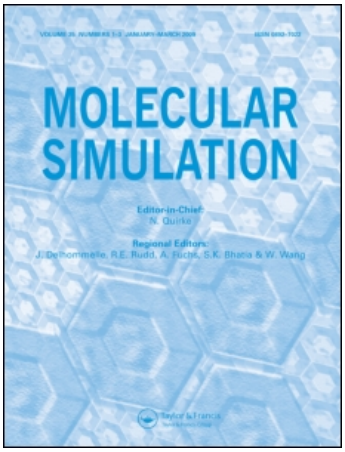

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Quantum chemical study on influence of substituents and solvents in reaction complexing ethylene with nickel dithiolene

Qing-Zhen Han[ab]; Yue-Hong Zhao[a]; Hao Wen[a]
[a] Multi-phase Reaction Laboratory, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, People's Republic of China [b] Graduate University of Chinese Academy of Sciences, Beijing, People's Republic of China

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Quantum chemical study on influence of substituents and solvents in reaction complexing ethylene with nickel dithiolene

Qing-Zhen Han[ab]*, Yue-Hong Zhao[a] and Hao Wen[a]

[a]*Multi-phase Reaction Laboratory, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, People's Republic of China;* [b]*Graduate University of Chinese Academy of Sciences, Beijing, People's Republic of China*

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The influences induced by various terminal substituents and solvents on the reaction mechanism and chemical dynamics of complexing ethylene with Ni dithiolene are theoretically studied by using B3LYP method and Onsager model. It is shown that the reaction should be a two-step process, and the first step is the rate-determining step. We find that the rate constant of the rate-determining step becomes small when the electron-donating ability of the substituents is increased, while it becomes large when the electron-withdrawing ability of the substituents is increased. Subsequently, we consider the solvent effects on the reaction adding ethylene to the simplified hydrogen-substituted nickel dithiolene. It is found that the solvents will make slight changes to the geometries of the reactants, transition states, intermediates and products. However, the corresponding molecular dipole moments become large with the increase of the solvent polarity, which is beneficial to accelerate the reaction. Moreover, we show that, as the solvent polarity becomes large, the activation energies of the reaction decrease exponentially, while the reaction rate constants increase exponentially. These results demonstrate that in polar solvents, the reaction complexing ethylene with Ni dithiolene may become easier and faster to occur, and the product rate is improved. We believe that this research can be seen as a reference for complex and solvent selection in olefin separation process.

Keywords: substituent effects; solvent effects; activation energy; rate constant

1. Introduction

As the largest volume feedstock in petrochemical industry, olefins are extensively applied to the production of polymers, acids, esters and ethers [1,2]. Therefore, the separation of olefins, especially ethylene, has become an important industrial process. Usually, olefins can be separated by either cryogenic distillation [3] or chemical gas absorption approach [4–8]. However, disadvantages of high energy consumption or low reagent selectivity exist in the above separation methods.

Recently, Wang et al. [1,9] proposed an effective method for olefin separation. They found that 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. They also discovered that this reaction is not poisoned by hydrogen, carbon monoxide, acetylene or hydrogen sulphide, which are commonly present in olefin streams, presumably because olefin binding occurs through the sulphur ligand rather than the metal centre. In addition, many researches have demonstrated that dithiolene complexes also display unusual structural, electronic, optical and redox properties [10,11]. Schrauzer et al. [12] reported that $M(S_2C_2Ph_2)_2$ (M = Ni, Pd, Pt; Ph = phenyl group) reacts with norbornadiene, and Wing et al. [13] proposed that $Ni[S_2C_2(CF_3)_2]_2$ reacts with norbornadiene and 2,3-dimethyl-1,3-butadiene to form 1/1 olefin adducts, where the olefin binds to ligand S atoms rather than the metal atoms.

Theoretically, Fan et al. [14] using density functional theory with B3LYP [15,16] investigated the reaction process of ethylene and $Ni(S_2C_2R_2)_2$ (R = H, CN, CF_3) in gas phase. It was found that this reaction is a two-step process, and the electron-withdrawing substituents can lower the barrier for the association of olefins and Ni dithiolene complexes, and can stabilise the intermediates and products relative to the reactants. However, there are few reports of the solvent effects on such reactions. It is necessary to study the solvent effects on the reaction of olefins and Ni dithiolene complexes, considering that solvents may present their influences on the geometries and electronic structures of molecules, and thus the processes of chemical reactions [17].

