ESTIMATION OF SOLVENT EFFECTS FOR THE COMPLEXING REACTION OF PROPYLENE AND NICKEL DITHIOLENE

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Introduction

■ **Nearly all of the actual approaches for olefins separation exhibit severe disadvantages: low reagent selectivity and high energy consumption.**

■ **Recently, Wang *et al.* found that the transition metal dithiolene complexes can reversibly and selectively react with simple olefins under mild conditions.**
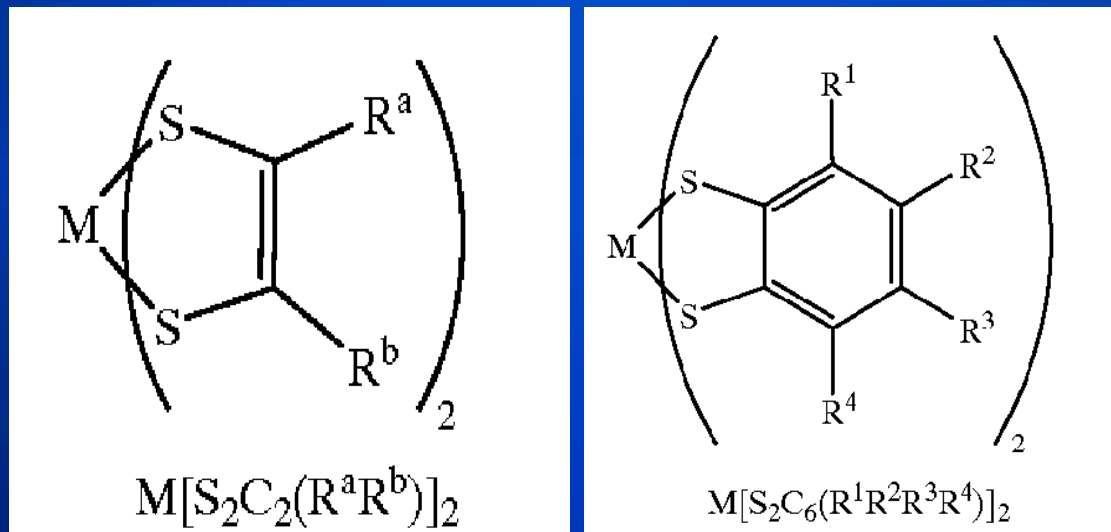

Figure 1: The geometries of the dithiolene complexes.

Introduction

■ Theoretical studies on the reaction of ethylene and $Ni(S_2C_2R_2)_2$ (R = H, CN, CF_3) in gas phase were performed by Fan *et al.*.

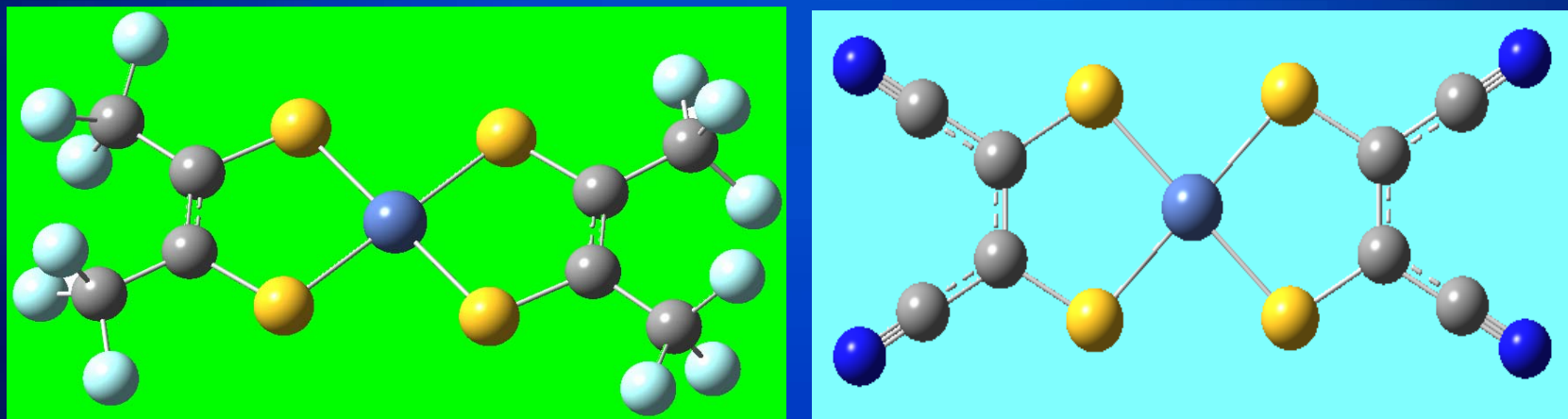■ There are few studies on the solvent effects of such reactions.

