

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

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### ABSTRACT

The formation of olefin complexes is of potential importance in the separation of olefins. The solvents affect the activation energies, and hence the rates and equilibrium constants of the complexing reactions, which performance should be well estimated for the purpose of industrial practice. The solvent effects on the complexing reaction of propylene and nickel dithiolene  $\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2 + \text{C}_2\text{H}_4=\text{CH}_2 \rightarrow \text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2 \cdot \text{C}_2\text{H}_4=\text{CH}_2$  are studied in this work, using density functional theory with B3LYP and an Onsager model. Complete optimizations of all the stagnation points are performed in benzene, toluene, tetrahydrofuran, dichloromethane, 1,2-dichloroethane, acetone, ethanol, methanol, 1,2,3-propanetriol, dimethylsulfoxide and water, respectively. The reaction of complexing nickel dithiolene with propylene is a two-step process: the first step coordinates the propylene to S atoms in dithiolene, forming a trans-structural intermediate. The second step then yields the cis-structural product. The activation energy of the first step is higher than that of the second, indicating that the first step is the rate-determining step. The solvents make slight changes in the geometries of the reactants, transition states, intermediates and products. However, the corresponding molecular dipole moment becomes large with increase of the solvent polarity, which is beneficial to accelerate the reaction. Furthermore, the activation energies of the first (or second) step will exponentially decrease from 125.0 to 113.0  $\text{kJ}\cdot\text{mol}^{-1}$  (or from 101.8 to 83.43  $\text{kJ}\cdot\text{mol}^{-1}$ ) when the dielectric constants of solvents increase from 1.00 to 78.39, while the reaction rates of the first (or second) step exponentially increase from  $0.7673 \times 10^{-9}$  to  $96.20 \times 10^{-9} \text{ s}^{-1}$  (or from 0.5503 to  $1.038 \text{ s}^{-1}$ ), and the equilibrium constants rapidly increase from 0.5066 to 343.4  $\text{l}\cdot\text{mol}^{-1}$ . The sharp variations of activation energies, rate constants, and equilibrium constants appear when the value of the dielectric constant of solvents lies between 1 and approximately 20, while these variations become mild when the dielectric constant of solvents is larger than 20. All of these results demonstrate that the complexing reaction of propylene and nickel dithiolene become much easier and faster to occur in polar solvents. The relationship between the equilibrium constants of the complexing reaction  $K_{\text{eq}}$  and the dielectric constants of solvents  $\epsilon$  can be presented mathematically as  $K_{\text{eq}} = A \cdot \exp\left(-\frac{\epsilon}{t}\right) + B$  with correlation parameters  $A = -378.4 \text{ l}\cdot\text{mol}^{-1}$ ,  $B = 350.7 \text{ l}\cdot\text{mol}^{-1}$  and  $t = 21.17$ . This relationship may be seen as a reference for solvent selection in olefin separation practice.

**Keywords:** Density functional theory, Solvent effects, Performance estimation, Olefins, Nickel dithiolene

## 1 INTRODUCTION

With the advance of the petrochemical industry, olefins have been extensively applied in the production of polymers, acids, esters, and ethers (Sundaram et al., 1995). The separation of olefins, especially of the approaches for olefin separation (Grantom & Royer, 1987; Suzuki et al., 1997; Blytas, 1992; Murata et al., 1994; Shibahara et al., 1996; McKenna et al., 1983) exhibit severe disadvantages of low reagent selectivity and high energy consumption.

Wang et al. found in recent years that the 1,2-enedithiolate (dithiolene) complexes can reversibly and selectively react with simple aliphatic olefins to form 1/1 adducts under mild conditions by the experimental method of UV-vis spectroscopy (Wang & Stiefel, 2000; 2001), which presents potential for olefin separation. They also discovered that the dithiolene complexes are not poisoned by hydrogen, carbon monoxide, acetylene or hydrogen sulfide, which are commonly present in olefin streams, presumably because olefin binding occurs through the sulfur ligand rather than the metal center. In addition, Schrauzer et al. reported that  $\text{M}(\text{S}_2\text{C}_2\text{Ph}_2)_2$  (M

