ELSEVIER

Journal of Molecular Structure: THEOCHEM 731 (2005) 139–147

THEO CHEM

www.elsevier.com/locate/theochem

# Quantum investigation on the mechanism of isomerization of 1-butylene catalyzed by Rh-complex

Xiaoling Luo[a], Dianyong Tang[b], Ming Li[a,*]

[a]Department of Chemistry, Southwest-China Normal University, Chongqing, 400715, People's Republic of China
[b]Key Laboratory of Green Chemistry and Technology, Ministry of Education, Faculty of Chemistry, Sichuan University, Chengdu, 610064, People's Republic of China

Received 29 March 2005; revised 5 June 2005; accepted 18 June 2005
Available online 24 August 2005

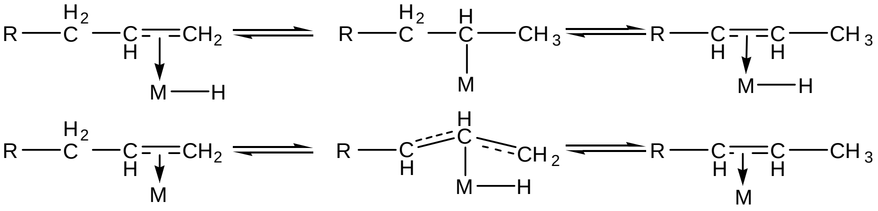
## Abstract

The mechanism of 1-butylene isomerization is studied by means of the density functional theory (DFT). As shown, the isomerization of 1-butylene goes mainly through coordination of 1-butylenen to the catalyst, insertion of the C1–C2 bond into the Rh-H bond, elimination of β-hydrogen, and dissociation of isomerized products. The C1–C2 bond insertion and the β-hydrogen elimination are accomplished through four-membered transition states consisted of H, Rh, and two C atoms. The rate-determining step for the catalytic cycle is the elimination of β-hydrogen. Trans-2-butylene is the preferred product and the selectivity for trans-2-butylene is kinetically and thermodynamically controlled.

*Keywords:* 1-Butylene; Isomerization; Rh catalyst; DFT; NBO

## 1. Introduction

Hydroformylation, as the prevailing homogeneous catalysis, have developed into an extremely important industrial process with over 6 million tons of oxo products obtained via this method worldwide in 1993. Butene is a popular reactant for hydroformylation[1]. In experimental conditions of hydroformylation, the butane easily isomerizes to 2-butene[2]. At the same time, alkene isomerization is an important organic reaction and attracts much attention of the experimental scientists[3–7]. Most of these isomerizations are accomplished by metal hydride (M–H) as proton source[8]. Based on the type of the catalyst employed, two general mechanisms are proposed. These are addition/elimination reactions of metal hydride complexs[9], M–H being present initially as catalyst or generated in situ (Eq. 1), versus a rearrangement through π-allyl intermediates, which proceeds by a reversible hydrogen transfer to generate the π-allyl M–H intermediates (Eq. 2). Most isomerizations appear to proceed via the addition/elimination mechanism [10], and iron carbonyl[11] and some palladium-catalyzed isomerizations are believed to proceed via the π-allyl complex[12].



$$R-\overset{H_2}{C}-\underset{H}{C}{=}CH_2 \cdots M{-}H \rightleftharpoons R-\overset{H_2}{C}-\underset{M}{\overset{H}{C}}-CH_3 \rightleftharpoons R-\underset{H}{C}{=}\underset{H}{C}-CH_3 \cdots M{-}H \quad (1)$$

$$R-\overset{H_2}{C}-\underset{H}{C}{=}CH_2 \cdots M \rightleftharpoons R-\underset{H}{C}\cdots\underset{M-H}{\overset{H}{C}}\cdots CH_2 \rightleftharpoons R-\underset{H}{C}{=}\underset{H}{C}-CH_3 \cdots M \quad (2)$$

Up to now, the isomerization of 1-butylene catalyzed by the rhodium-catalyst has hardly been studied theoretically. It is unclear what mechanism (Eq. 1 or Eq. 2) the 1-butylene isomerization catalyzed by the Rh-catalyst would go

---

* Corresponding author.
*E-mail address:* liming@swnu.edu.cn (M. Li).