Figure 2: The geometries of $Ni[S_2C_2(CF_3)_2]_2$, $Ni[S_2C_2(CN)_2]_2$.

Computational methods

■ **The geometries of all the stagnation points, and the corresponding frequency calculations, are achieved by means of DFT.**

■ **The influences of different solvents have been investigated based on the Onsager model.**

Reaction process of complexing propylene with Ni Dithiolene
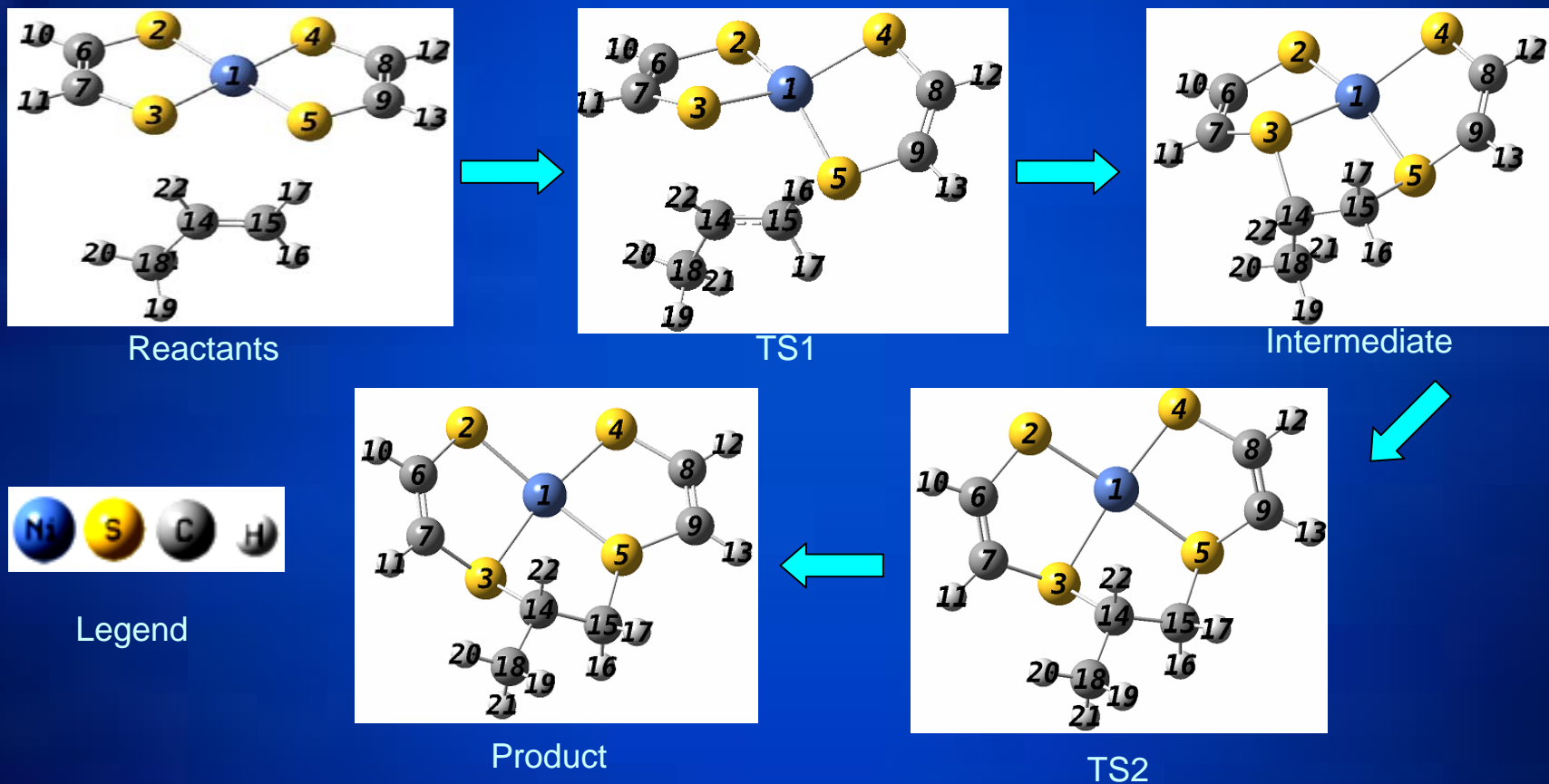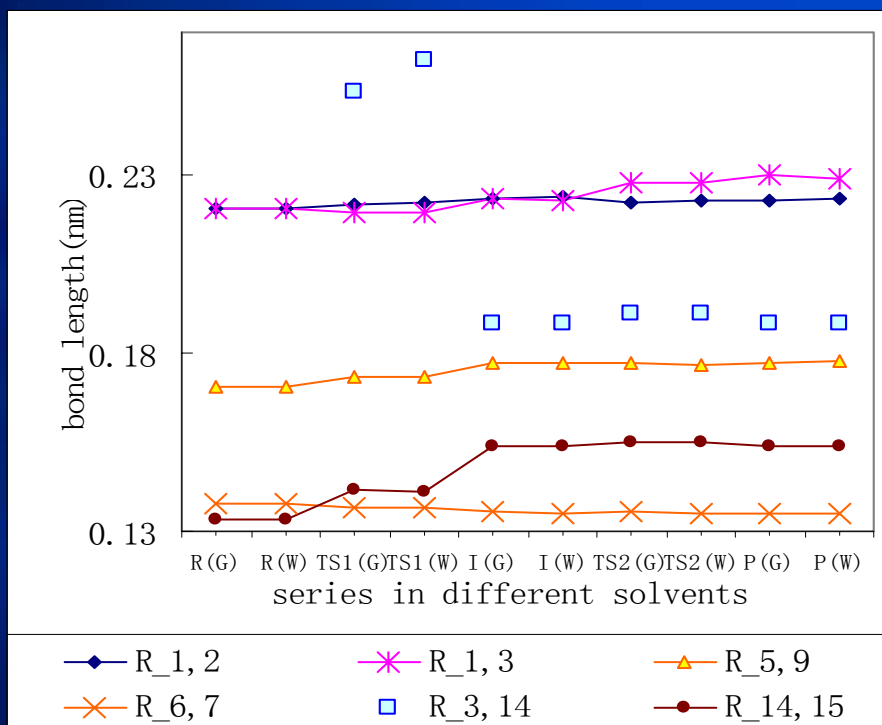