= Ni, Pd, Pt; Ph = Phenyl group) reacts with norbornadiene (Schrauzer & Mayweg, 1965; Schrauzer & Rabinowitz, 1968; Schrauzer et al., 1970), and Wing et al. also proposed that  $\text{Ni}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2$  reacts with norbornadiene and 2,3-dimethyl-1,3-butadiene to form 1/1 olefin adducts (Wing *et al.*, 1970), where the olefin binds to ligand S atoms rather than the metal. Theoretical studies on the reaction of ethylene and  $\text{Ni}(\text{S}_2\text{C}_2\text{R}_2)_2$  ( $\text{R} = \text{H}, \text{CN}, \text{CF}_3$ ) in gas phase were performed by Fan et al. (2002), using density functional theory (DFT) with B3LYP (Becke, 1993; Lee et al., 1988). It was found that this reaction is a two-step process, and the electron-withdrawing groups lower the barrier for the association of olefins and Ni dithiolene complexes and stabilize the intermediates and products relative to the reactants.

However, few of these studies discuss the solvent effects on such reactions. It is beneficial to study the solvent effects on the reaction of olefins and Ni dithiolene complexes forming, considering that solvents may influence the geometries and electrical structures of molecules, and thus the processes of chemical reactions (Field & Bash, 1990). The solvent effects on the reaction mechanism, rate and equilibrium constants of the reaction between propylene and Ni dithiolene are studied in the present work, using density functional theory (DFT) with B3LYP and an Onsager model. The whole optimization of all stagnation points existing in the reaction potential profiles are carried out in the gas phase, as well as solvents benzene, toluene, tetrahydrofuran, dichloromethane, 1,2-dichloroethane, acetone, ethanol, methanol, 1,2,3-propanetriol, dimethylsulfoxide and water, respectively. It is shown that this reaction is a two-step process, and the first step is rate-determining. In addition, the solvents make slight changes in the geometries of the reactants, transition states, intermediates and products. However, the rapid increase on the corresponding molecular dipole moment (MDM) is observed with increasing solvent polarity, which is beneficial to accelerate the reaction. Furthermore, the activation energy of the reaction decreases exponentially, as the dielectric constants of solvents become large, while the reaction rates and the equilibrium constants increase exponentially to be saturated. These demonstrate that the reaction of complexing propylene to Ni dithiolene may become easier and faster and may attain higher rate of product in the strong polarity solvents, in agreement with a great many experimental studies.

## 2 COMPUTATIONAL METHODS

All calculations of the present work are performed with Gaussian03 program package (Frisch *et al.*, 2003). The geometries of reactants, transition states, intermediates and products are optimized, as well as the corresponding frequency calculations, by means of DFT with B3LYP. A slightly modified version of Hay and Wadt's LANL2DZ (Hay & Wadt, 1985; Wadt & Hay, 1985) with the two outermost  $p$  functions replaced by a new function with (41) split (Couty & Hall, 1996), and a relativistic effective core potential (ECP) (Schwefdtfefer et al., 1989; Andrae et al., 1990) is used for Ni, while the 6-31G(d) (Ditchfield et al., 1971; Hehre et al., 1972; Hariharan & Pople, 1973; Hariharan & Pople, 1974) basis set is utilized for all the other atoms. In addition, the nature of all transition states is characterized by the imaginary frequency and verified by the intrinsic reaction coordinate (IRC) approach (Gonzalez et al., 1990; Gonzalez & Schlegel, 1990; Harding *et al.*, 1980). Moreover, the influence of different solvents has been investigated based on an Onsager model (Onsager, 1938; Wiberg et al., 1987; Wiberg et al., 1995; Wong et al., 1992). All of the calculations are performed at temperature  $T = 298.15$  K and pressure  $P = 101.33$  kPa, and the energies have been modified by zero point corrections.