In the present work, we use the B3LYP method and Onsager model to study the effects of substituents and solvents on the reaction between ethylene and Ni

*Corresponding author. Email: qzhan@home.ipe.ac.cn

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dithiolene. The optimisations of all the stagnation points existing in the reaction potential profiles are carried out with different substituents (—CH_3, —H, —CN and —CF_3) on dithiolene in gas phase and toluene. Subsequently, a detailed analysis and optimisation of all the points are also performed with the simplified hydrogen-substituted dithiolene in 11 polar and nonpolar solvents, respectively. It is shown that this reaction is a two-step process with the first being the rate-determining step. The rate constants may increase with the increase of electronegativity of substituents. In addition, it is found that the overall mechanism does not change no matter what solvent is used. However, as the polarity of the solvent is increased, the activation energies of the reaction are reduced exponentially, while the corresponding molecular dipole moment (MDM) and the reaction rate constants will increase exponentially to be saturated, which is beneficial to accelerate the reaction. These demonstrate that the reaction of complexing ethylene with Ni dithiolene may become much easier and faster, and can attain a higher product rate in the strong polarity solvents, in agreement with a great many experimental studies [1,9].

2. Computational methods

The substituent (e.g. —CH_3, —H, —CN and —CF_3) effects and the solvent effects (e.g. benzene, toluene, tetrahydrofuran, dichloromethane, 1,2-dichloroethane, acetone, ethanol, methanol, 1,2,3-propanetriol, dimethylsulfoxide and water) on the reaction of $Ni(S_2C_2R_2)_2 + C_2H_4 \rightarrow Ni(S_2C_2R_2)_2{\cdot}C_2H_4$ (R = —CH_3, —H, —CN and —CF_3) at temperature $T = 298.15$ K and pressure $P = 1$ atm are considered in the present work.

All of the calculations are performed with Gaussian03 program package [18]. The optimisations of the geometries of reactants, transition states, intermediates and products, as well as the corresponding frequency calculations, are achieved by means of density functional theory with B3LYP. A slightly modified version of Hay and Wadt's LANL2DZ [19] with the two outermost p functions replaced by a new function with (41) split [20], and a relativistic effective core potential [21] are used for Ni, while the 6-31G(d) basis set is utilised for all of the rest atoms in the simplified hydrogen-substituted model. Furthermore, an f-polarisation function [22] is added to nickel atoms in the cyano- and trifluoromethyl-substituted complexes. The 6-31G(d) basis set is also used for all atoms (C and N) in cyano substituent, and the 6-31 basis set is used for all atoms (C and F) in trifluoromethyl substituent. In addition, the nature of all transition states is characterised by the imaginary frequency and verified by the intrinsic reaction coordinate approach [23]. Moreover, the influences of different solvents have been investigated based on Onsager model [24], and all of the energies have been modified by zero point corrections.

In order to find the rate constant of the reaction at temperature T, the general statistical thermodynamics [25] and Eyring transition state theory [26] are used to calculate the rate constants from partition functions:

$$k(T) = \frac{N_A k_B T}{h}\left[\frac{Q_{TS}^{\neq}/V_{TS}}{\prod_i (Q_{Ri}/V_{Ri})}\right]\exp\left(-\frac{\Delta E_0}{RT}\right), \qquad (1)$$

where $N_A = 6.022 \times 10^{23}\,\mathrm{mol}^{-1}$ is the Avogadro number, $k_B = 1.380662 \times 10^{-26}\,\mathrm{kJ\,K}^{-1}$ the Boltzmann constant, $h = 6.626176 \times 10^{-37}\,\mathrm{kJ\,s}^{-1}$ the Planck's constant, $R = 8.314 \times 10^{-3}\,\mathrm{kJ\,mol}^{-1}\,\mathrm{K}^{-1}$ the gas constant, $Q_{TS}^{\neq}$ and Q_{Ri} (V_{TS} and V_{Ri}) represent the molecular total partition functions (molar volume) of transition state and reactant i, and ΔE_0 the energy barrier of activation after zero point corrections.

