



Mechanism of Mo-catalyzed C–S cleavage of thiophene



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ABSTRACT

The Mo(PMe₃)₆-catalyzed C–S cleavage of thiophene was studied using density functional theory (DFT). A comparison of several possible pathways shows that, the five- and four-coordinated species are determined as two most active catalyst species, and this reaction is the most likely to undergo consecutively the dissociation of two PMe₃ groups from Mo(PMe₃)₆ to give the four-coordinated Mo(PMe₃)₄, the binding of thiophene to Mo(PMe₃)₄ in η¹-S-mode to give Mo(PMe₃)₄(η¹-S-thiophene), the transformation of Mo(PMe₃)₄(η¹-S-thiophene) into the Mo(PMe₃)₄(η²-C²,S-thiophene), and the cleavage of the C–S bond of thiophene to give the ring-opened species Mo(PMe₃)₄(κ²-C²,S-thiophene). The butadiene–thiolate complex (η⁵-C₄H₅S)Mo(PMe₃)₂(η²-CH₂PMe₂) may generate in the ring-opened species through the departure of one PMe₃ group, hydrogen transfer and structural transformation. The thiophene adduct Mo(PMe₃)₃(η⁵-thiophene) may originate in Mo(PMe₃)₄(η²-C²,C³-thiophene) by removing one PMe₃ group and changing the η²-coordination mode into η⁵-coordination mode. The highest formation energy barrier of the thiophene adduct and butadiene–thiolate complex is 20 and 10.4 kcal/mol, respectively, which is easy to cross and supports the facts that the two species can be experimentally observed.

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1. Introduction

The hydrodesulphurization (HDS) technology is one of the most effective ways to decrease the sulfur content in fuel oil, reducing the erosion of sulfur compounds to oil refining machines and alleviating the damage of the sulfur oxide to the environment [1,2]. Though the existed HDS catalysts can partly remove common organosulfur compounds, their efficiency still need to be improved to meet the required specifications for ultra low sulfur diesel (ULSD) [3,4]. Besides, the HDS reactions usually need to be carried out under harsh conditions [3], which results in higher cost and inconvenient operation. Therefore, the exploitation of novel catalyst, especially homogeneous transition metal complex catalyst, is of significance to promote the efficiency of HDS technology.

In the past decades, the complex [Ru₃(CO)₁₂] and [Rh(μ-Cl)(CO)₂]₂ were employed to break the C–S bond of pyridyl-substituted dibenzothiophenes to generate thiolate-containing pincer frameworks, finding that the pre-coordination of the adjacent pyridyl group can promote the oxidative addition of the C–S bond by laying the C–S bond to the vacant site on the metal center [5]. The complex [(dippe)Ni(μ-H)]₂ was used to catalyze the C–S bond cleavage of the biphenyl-2-thiol by variable temperature

NMR experiments, and a bimetallic intermediate [(dippe)₂Ni₂(μ-H)(μ-S-2-biphenyl)] was discovered, indicating that the bimetallic intermediate plays a key role in the whole HDS process [6]. The C–S bond activation of thiophene by the complex [(dppp)₂Pt₂H₃]ClO₄ (dppp = Ph₂P(CH₂)₃PPh₂) to give [(dppp)Pt(SC₄H₄-C,S)] and [(dppp)₂Pt₂(μ-SC₄H₅-C,S)]ClO₄ had been experimentally and computationally studied [7]. In addition, the transition metal complex catalysts, including Ir [8], Rh [9], Fe [10], Pd [11], and so on, are also investigated. However, all of these catalysts are still not ideal for HDS.

Among all the homogeneous transition metal catalysts used in HDS, the Mo/W catalysts are recently reported powerful catalysis activities and attract a lot of attentions from academic and industrial circles [12–14], because they can break the C–S bond of thiophene and extract the sulfur in thiophene or even in dibenzothiophene under extremely mild conditions. Furthermore, these transition metal catalysts are inexpensive and their application in industry would certainly reduce the cost for production. However, the ligand PMe₃ in these catalysts is toxic and may be pyrophoric. Therefore, it is very necessary to optimize and redesign these homogeneous Mo/W catalysts.