The key formula presented in Equation (1) is adopted, in order to find the rate constants of the reaction  $\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2 + \text{C}_2\text{H}_4=\text{CH}_2 \rightarrow \text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2 \cdot \text{C}_2\text{H}_4=\text{CH}_2$  at temperature  $T$ .

$$k(T) = \frac{N_A k_B T}{h} \left[ \frac{Q_{\text{TS}}^\ddagger / V_{\text{TS}}}{\prod_i (Q_{\text{R}_i} / V_{\text{R}_i})} \right] \exp\left(-\frac{\Delta E_0}{RT}\right), \quad (1)$$

where  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$  is the Avogadro number,  $k_B = 1.380662 \times 10^{-26} \text{ kJ} \cdot \text{K}^{-1}$  the Boltzmann constant,  $h = 6.626176 \times 10^{-37} \text{ kJ} \cdot \text{s}^{-1}$  the Planck's constant, and  $R = 8.314 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  the gas constant  $Q_{\text{TS}}^\ddagger$  and  $Q_{\text{R}_i}$  represent the molecular total partition function of transition state and reactant  $i$ ,  $V_{\text{TS}}$  and  $V_{\text{R}_i}$  the volume of transition states and reactant  $i$ , and  $\Delta E_0$  is the energy barrier of activation by zero point corrections. The equilibrium constant  $K_{\text{eq}}$  can be obtained directly by the thermodynamic relationship.

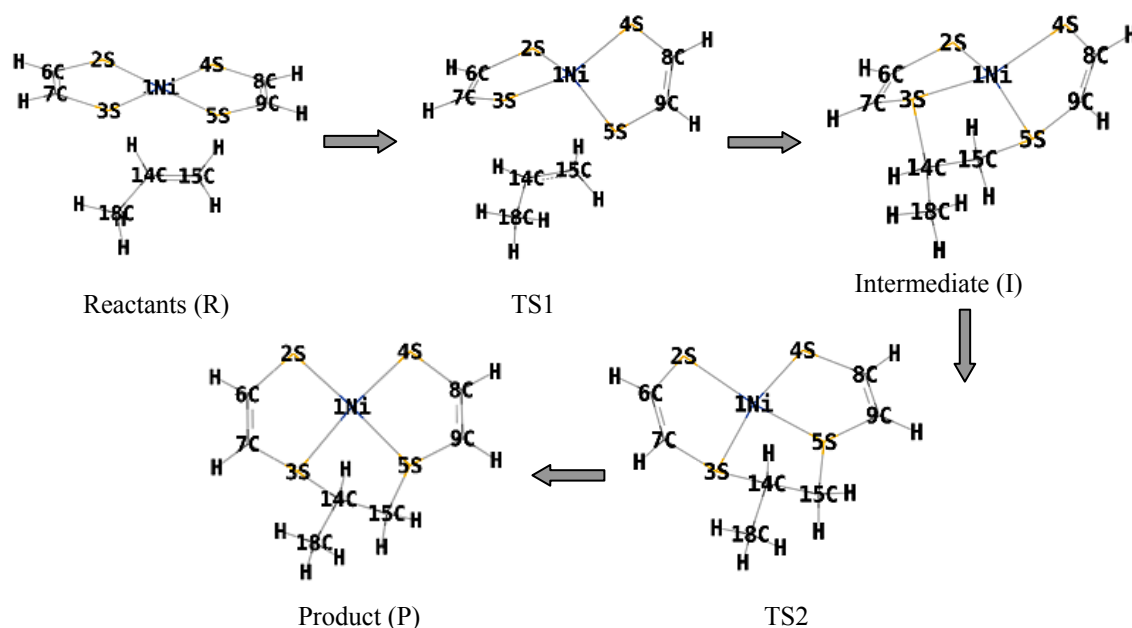
$$\Delta G = -RT \ln K_{\text{eq}} + \Delta n RT, \quad (2)$$

where  $\Delta G$  and  $\Delta n$  represent the Gibbs free energy gap and the gas molecular difference before and after the reaction, respectively. The equilibrium constant can further be expressed as

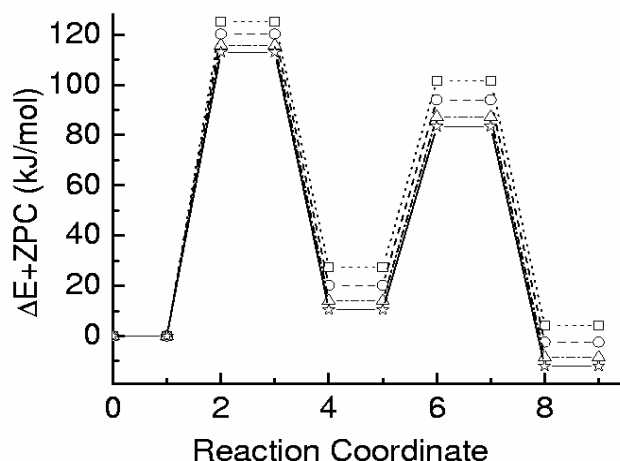
$$K_{eq} = \exp\left(-\frac{\Delta G}{RT} + \Delta n\right). \quad (3)$$