3. Results and discussions

The reaction mechanism of complexing ethylene with Ni dithiolene is schematically presented in Figure 1. It is shown that this reaction belongs to a two-step process, and the intermediate (or product) is in trans-structure (or cis-structure). The first step of this reaction is coordinating the ethylene molecule to S atoms in dithiolene to form a trans-structural intermediate $Ni(S_2C_2H_2)_2{\cdot}C_2H_4$. In this process the empty 3p orbit of S atoms in dithiolene, an electron acceptor, will attack the π-electron of ethylene. This can be understood well according to the matching principle of symmetry in the frontier orbit theory, and the shapes of HOMO and LUMO of ethylene and Ni dithiolene. The second step is that the trans-structural intermediate is quickly transformed into the steady cis-structural product, since the trans-structural intermediate is unstable.

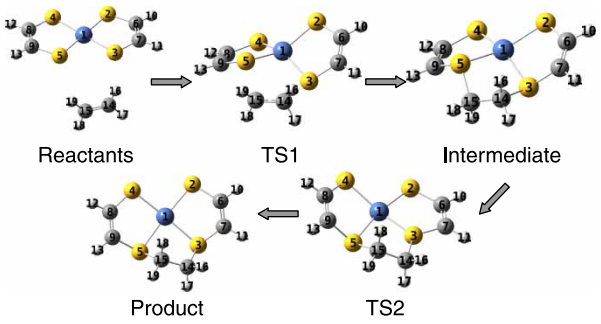

Figure 1. Optimised geometries of all the stagnation points in the reaction of complexing ethylene with nickel dithiolene.

Table 1. The rate constants of the rate-determining step k_1 (in unit of $1\,mol^{-1}\,s^{-1}$) in the reaction adding ethylene to Ni dithiolene with different substituents.

Solvent	—CH_3	—H	—CN	—CF_3	—CF_3
–	$k_1 \times 10^{14}$	$k_1 \times 10^{11}$	$k_1 \times 10^{4}$	$k_1 \times 10^{4}$	$k_1 \times 10^{4}$
Gas phase	6.894	1.177	1.012	5.458	–
Toluene	30.50	5.851	2.999	13.91	9.0[a]

[a] This is the experimental result from Refs. [1,9].

3.1 Substituent effects

The electronegativity effects of substituents in terminal ligands on the complexing reaction in gas phase and toluene are given in Table 1. In the solvent of toluene, the rate constant of the rate-determining step for R = —CF_3 is found to be $13.91 \times 10^{-4}\,l\,mol^{-1}\,s^{-1}$, consistent with the related experimental value ($9.0 \times 10^{-4}\,l\,mol^{-1}\,s^{-1}$) obtained by Wang et al. [1,9]. It can be found that when the hydrogen-substituent is replaced by the electron-withdrawing substituent —CN (—CF_3), the rate constant k_1 for the first step is increased from 5.851×10^{-11} to $2.999 \times 10^{-4}\,l\,mol^{-1}\,s^{-1}$ ($13.91 \times 10^{-4}\,l\,mol^{-1}\,s^{-1}$). However, k_1 is decreased from 5.851×10^{-11} to $3.050 \times 10^{-13}\,l\,mol^{-1}\,s^{-1}$ when —H is replaced by —CH_3 (an electron-donating substituent). Obviously this phenomenon is also the case in the gas phase. It is demonstrated that the rate constant of the first step will increase (decrease) with the increasing (decreasing) of the substituent electronegativity. These are because the electron-withdrawing substituents can lower the barrier for the first step of the reaction, and stabilise both cis- and trans-products relative to the reactants through stabilising the LUMO of the Ni complexes [14]. Therefore, the introduction of the electron-withdrawing substituents is favourable for the complexing of ethylene and Ni dithiolene. This implies that the reaction rate in the practical olefin separation can be adjusted by selecting suitable electronegative substituents on the Ni dithiolene.

3.2 Solvent effects

3.2.1 Molecular geometries and dipole moment

The influences on main bond lengths of optimised geometries and MDM induced by solvents, corresponding to the reactants (R), intermediates (I), transition states (TS1 and TS2) and products (P) of the reaction occurring in different solvents, are presented in Tables 2 and 3, respectively.