Reactants

TS1

Intermediate

Legend

Product

TS2

Figure 3: Optimized geometries of all the stagnation points in the reaction process .

Solvent effects

Molecular Geometry Structure

1) The C−C bond length ($R_{14,15}$) of propylene and the length of the dithiolene C−S bond is increased during the reaction.

2) The solvents only make slight effects on the geometries of the R, TS, I, and P.

Figure 4: Bond Length (nm) of Reactants, Intermediates, Transition States, and Products in Typical Solvents.

Solvent effects

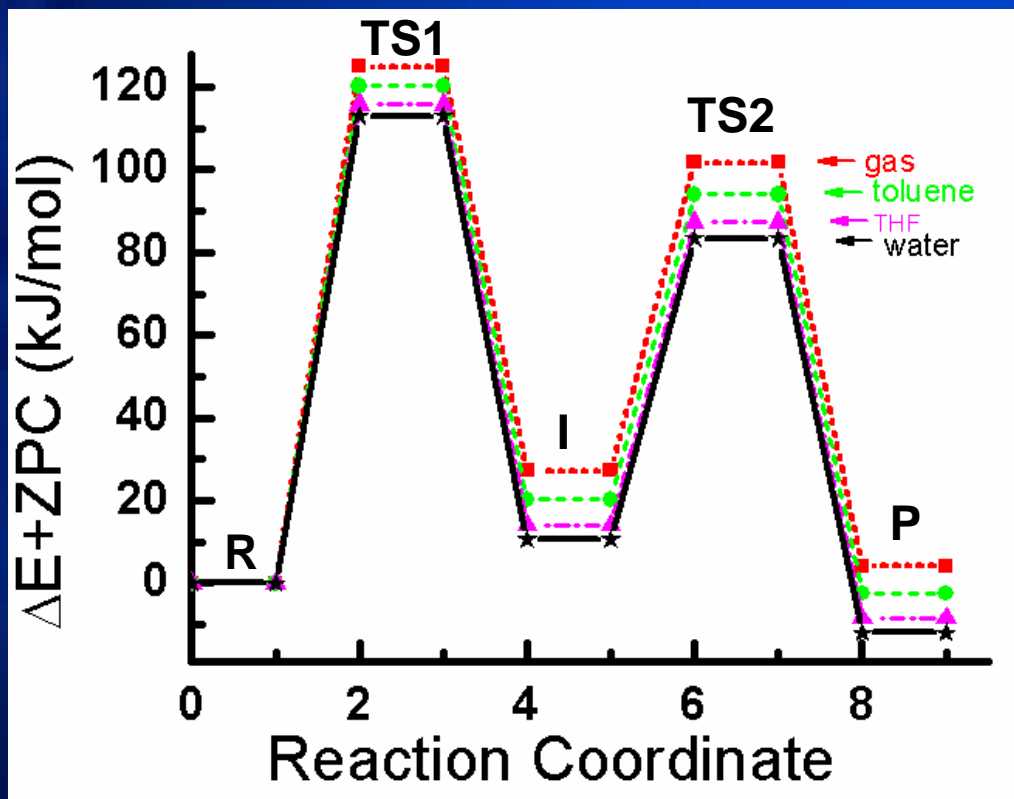## Molecular Dipole Moment (MDM)
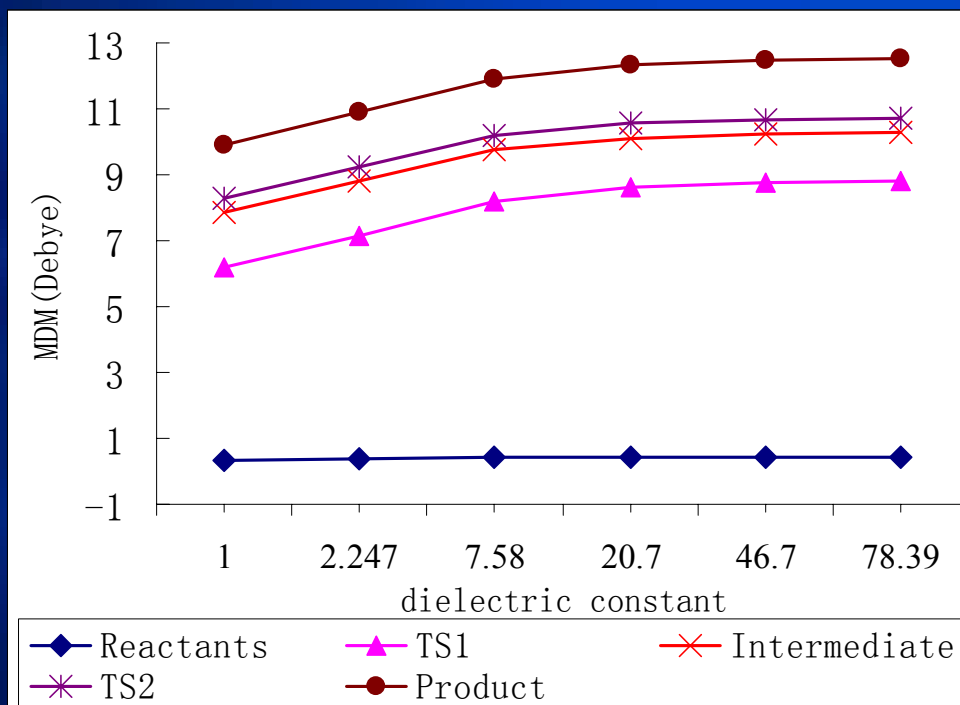
1) **This reaction is a MDM-increasing process in any solvent.**

2) **The MDM in any stage will increase monotonously when the the solvent polarity is increased.**

Figure 5: Molecular Dipole Moments (Debye) Corresponding to the Reaction Process in Different Typical Solvents.