Toward molecular-level understanding of the HDS process of thiophene, several mechanisms of thiophene activated by homogeneous catalysts have been theoretically investigated in the past decades [1,2]. For example, the mechanism of the Cp*Rh(PMe₃)-catalyzed desulphurization of the thiophene was studied by several

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groups [15–17], and this reaction is finally proved to be a stepwise process. The platinum dimethylphosphine-catalyzed desulphurization of the thiophene has been studied using density functional theory (DFT). The calculations show that the initial η^2 -C,C-coordinated thiophene is kinetically favorable [18]. The selectivity in activation of C–S bond of substituted thiophene with $(C_5Me_5)Rh(PMe_3)$ has been studied by Tülay and coworkers. Their calculations reveal that all of the other experimental products correlate with thermodynamically products except one [19].

Herein, we plan to take $Mo(PMe_3)_6$ as the representative catalyst and thiophene as the representative compound containing sulfur in fuel oil to study the mechanism of the HDS reactions using computational tools. This work hopes to provide insight into the desulphurization of thiophene activated by $Mo(PMe_3)_6$, and supply a guideline to design novel homogeneous Mo catalyst with higher performance.

2. Computational details

All the calculations were carried out using the Gaussian09 program [20]. The Becke three-parameter hybrid functional with the Lee–Yang–Parr correlation potential (B3LYP) [21–23], which has been proved to give reliable thermodynamic results for transition metal compounds [24–27], was used to optimize geometries of all species. To accurately account for relativistic effects and substantially reduce the computational cost, the modified Los Alamos National Laboratory 2-double-zeta (LANL2DZ) [28] basis set was utilized for Mo, P, S atoms, a set of d-polarization functions were added to P and S atoms [29], and a set of f-polarization functions were added to Mo atom [30]. The 6-31G(d, p) basic set [31–35] was applied for C and H atoms. Frequency analysis was carried out to verify the stationary points as either minima or transition states, and obtain the zero point energy (ZPE) and free energy of each species. The intrinsic reaction coordinate (IRC) [36–38] calculations were performed to confirm whether the transition states truly connected the reactants and the products. To evaluate the effects of solvent environment on the reaction, the polarized continuum model (PCM) [39–41] (with the toluene as solvent) was used to estimate the solvation free energy of each species. The molecular cavity was treated using the united atom Hartree–Fock (UAHF) parameterization [42]. The partial atomic charges were analyzed using natural bond orbital (NBO) [43] method to determine the electronic distribution of some key atoms. The contour line maps of the density difference function of key intermediates were drawn by Multiwfn [44].

3. Results and discussion

$Mo(PMe_3)_6$ (**1**) is a relatively stable (18e system) catalyst precursor, and it is assumed to take effect via dissociating one, two or three PMe_3 groups continually to give active five-(**2**), four-(**3** and **4**) or three-coordinated catalyst species (**5** and **6**). And this work is correspondingly divided into the determination of the active catalyst species, the C–S cleavage of thiophene mediated by the active catalyst species and the formation of two species observed by experiment (see Schemes 1–6).

3.1. The determination of the active catalyst species

3.1.1. Five coordinated-catalyst species

In the catalyst precursor **1**, six equivalent PMe_3 groups surround the metal center Mo and construct a configuration of distorted octahedron. The distance of Mo–P bond is calculated to range from 2.528 to 2.550 Å, which is in good agreement with the crystallography value (2.467 Å) [45]. In **2**, four PMe_3 groups and the metal