In Table 2, two typical solvents with dielectric constants $\varepsilon = 1$ (gas phase) and 78.39 (water) are considered. Since the calculations are performed on the basis of Onsager model and the reactants have the D_{2h} symmetry, the geometry parameters of the reactants are kept constant, as expected [24], even in different solvents. It is obvious that, for the case of gas phase, the ethylene C—C bond length $R_{14,15}$ in product (0.1533 nm) is longer approximately by 0.02 nm than that in reactants (0.1331 nm), and the average length of dithiolene C—S bonds ($R_{4,8}$ and $R_{5,9}$) is increased by 0.0048 nm during the reaction process, in agreement with the results obtained by Fan and Hall [14]. Furthermore, it can be found by a simple calculation that the solvent-induced variation rate $(R_{i,j} - R_{i,j}^{Gas})/R_{i,j}^{Gas}$ is not larger than 0.5% for any bond, which indicates that the whole 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. Therefore, it can be readily concluded that the solvents will make slight effects on the whole geometries of the reactants, transition states, intermediates and products.

By a comprehensive analysis on the MDM presented in Table 3, two apparent characteristics can be found: (i) the reaction of complexing ethylene with nickel dithiolene is a MDM-increasing process in any solvent, and (ii) the MDM of transition states, intermediates and products will increase monotonically with the increasing of the solvent polarity. For example, the MDM P of reactant, transition states, intermediates and products will increase from the initial 0 Debye (R) to 5.527 (TS1), 7.604

Table 2. Main bond lengths (nm) of reactants (R), intermediates (I), transition states (TS1 and TS2) and products (P) in typical solvents. $R_{i,j}$ ($i, j = 1, 2, \ldots, 15$) represents the distance between atoms i and j.

Species	Solvent	R_{1-2}	R_{1-3}	R_{4-8}	R_{5-9}	R_{6-7}	R_{3-14}	R_{14-15}
R	Gas phase and water	0.2206	0.2206	0.1706	0.1706	0.1378	–	0.1331
TS1	Gas phase	0.2219	0.2183	0.1727	0.1733	0.1366	0.2377	0.1411
	Water	0.2224	0.2181	0.1729	0.1734	0.1365	0.2407	0.1407
I	Gas phase	0.2235	0.2239	0.1748	0.1771	0.1353	0.1860	0.1532
	Water	0.2244	0.2234	0.1756	0.1772	0.1350	0.1861	0.1531
TS2	Gas phase	0.2260	0.2151	0.1744	0.1772	0.1348	0.1834	0.1542
	Water	0.2268	0.2150	0.1753	0.1775	0.1347	0.1839	0.1541
P	Gas phase	0.2229	0.2295	0.1739	0.1769	0.1349	0.1871	0.1533
	Water	0.2235	0.2291	0.1745	0.1771	0.1347	0.1872	0.1532

Table 3. MDMs (Debye) corresponding to the reaction process in different typical solvents. The MDM's of R in different solvents are always kept to be zero (not presented here).

Solvents (ε)	TS1	I	TS2	P
Gas phase (1.0)	5.527	7.604	8.131	9.603
Benzene (2.247)	6.272	8.654	9.315	10.42
THF (7.58)	7.027	9.722	10.54	11.23
Acetone (20.7)	7.310	10.12	11.01	12.57
DMSO (46.7)	7.411	10.26	11.17	12.65
Water (78.39)	7.445	10.31	11.23	12.87

(I), 8.131 (TS2) and 9.603 Debye (P), when the reaction occurs in gas phase, which implies that the molecular structures evolve from symmetrical into asymmetrical one. It can be readily found that the *solvent*-induced variation rates of MDM $(P_{\text{solvent}} - P_{\text{gas}})/P_{\text{gas}}$, e.g. in water, are 34.7% (TS1), 35.6% (I), 38.1% (TS2) and 34.0% (P), respectively. This phenomenon verifies that obvious variations on MDM have happened when the dielectric constant of solvents increases from 1 (gas phase) to 78.39 (water). Actually, one of the most eminent phenomena induced by MDM in solvent medium is that the MDM is able to produce the inducted dipole moment (IDM) of medium. It is the interplay between MDM and IDM that will stabilise the system of the molecule in the medium. Obviously, the stabilisation of the molecule system should promote a reaction to be carried out more easily. Therefore, the ε-induced increase in MDM will make the product more stable in medium, which is beneficial to accelerate the reaction.