### 3 RESULTS AND DISCUSSIONS

Figure 1 shows the reaction process of complexing propylene with Ni dithiolene. It is shown that the complexing reaction presents a two-step process, and the intermediate (or product) is trans-structural (or cis-structural). The first step of this reaction is coordinating the propylene molecule to S atoms in dithiolene molecule, consequently forming a new complex  $\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2 \cdot \text{C}_2\text{H}_4=\text{CH}_2$ . Based on the matching principle of symmetry in the frontier orbit theory, and the shapes of HOMO and LUMO of propylene and Ni dithiolene, this reaction may bring into being the trans-structural intermediate first, and then the intermediate is quickly transformed into the steady cis-structural product as it is unstable. Figure 2 schematically shows the potential energy surfaces of this reaction. It can be found that the energies of transition states (TS1 and TS2) are higher than those of reactants (R), intermediates (I), and products (P), implying that two energy barriers, or two steps exist in the reaction process.



**Figure 1.** Optimized geometries of all the stagnation points in the reaction process.



**Figure 2.** Schematic presentations of potential energy surface of the reaction in four typical solvents.  
 (□: Gas phase; ○: Toluene; △: Tetrahydrofuran; ☆: Water)

### 3.1 Molecular Geometry Structures and Dipole Moment

Table 1 shows the main bond lengths of the optimized geometries corresponding to the reactants (R), intermediates (I), transition states (TS1 and TS2), and products (P) of the reactions in two typical solvents with dielectric constants  $\epsilon = 1.000$  (gas phase), and 78.39 (water). It is obvious that, in the case of gas phase, the C–C bond length of propylene  $R_{14,15}$  (0.1538 nm) in product is longer approximately by 0.02 nm than that of reactants (0.1333 nm), and the average length of the dithiolene C–S bonds ( $R_{4,8}$  and  $R_{5,9}$ ) is increased by 0.0055 nm during the reaction process. Furthermore, in the case of water solvent, it can be found by a simple calculation that the solvent-induced variation rate  $(R_{i,j} - R_{i,j}^{\text{gas}})/R_{i,j}^{\text{gas}}$  is not larger than 0.4% for any bond, which indicates that all geometry structures of the reactants, intermediates, transition states, and products are slightly changed. This is also the case for the other solvents studied in the present work. It can be readily concluded, therefore, that the solvents only have slight effects on the geometries of the reactants, transition states, intermediates, and products.

**Table 1.** Bond Lengths (nm) of Reactants, Intermediates, Transition States, and Products in Typical Solvents.  $R_{i,j}$  ( $i, j = 1; 2, \dots, 15$ ) represents the distance between atoms  $i$  and  $j$ .

	Solvent	$R_{1,2}$	$R_{1,3}$	$R_{4,8}$	$R_{5,9}$	$R_{6,7}$	$R_{3,14}$	$R_{14,15}$	$R_{14,18}$
R	Gas phase	0.2207	0.2206	0.1706	0.1706	0.1378	–	0.1333	0.1502
	Water	0.2206	0.2206	0.1706	0.1706	0.1378	–	0.1334	0.1502
TS1	Gas phase	0.2218	0.2192	0.1726	0.1735	0.1366	0.2533	0.1416	0.1502
	Water	0.2221	0.2192	0.1728	0.1735	0.1364	0.2625	0.1413	0.1497
I	Gas phase	0.2232	0.2234	0.1749	0.1773	0.1354	0.1882	0.1540	0.1527
	Water	0.2240	0.2229	0.1754	0.1773	0.1351	0.1883	0.1539	0.1526
TS2	Gas phase	0.2223	0.2280	0.1766	0.1771	0.1355	0.1910	0.1552	0.1524
	Water	0.2228	0.2276	0.1770	0.1768	0.1352	0.1910	0.1551	0.1524
P	Gas phase	0.2228	0.2300	0.1743	0.1774	0.1352	0.1883	0.1538	0.1527
	Water	0.2234	0.2290	0.1749	0.1776	0.1349	0.1884	0.1537	0.1527

