24 to 125.4 mPa s) variation. Experimental evidence is displayed for the crucial roles of polarity and viscosity in isomerization of diradicals with  $\pi$ -single bonding character to the  $\sigma$ -bonded isomer. Particularly, it was discovered that in low- $\eta$  solvents ( $\eta < 1$  mPa s) such as *n*-hexane and diethyl ether, isomerization process described by lifetime parameter of diradicals is more dependent of solvent polarity. In high- $\eta$  solvents ( $\eta > 2$  mPa s), specifically in a binary mixed solvent system of [BMIM][PF<sub>6</sub>] and GTA or DMSO, the rate of isomerization was largely influenced by  $\eta$  in addition to  $\pi^*$ . Slower isomerization of diradicals were observed in more viscous solvents.

Moreover, the singlet diradical **S-DR5** with a long alkyl chain at the remote position from the reaction site was generated from the corresponding azoalkane **AZ5**, and the solvent effect on the reactivity of **S-DR5** was compared with that in the case of **S-DR4b**. The difference in the reactivities of **S-DR4b** and **S-DR5** would clarify the relative motion of cyclopentane moiety rather than the alkoxy group during the isomerization of the planar **S-DR4b** and **S-DR5** to **CP4b** and **CP5** having puckered structures, respectively.

Finally, the regression analysis clarified that  $\tau_{293}$  was determined by the effects of both  $\pi^*$  and  $\eta$ . The present study provides insight into the nature of singlet diradicals and guidelines for further extending the lifetime of the  $\pi$ -single bonding compounds.