3.2.2 *Activation energy and rate constants*

Figure 2 schematically shows the potential energy surfaces of the reaction of complexing ethylene with Ni dithiolene in gas phase ($\varepsilon = 1$), toluene ($\varepsilon = 2.379$), tetrahydrofuran ($\varepsilon = 7.58$) and water ($\varepsilon = 78.39$). The energies of transition states (TS1 and TS2) in gas phase are higher than those of R, I and P, implying that two barriers are formed in the reaction process. It is clear that the barrier corresponding to TS1 is higher than that corresponding to TS2. As the polarity, in other words, the dielectric constant ε of solvents increases, both barriers corresponding to TS1 and TS2 will be lowered. This phenomenon indicates that polar solvents are more favourable for the reaction. It can also be found that the energies of the products will decrease with increasing ε, indicating that the products become more stable in polar solvents. This result can also be found from the MDM variation of the product in Table 3.

More detailed calculations of the activation energies, rate constants and equilibrium constants of the reaction in gas phase and in benzene, toluene, tetrahydrofuran, dichloromethane, 1,2-dichloroethane, acetone, ethanol, methanol, 1,2,3-propanetriol, dimethylsulfoxide and

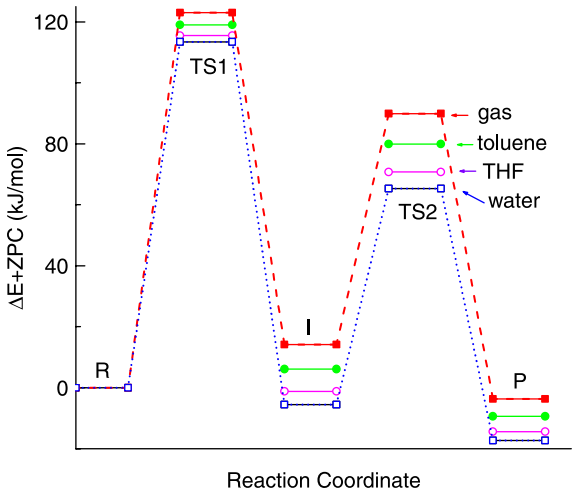

Figure 2. Schematic presentation of potential energy surface of the reaction in different solvents. Only four cases corresponding to gas phase, toluene, tetrahydrofuran (THF) and water are shown for clarity.

water are presented in Table 4. It can be found that the activation energy of step-1 $\Delta^{\neq}E_1$ will decrease from 123.0 to 113.4 kJ mol^{-1}, when the dielectric constant ε of solvents increases from 1.000 to 78.39, while the activation energy of step-2 $\Delta^{\neq}E_2$ will decrease from 89.90 to 65.31 kJ mol^{-1}. A more thorough comparison shows that both $\Delta^{\neq}E_1$ and $\Delta^{\neq}E_2$ will present sharp variations when ε is approximately less than 20, and they will mildly approach to certain thresholds as ε is increased to the values larger than 20. The variations of the activation energy $\Delta^{\neq}E_1$ and $\Delta^{\neq}E_2$ as functions of ε are further plotted in Figure 3 for clarity. The relationship of activation energy and dielectric constant of solvents can be expressed mathematically in an exponential manner as

$$\Delta^{\neq}E_i = a_i \exp\left(-\frac{\varepsilon}{\beta_i}\right) + b_i. \qquad (2)$$

Here, $\Delta^{\neq}E_i$ ($i = 1, 2$) is the activation energy corresponding to the reaction process of step-i, ε is the dielectric constant of solvents, a_i, b_i and β_i ($i = 1, 2$) are the correlation parameters. For step-1, $a_1 = 11.24$ kJ mol^{-1}, $b_1 = 113.8$ kJ mol^{-1} and $\beta_1 = 3.609$, while $a_2 = 19.29$ kJ mol^{-1}, $b_2 = 65.87$ kJ mol^{-1} and $\beta_2 = 6.156$ for step-2.