The main influences of molecular dipole moment (MDM) induced by solvents are presented in Table 2, corresponding to the R, I, TS1 and TS2 and P of the reaction occurring in different solvents. By a comprehensive analysis on MDM presented in Table 2, two visible characteristics can be found: the reaction of complexing propylene to nickel dithiolene is an MDM-increasing process in any solvent, and the MDM of reactions, transition states, intermediates and products increase monotonously with increase of the solvent polarity. For example, the MDM values of reactant, transition states, intermediate and product will be 0.3551 Debye (R), 6.183 Debye (TS1), 7.868 Debye (I), 8.265 Debye (TS2) and 9.895 Debye (P) when the reaction occurring in gas phase, which implies that the molecular structures evolve from symmetrical into asymmetrical.

It can be readily found that the *solvent*-induced variation rates of MDM ( $(\nu_{\text{solvent}} - \nu_{\text{gas}})/\nu_{\text{gas}}$ ), e.g. in water, are 22.5% for R, 43.6% for TS1, 30.5% for I, 29.7% for TS2, and 26.4% for P, respectively. This phenomenon verifies that obvious variations on MDM are found when the dielectric constant of solvents increases from 1.000 (gas phase) to 78.39 (water). Actually, one of the most prominent phenomena induced by MDM in solvent medium is that the MDM is able to produce the induced dipole moment (IDM) of medium. It is the interplay between MDM and IDM that will be inclined to stabilize the system of the molecule in the medium. Obviously, the stabilization of the molecule system should promote a reaction to be carried out more easily. Therefore, the  $\epsilon$ -induced increase in MDM makes the product more stable in medium, which is beneficial to accelerate the reaction.

**Table 2.** Molecular Dipole Moments (Debye) Corresponding to the Reaction Process in Typical Solvents.

Solvents	$\epsilon$	R	TS1	I	TS2	P
Gas phase	1.000	0.3551	6.183	7.868	8.265	9.895
Benzene	2.247	0.3882	7.135	8.823	9.239	10.88
Tetrahydrofuran	7.58	0.4191	8.182	9.762	10.20	11.92
Acetone	20.7	0.4300	8.613	10.11	10.55	12.33
Dimethylsulfoxide	46.7	0.4338	8.775	10.23	10.68	12.47
Water	78.39	0.4351	8.828	10.27	10.72	12.51

### 3.2 Activation Energy, Rate Constants, and Equilibrium Constants

Table 3 presents the activation energies, rate constants, and equilibrium constants of the reaction complexing propylene with Ni dithiolene in gas phase, benzene, toluene, tetrahydrofuran, dichloromethane, 1,2-dichloroethane, acetone, ethanol, methanol, 1,2,3-propanetriol, dimethylsulfoxide and water. The influence of solvent polarity on potential energy surfaces of this reaction are schematically shown in Figure 2, in which the dielectric constant of solvents  $\epsilon$  varying from 1.000 to 78.39.

**Table 3.** Thermodynamic Parameters of the Reaction  $\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2 + \text{C}_2\text{H}_4=\text{CH}_2 \rightarrow \text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2 \cdot \text{C}_2\text{H}_4=\text{CH}_2$  in Different Solvents.

Solvents	$\epsilon$	$\Delta^\ddagger E_1$ kJ·mol <sup>-1</sup>	$\Delta^\ddagger E_2$ kJ·mol <sup>-1</sup>	$\Delta E$ kJ·mol <sup>-1</sup>	$10^{-9}k_1$ s <sup>-1</sup>	$k_2$ s <sup>-1</sup>	$K_{eq}$ l·mol <sup>-1</sup>
Gas phase	1.000	125.0	101.8	4.165	0.7673	0.5503	0.5066
Benzene	2.247	120.5	94.47	-2.018	4.720	0.7150	6.135
Toluene	2.379	120.2	94.01	-2.409	5.306	0.7259	7.183
Tetrahydrofuran	7.580	115.8	87.28	-8.414	31.96	0.9133	80.91
Dichloromethane	8.930	115.4	86.69	-8.945	37.70	0.9317	100.3
1,2-Dichloroethane	10.36	115.1	86.23	-9.380	43.05	0.9473	119.7
Acetone	20.70	114.0	84.64	-10.83	67.05	0.9963	214.6
Ethanol	24.55	113.8	84.39	-11.07	72.17	1.005	236.2
Methanol	32.63	113.5	84.06	-11.39	79.81	1.018	268.7
1,2,3-Propanetriol	42.50	113.3	83.80	-11.64	85.79	1.025	297.1
Dimethylsulfoxide	46.70	113.2	83.72	-11.70	87.70	1.028	305.5
Water	78.39	113.0	83.43	-11.99	96.20	1.038	343.4