Solvent effects

Activation Energy

1) **The energy barriers corresponding to TS1 and TS2 will be lowered as the dielectric constant of the solvent is increased.**

2) **The energy barrier of TS1 is larger than that of TS2.**

Figure 6: Schematic presentations of potential energy surface of the reaction in four typical solvents.
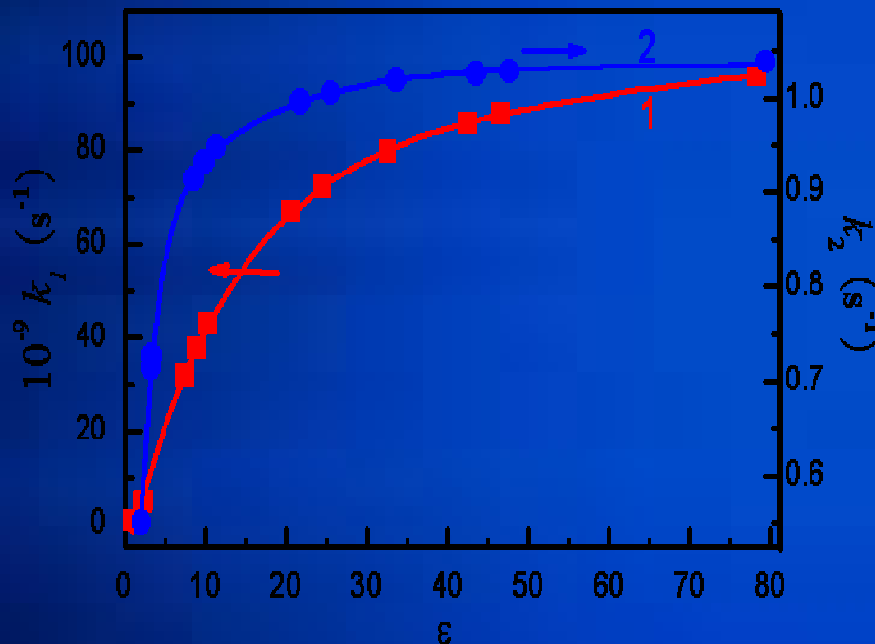
Solvent effects

Activation Energy

Figure 7: Variations of the activation energies of TS1 (1) and TS2 (2) with the dielectric constants ε.
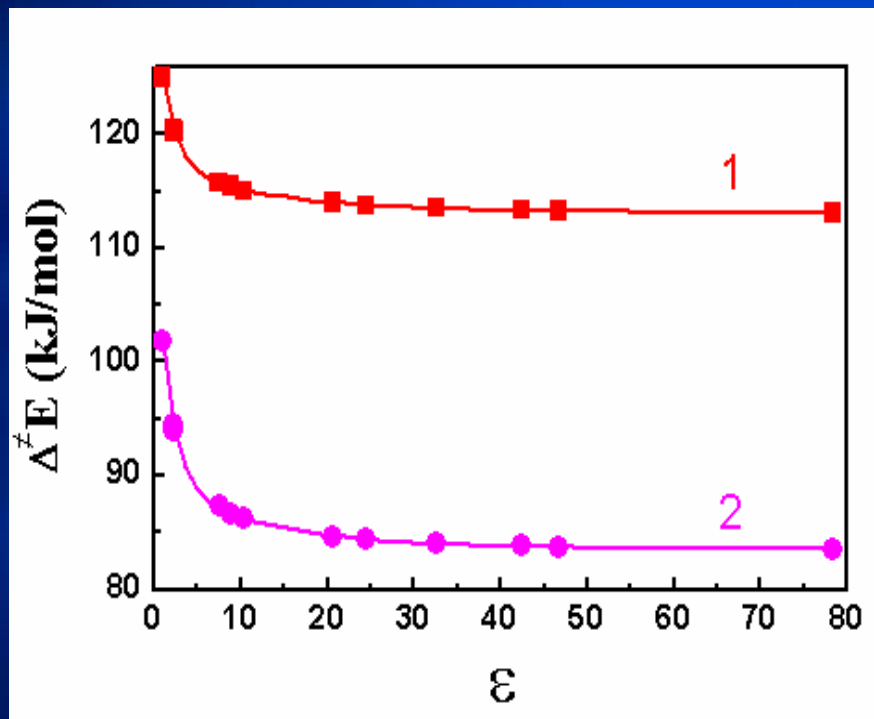
1) The energy rapidly decreases when ε less than 20, and then slowly approaches a certain threshold.