It also can be seen from Table 4 that the rate constants of step-1 (k_1) and step-2 (k_2) improve from 1.177×10^{-11} l mol^{-1} s^{-1} to 89.45×10^{-11} l mol^{-1} s^{-1} and from 0.1923 to 1.398 s^{-1}, respectively, as ε increases from 1.000 to 78.39. Furthermore, the sharp variations of rate constants can be observed when ε is approximately less than 20, and the variations of rate constants will become mild as the value of ε is larger than 20. The variation of rate constants can also be described with

Table 4. Thermodynamic and dynamic parameters of the reaction adding ethylene to Ni dithiolene in different solvents. Here the unit of energy ($\Delta^{\neq}E_1$, $\Delta^{\neq}E_2$ and ΔE) is kJ mol^{-1}, while that of the rate constant k_1 is l mol^{-1} s^{-1}, and that of k_2 is s^{-1}.

Solvents	ε	$\Delta^{\neq}E_1$	$\Delta^{\neq}E_2$	ΔE	$k_1 \times 10^{11}$	$k_2 \times 10$
Gas phase	1.000	123.0	89.90	−3.706	1.177	1.923
Benzene	2.247	119.3	80.50	−9.079	5.318	3.931
Toluene	2.379	119.0	79.91	−9.413	5.850	4.122
Tetrahydrofuran	7.580	115.5	70.77	−14.42	24.84	8.728
Dichloromethane	8.930	115.2	69.94	−14.86	28.33	9.356
1,2-Dichloroethane	10.36	114.9	69.28	−15.21	31.41	9.900
Acetone	20.70	114.1	67.08	−16.39	44.37	11.98
Ethanol	24.55	113.9	66.72	−16.58	46.99	12.37
Methanol	32.63	113.7	66.22	−16.84	50.76	12.91
1,2,3-Propanetriol	42.50	113.6	65.86	−17.03	53.68	13.32
Dimethylsulfoxide	46.70	113.5	65.76	−17.09	95.99	13.45
Water	78.39	113.4	65.31	−17.32	96.45	13.98

an exponential function as

$$n_i k_i = a_i \exp\left(-\frac{\varepsilon}{\beta_i}\right) + b_i. \quad (3)$$

Here, k_i ($i = 1, 2$) is the rate constant corresponding to step-i, ε is the dielectric constant of solvents, a_i, b_i and β_i ($i = 1,2$) are the correlation parameters. For step-1, $n_1 = 10^{-11}$, $a_1 = -60.101\,\text{l mol}^{-1}\,\text{s}^{-1}$, $b_1 = 56.211\,\text{l mol}^{-1}\,\text{s}^{-1}$ and $\beta_1 = 12.25$, while $n_2 = 1$, $a_2 = -1.263\,\text{s}^{-1}$, $b_2 = 1.336\,\text{s}^{-1}$ and $\beta_2 = 7.986$ for step-2. The exponential functions for k_1 and k_2 with ε are presented in Figure 4, which illuminates that the influences of ε on the rate constants are sensitive in a certain range of ε, and the rate constants will be immune to ε when ε is larger than approximately 20. The controlling of the reaction rate in actual industrial process, therefore, is possible by employing solvent with polarity in a certain range of ε. On account of $k_1 \ll k_2$, step-1 should be the rate-determining step of the reaction, and the intermediate will be promptly transformed into product once it comes into being. This result can also be observed from Figure 2, since the barrier of TS1 is larger than that of TS2.

4. Conclusion

In conclusion, the mechanism and chemical dynamics of the reaction complexing ethylene with Ni dithiolene, and the influences induced by the terminal substituents on Ni dithiolene and solvents are theoretically studied. It is shown that the reaction complexing ethylene with Ni dithioloene is a two-step process with the first being the rate-determining one. The rate constant becomes large with the increase of the electronegativity of the substituent on Ni dithiolene. In addition, the solvent-induced variation rate of any bond length is no larger than 0.5%, demonstrating that slight changes of the geometries of reactants, transition states, intermediates and products will be made by solvents. However, the reaction of complexing ethylene with nickel dithiolene is a MDM-increasing process in any solvent, and the MDM of transition states, intermediates and products will