Both Table 3 and Figure 2 indicate that the energy barriers corresponding to TS1 and TS2 are lowered as the dielectric constant of solvents  $\epsilon$  increased. The activation energy of the first step  $\Delta^\ddagger E_1$  decreases from 125.0 to 113.0 kJ·mol<sup>-1</sup>, when  $\epsilon$  is increased from 1.000 to 78.39, while the activation energy of the second step  $\Delta^\ddagger E_2$  decreases from 101.8 to 83.43 kJ·mol<sup>-1</sup>. These results indicate that polar solvents are more favored of the reaction. It can also be found that the energies of the products decrease with  $\epsilon$  increasing, indicating that the products become more stable in polar solvents.

By a more detailed comparison, it can also be found that both  $\Delta^\ddagger E_1$  and  $\Delta^\ddagger E_2$  rapidly decrease when  $\epsilon$  less than approximately 20, and then slowly approach a certain threshold. For clarity, the values of activation energies  $\Delta^\ddagger E_1$  and  $\Delta^\ddagger E_2$  are further plotted in Figure 3. The relationship between activation energy and  $\epsilon$  can be expressed in an exponential manner

$$\Delta^\ddagger E_i = A_i \exp\left(-\frac{\epsilon}{n_i}\right) + B_i \exp\left(-\frac{\epsilon}{t_i}\right) + C_i, \quad (4)$$

with correlation parameters

$A_1 = 4.425 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $B_1 = 14.11 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $C_1 = 131.1 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $n_1 = 12.77$ ,  $t_1 = 1.684$ , for  $i = 1$ , and  $A_2 = 6.436 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $B_2 = 23.01 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $C_2 = 83.54 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $n_2 = 12.12$ ,  $t_2 = 1.593$ , for  $i = 2$ .

Here,  $\Delta^\ddagger E_i$  ( $i = 1, 2$ ) is the activation energy corresponding to the  $i$ th step of reaction process and  $\epsilon$  the dielectric constant of solvent. As it obvious in Figure 3 that the activation energies of the reaction decrease with increasing polarity of solvent, which indicates that high solvent polarity is more favored of the carrying out of the reaction. This phenomenon can be observed more clearly in the schematic potential energy surfaces of the reactions in Figure 2.

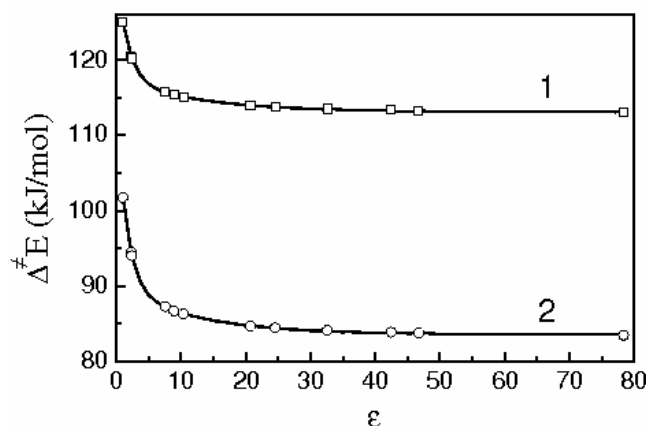


Figure 3. Variations of the activation energies of TS1 (1) and TS2 (2) with the dielectric constants  $\epsilon$ .