2) The relationship between $\Delta^{\neq}E$ and ε can be expressed in an exponential manner.

$$\Delta^{\neq} E_i = A_i \exp\left(-\frac{\varepsilon}{n_i}\right) + B_i \exp\left(-\frac{\varepsilon}{t_i}\right) + C_i$$

Solvent effects

Rate Constants

1) Due to $k_1 \ll k_2$, step-1 of the reaction should be the rate-determining step.

2) The variations of k_1, k_2 with ε are also in conformity with an exponential functions.
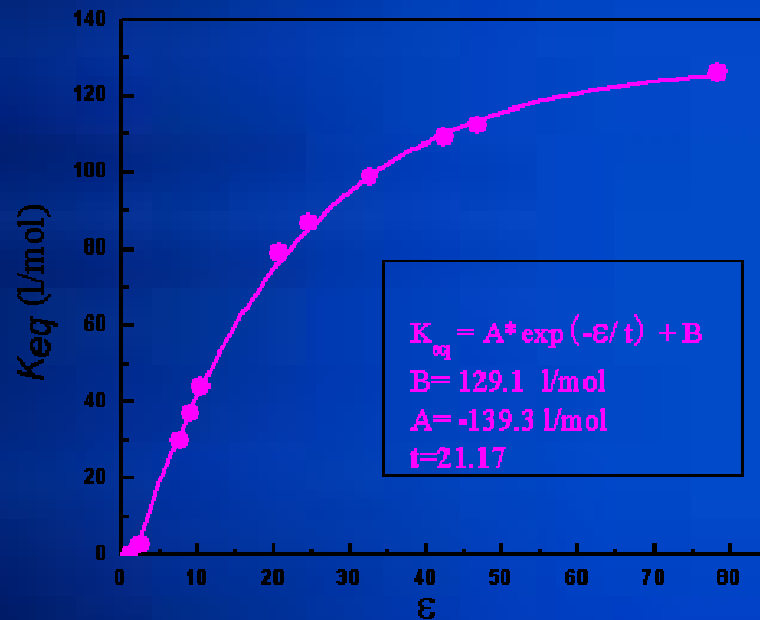
$$m_i k_i = A_i \cdot \exp\left(-\frac{\varepsilon}{n_i}\right) + B_i \cdot \exp\left(-\frac{\varepsilon}{t_i}\right) + C_i$$

Figure 8: Variations of the rate constants with the dielectric constants ε in different solvents.

Solvent effects

Equilibrium Constants

1) The solvent effect on K_{eq} is obvious in the appropriate range of ε.

2) The relationship between the K_{eq} and ε can be also expressed with an exponential formula.

Figure 9: Variations of the equilibrium constants with the dielectric constants εin different solvents.

Conclusion

- The reaction is a two-step process, and the first step is the rate-determining step.

- The solvents will make slight changes on the geometries of all the stagnation points.

- This reaction is a MDM-increasing process in any solvent, and the MDM of R, TS, I and P will increase when the solvent polarity is increased.

- The activation energies ($\Delta^{\neq}E$) will decrease exponentially when the dielectric constant of solvents increases, indicating that the barriers of the reaction potential energies will decrease and the reaction becomes easier to occur.

- The k_i and the K_{eq} will increase exponentially with the polarity of solvent increasing. This demonstrates that the reaction rate, as well as the rate of producing complex may be controlled by selecting the solvents.

- All of these relationship may be seen as a reference for solvent selection in olefin separation practice.

Thank You!

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