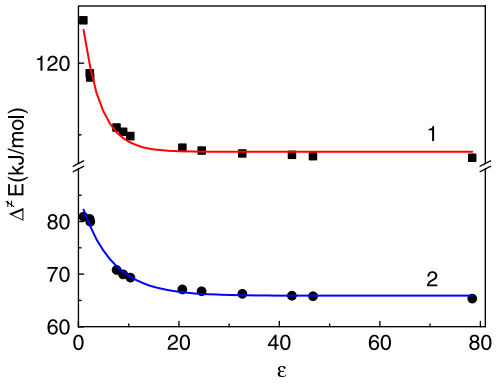

Figure 3. Variations of the activation energies of TS1 (1) and TS2 (2) with the dielectric constants ε. All the calculated data are further fitted and plotted.

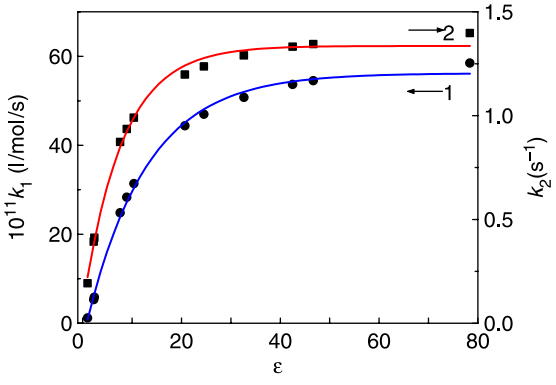

Figure 4. Variations of the rate constants corresponding to the first (1) and second (2) step reactions with the dielectric constants ε. All the calculated data are further fitted and also plotted.

increase monotonously with the increase of 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 step-1 and step-2 processes 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. Moreover, the rate constants of step-1 and step-2 processes will increase exponentially with increasing the polarity of solvent. This demonstrates that the reaction rate may be adjusted by selecting the terminal substituents on dithiolene and the solvents.

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References

[1] K. Wang and E.I. Stiefel, *Toward separation and purification of olefins using dithiolene complexes*, Science 291 (2001), pp. 106–109.

[2] K.M. Sundaram, M.M. Shreehan, and E.F. Olszewski, *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, New York, 1995.

[3] R.L. Grantom and D.J. Royer, *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, New York, 1987.

[4] T. Suzuki, R.D. Nobel, and C.A. Koval, *Electrochemistry, stability, and alkene complexation chemistry for copper(I) triflate in aqueous solution. Potential use for electro-chemically modulated complexation based separation processes*, Inorg. Chem. 36 (1997), pp. 136–140.

[5] P.A. Terry, R.D. Noble, D. Swanson, and C.A. Koval, *Electrochemically modulated complexation process for ethylene/ethane separation*, AICHE J. 43 (1997), pp. 1709–1716.

[6] T. Murata, Y. Mizobe, H. Gao, Y. Ishii, T. Wakabayashi, F. Nakano, T. Tanase, S. Yano, M. Hidai, I. Echizen, H. Nanikawa, and S. Motomura, *Syntheses of mixed-metal sulfide cubane-type clusters with the novel $PdMo_3S_4$ core and reactivities of the unique tetrahedral Pd site surrounded by sulfide ligands toward alkenes, CO, tBuNC, and alkynes*, J. Am. Chem. Soc. 116 (1994), pp. 3389–3398.

[7] T. Shibahara, G. Sakane, M. Maeyama, H. Kobashi, T. Yamamoto, and T. Watase, *Uptake of ethylene by sulfur-bridged cubane-type molybdenum/tungsten–nickel clusters $[M_3NiS_4(H_2O)_{10}]^{4+}$ ($M_3 = Mo_3$, Mo_2W, MoW_2, W_3): syntheses, structures and ^1H NMR spectra*, Inorg. Chim. Acta 251 (1996), pp. 207–225.

[8] M. McKenna, L.L. Wright, D.J. Miller, L. Tanner, R.C. Haltiwanger, and M.R. DuBois, *Synthesis of inequivalently bridged cyclopentadienyl dimers of molybdenum and a comparison of their reactivities with unsaturated molecules and with hydrogen*, J. Am. Chem. Soc. 105 (1983), pp. 5329–5337.