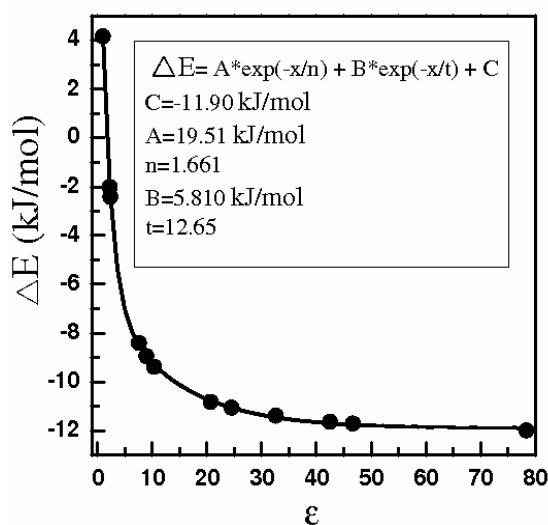


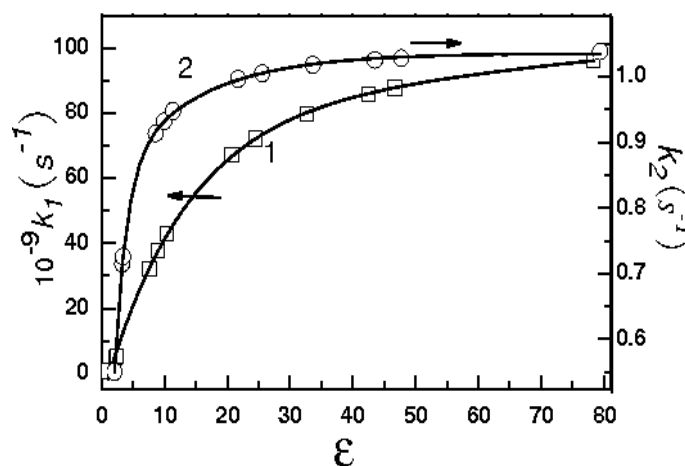
Figure 4. Variation of total energy  $\Delta E$  with the dielectric constants  $\epsilon$  of different solvents.

In addition, the total energy of the reaction  $\Delta E$  also decreases from  $4.165$  to  $-11.99 \text{ kJ}\cdot\text{mol}^{-1}$  with  $\epsilon$  increasing from  $1.000$  to  $78.39$ , as indicated in Table 3. This variation is also shown in Figure 4, which shows that a sharp

decrease of the total energy appears when the value of dielectric constant lies between 1 and approximately 20, while the decrease becomes mild when the dielectric constant of solvents is larger than 20. The variation of the total energy  $\Delta E$  with the polarity of solvent is also expressed in an exponential manner

$$\Delta E = A \exp\left(-\frac{\varepsilon}{n}\right) + B \exp\left(-\frac{\varepsilon}{t}\right) + C, \quad (5)$$

with correlation parameters  $A = 19.51 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $B = 5.81 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $C = -11.90 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $n = 1.661$  and  $t = 12.65$ .



**Figure 5.** Variations of the rate constants with the dielectric constant of solvents  $\varepsilon$ .

The rate constants  $k_1$  and  $k_2$  of the first and second step in the reaction process are also presented in Table 3. The rate constant  $k_1$  increases from  $0.7673 \times 10^{-9}$  to  $96.20 \times 10^{-9} \cdot \text{s}^{-1}$  and  $k_2$  from  $0.5503$  to  $1.038 \cdot \text{s}^{-1}$ , respectively, as  $\varepsilon$  increases from  $1.000$  to  $78.39$ . On account of  $k_1 \ll k_2$ , the first step of the reaction should be the rate-determining step, and the intermediate transforms promptly into product once it comes into being. This result can also be observed in Figure 2, as the energy barrier of TS1 is larger than that of TS2. Furthermore, the rapid increase of rate constants occurs when  $\varepsilon$  is less than approximately 20, and then approaches slowly to certain thresholds as  $\varepsilon$  becomes large. This variation is also in conformity with an exponential function:

$$m_i k_i = A_i \exp\left(-\frac{\varepsilon}{n_i}\right) + B_i \exp\left(-\frac{\varepsilon}{t_i}\right) + C_i, \quad (6)$$

with correlation parameters

$m_1 = 10^9$ ,  $A_1 = -89.52 \text{ s}^{-1}$ ,  $B_1 = -165.7 \text{ s}^{-1}$ ,  $C_1 = 249.6 \text{ s}^{-1}$ ,  $n_1 = 13.21$ , and  $t_1 = 817.9$ , for  $i = 1$ , and

$m_2 = 1$ ,  $A_2 = -0.1948 \text{ s}^{-1}$ ,  $B_2 = -0.5167 \text{ s}^{-1}$ ,  $C_2 = 1.035 \text{ s}^{-1}$ ,  $n_2 = 13.18$ , and  $t_2 = 1.886$ , for  $i = 2$ .