center Mo are approximately located in one plane, and the fifth PMe_3 group (P^5Me_3) is vertical to this plane (see Fig. 1), indicating that **2** is in a typical tetragonal-pyramid configuration. The distance of Mo–P⁵ (P atom in the apical PMe_3 group) bond is calculated to be 2.382 Å, which is shorter than other Mo–P bond distance ranging from 2.467 Å to 2.526 Å. The difference in the distance of Mo–P bond indicates that the Mo atom has stronger interaction on the PMe_3 group at the apical vertex of the tetragonal pyramid than the PMe_3 groups at the basal vertices. This can be attributed to four bulky PMe_3 groups in one plane spatially repelling each other. From **1** to **2**, the distance of Mo–P bonds is more or less shortened because of the reduced steric strain resulting from the departure of one PMe_3 group. The NBO charge of Mo increases from –2.596 eu to –1.937 eu by dissociating one PMe_3 group, showing that the electrons are donated from PMe_3 group to Mo atom. This step is calculated to be exothermic by 7.7 kcal/mol with an energy barrier of 5.6 kcal/mol (see Fig. 2), being consistent with the experimental findings that it is very easy for $Mo(PMe_3)_6$ to dissociate one PMe_3 group [45,46]. In addition, many efforts were made to optimize the trigonal-bipyramidal geometry of **2**, however, it is unsuccessful. The optimization of trigonal-bipyramidal geometry always leads to the tetragonal-pyramidal configuration. Clearly, it is unstable for **2** to adopt the trigonal-bipyramidal geometry, and this configuration is not considered any more.

3.1.2. Four-coordinated catalyst species

The five-coordinated catalyst species **2** can still dissociate one PMe_3 group to give a four-coordinated catalyst species. Since **2** has two kinds of PMe_3 group, four locate at the basal vertices and one sits at the apical vertex of the tetragonal pyramid, the PMe_3 group at the apical vertex dissociates to give a four-coordinated catalyst species $Mo(PMe_3)_4$ **3**, and the PMe_3 group at the basal vertex dissociates to give another four-coordinated catalyst species $Mo(PMe_3)_4$ **4**. Seen from Fig. 1, **3** is a peri-square planar structure, and **4** is a tetrahedral structure. The average bond distance between Mo and P atoms in **3** is longer than that in **4**, indicating that the intramolecular strain in **3** is larger than that in **4**. The NBO charge of Mo increases from –1.937 eu to –1.093 eu when **2** converts into **3**, and increases to –1.333 eu when **2** converts into **4**. This may be because P atoms in **4** are closer to Mo than that in **3**, donating more electrons into Mo atom. The process from **2** to **3** is calculated to be endothermic by 18.8 kcal/mol with an energy barrier of 29.2 kcal/mol, and the process from **2** to **4** is calculated to be exothermic by 4.0 kcal/mol with an energy barrier of 7.3 kcal/mol, revealing that the PMe_3 group at the basal vertices is much easier to dissociate than that at the apical vertex of the tetragonal pyramid. Clearly, **4** is a reasonable four-coordinated active catalyst, and **3** is no longer considered.

3.1.3. Three coordinated-catalyst species

It also needs to consider for $Mo(PMe_3)_4$ to dissociate one PMe_3 groups to give three-coordinated catalyst species. As shown in Fig. 1, **4** is in a distorted tetrahedron configuration, and has two kinds of PMe_3 groups. The dissociation of the P^1Me_3 group would give the three coordinated-catalyst species **5**, and the dissociation of the P^5Me_3 group would give **6** (see Scheme 1). **5** is a pyramid structure, and **6** shows a planar structure. The bond distance between Mo and P atoms in **5** is shorter than that in **6**. The NBO charge of Mo increases from –1.333 eu to –0.810 eu when **4** converts into **5**, and increases to –0.625 eu when **4** converts into **6**. The reason is similar to the transformation from **2** into **3** or **4**. Many attempts were made to optimize the transition state connecting **4** and **5/6**, however, it is unavailing. To understand the two processes from the viewpoint of energy, the flexible potential energy surface scan is made for the dissociation of P^1Me_3 and P^5Me_3 group. The energy increases with the elongation of the Mo–P bond and no clear peak

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