[9] K. Wang and E.I. Stiefel, United States Patent 6120692 (2000).

[10] T.B. Rauchfuss, C.L. Beswick, M.K. Johnson, K. Wang, S.D. Cummings, K.A. Van Houten, C. Faulmann, S.J.N. Burgmayer, J. Mcmaster, and D. Sellmann, *Dithiolene Chemistry Synthesis, Properties, and Applications*, Wiley, New Jersey, 2004.

[11] D.J. Harrison, N. Nguyen, A.J. Lough, and U. Fekl, *New insight into reactions of $Ni(S_2C_2(CF_3)_2)_2$ with simple alkenes: Alkene adduct versus dihydrodithiin product selectivity is controlled by $[Ni(S_2C_2(CF_3)_2)_2]^-$ anion*, J. Am. Chem. Soc. 128 (2006), pp. 11026–11027.

[12] G.N. Schrauzer, R.K.Y. Ho, and R.P. Murillo, *Structure, alkylation, and macrocyclic derivatives of bicyclo[2.2.1]hepta-2,5-diene adducts of metal dithienes*, J. Am. Chem. Soc. 92 (1970), pp. 3508–3509.

[13] R.M. Wing, C. Gerald, G.C. Tustin, and W.H. Okamura, *Oxidative cycloaddition of metal dithiolenes to olefins. Synthesis and characterization of norbornadiene-bis-*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)nickel*, J. Am. Chem. Soc. 92 (1970), pp. 1935–1939.

[14] Y.B. Fan and M.B. Hall, *How electron flow controls the thermochemistry of the addition of olefins to nickel dithiolenes: Predictions by density functional theory*, J. Am. Chem. Soc. (Communication) 124 (2002), pp. 12076–12077.

[15] A.D. Becke, *Density-functional thermochemistry. III. The role of exact exchange*, J. Chem. Phys. 98 (1993), pp. 5648–5652.

[16] C. Lee, W. Yang, and R.G. Parr, *Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density*, Phys. Rev. B 37 (1988), pp. 785–789.

[17] M.J. Field, P.A. Bash, and M. Karplus, *A combined quantum mechanical and molecular mechanical potential for molecular dynamics simulations*, J. Comput. Chem. 11 (1990), pp. 700–733.

[18] M.J. Frisch, G.W. Trucks, and H.B. Schlegel, *Gaussian 03, Revision B.05*, Gaussian, Inc., Pittsburgh, 2003.

[19] P.J. Hay and W.R. Wadt, Ab initio *effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg*, J. Chem. Phys. 82 (1985), pp. 270–283.

[20] M. Couty and M.B. Hall, *Basis sets for transition metals: Optimized outer p functions*, J. Comput. Chem. 17 (1996), pp. 1359–1370.

[21] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, and H. Preuss, Ab initio *energy-adjusted pseudopotentials for elements for groups. 13–17*, Mol. Phys. 80 (1993), pp. 1431–1441.

[22] A.W. Ehlers, M. Boehme, S. Dapprich, A. Gobbi, A. Hoellwarth, V. Jonas, K.F. Koehler, R. Stegmann, A. Veldkamp, and G. Frenking, *A set of f-polarization functions for pseudo-potential basis sets of the transition metals Sc–Cu, Y–Ag and La–Au*, Chem. Phys. Lett. 208 (1993), pp. 111–114.

[23] C. Gonzalez and H.B. Schlegel, *Reaction path following in mass-weighted internal coordinates*, J. Phys. Chem. 94 (1990), pp. 5523–5527.

[24] M.W. Wong, K.B. Wiberg, and M.J. Frisch, *Solvent effects. 2. Medium effect on the structure, energy, charge density, and vibrational frequencies of sulfamic acid*, J. Am. Chem. Soc. 114 (1992), pp. 523–529.

[25] P.W. Atkins, *Physical Chemistry*, 6th ed., Oxford University Press, Oxford, 1998.

[26] H. Eyring, *Physical Chemistry: An Advanced Treatise*, Thermodynamics Vol. 1, Academic Press, New York, 1971.