Here,  $k_i$  ( $i = 1, 2$ ) are the rate constants corresponding to the  $i$ th step of reaction process. The exponential functions of  $k_1$  and  $k_2$  vary with the dielectric constant of solvents as given in Figure 5, which illuminate that the influences of  $\varepsilon$  on the rate constants are sensitive in the appropriate range of  $\varepsilon$ . Therefore, it may be possible to control the reaction rate by selecting the polarity of solvent in a certain range of  $\varepsilon$  in actual production.

The variation of equilibrium constant  $K_{eq}$  of the reaction with increasing  $\varepsilon$  is listed in the rightmost column of Table 3, in which  $K_{eq}$  sharply increases from  $0.5066$  to  $343.4 \text{ l}\cdot\text{mol}^{-1}$  as  $\varepsilon$  increases from  $1.000$  to  $78.39$ . The relationship between  $K_{eq}$  and  $\varepsilon$  can also be expressed with an exponential formula

$$K_{eq} = A \exp\left(-\frac{\varepsilon}{t}\right) + B, \quad (7)$$

with correlation parameters  $A = -378.4 \text{ l}\cdot\text{mol}^{-1}$ ,  $B = 350.7 \text{ l}\cdot\text{mol}^{-1}$  and  $t = 21.17$ , as shown in Figure 6. A sharp variation of  $K_{eq}$  appears when the value of  $\varepsilon$  is placed between 1 and approximately 20, which demonstrates that the solvent effect on equilibrium constants is obvious in the appropriate range of  $\varepsilon$ . The equilibrium

constant  $K_{eq}$ , and therefore the rate of producing complex, can also be improved by increasing the solvent polarity in a certain range.

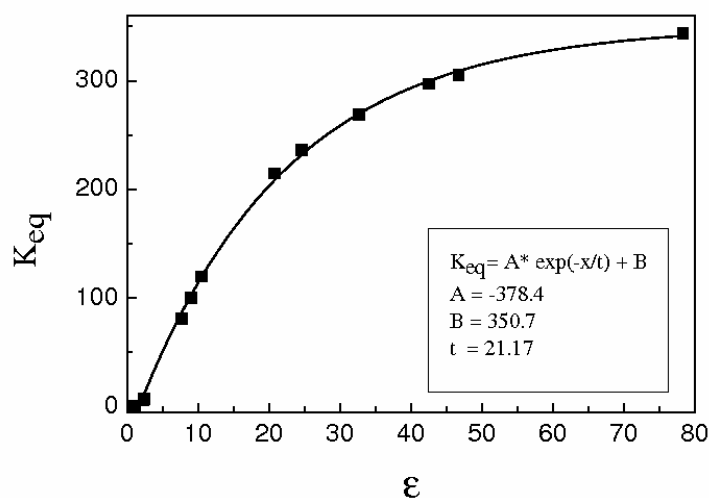


Figure 6. Variation of equilibrium constants with the dielectric constant of solvents  $\epsilon$ .

## 4 CONCLUSION

In conclusion, the mechanism and chemical thermodynamics of the reaction complexing propylene with nickel dithiolene and the influences induced by solvents are theoretically studied. It is shown that this reaction is a two-step process, and the first step is the rate-determining step. The solvent-induced variation rate on bond length is no more than 0.4%, demonstrating that the solvents make slight changes on the geometries of reactants, transition states, intermediates and products. However, this reaction is a MDM-increasing process in any solvent, and the MDM of reactants, transition states, intermediates and products increases with increasing solvent polarity. It indicates that the strong polar solvents may increase the stability of the molecules in medium and accelerate the reaction. The activation energies of the first and second step processes *decrease* exponentially when the dielectric constant of solvents increases, indicating that the barriers of the reaction potential energies decrease, and the reaction becomes easier to occur. Moreover, the rate constants of the first and second step processes, and the equilibrium constant, *increase* exponentially with increasing the polarity of solvent. This demonstrates that the reaction rate, as well as the rate of producing complex, may be controlled by selecting the solvents.

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