0166-1280/$ - see front matter
doi:10.1016/j.theochem.2005.06.020

through. Therefore, the 1-butylene isomerization catalyzed by $HRh(CO)(PH_3)_2$ is investigated in the present paper.

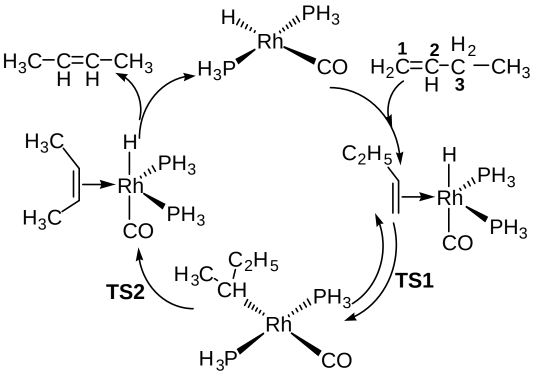
## 2. Computational models and methods

$PH_3$ is chosen to mimic the organic phosphorus ligand $PPh_3$ for minimizing computational time. All the computations are carried out in the density functional theory framework by use of the Becke's three-parameter hybrid exchange functional[13] and the gradient-corrected correlation functional of Lee, Yang, and Parr[14], B3LYP, with the Gaussian 03 program [15]. For rhodium and phosphorus, the double-ζ quality, Hay and Wadt LANL2DZ[16] basis set for the valence and penultimate shells, with effective core potential, is used and the f-polarization function with 1.35[17] of exponent is added for rhodium and the d-polarization function with 0.371[18] of exponent for phosphorus. For all other atoms, the 6–31G(d,p)[19] basis set is utilized. The vibrational analysis and internal reaction calculations (IRC) are performed to verify all transition states. The Wiberg bond index analysis is carried out with the NBO[20] program in Gaussion 03. The charge density diversion of some structures is also calculated to track the reaction mechanism by using AIM2000 program[21].

## 3. Results and discussion

Based on the Wilkinson mechanism[22] of alkene isomerizations, the catalytic cycle of the rhodium-catalyzed 1-butylene isomerization is proposed (Scheme 1). In the following sections, 1-butylene association and insertion will be studied in Section 1, then β-hydrogen elimination with catalyst regeneration will be studied in Section 2, and finally, these results are combined to construct the potential energy profile for the entire catalytic cycle, which is discussed in Section 3.

The atomic labels are presented in Scheme 1. The geometries of all structures are given in Figs. 1,2 and 5. Total energies (E), enthalpies (H, 298.15K, 1atm), free energies (G, 298.15K, 1atm) and their corresponding relative energies (ΔE, ΔH, and ΔG) for intermediates are given in Table 1. The Wiberg bond indexes (WBI) and Mulliken overlap populations (M) of some bonds in the 1-butylene isomerization are shown in Table 2. Total energies, activation energies, and vibrational frequencies for transition states are summarized in Table 3. The transition states are located until the Hessian matrix had the sole imaginary eigenvalue and are also verified by animating the negative eigenvector coordinates with a visualization program and by the IRC calculations (Fig. 3).



Scheme 1.

### 3.1. -Butylene association and insertion into Rh-H bond

As proposed mechanism, the first step of olefin isomerization is olefin association with catalyst **1**. The active catalyst has two possible isomers, **1a** and **1b** shown in Fig. 1. The coordination of t 1-butylene with the catalyst **1** leads to the $\eta^2$-type intermediates **2** which are of trigonal bipyramidal structure. The 1-butylene coordinates with **1** in an equatorial position, whereas the hydride is axial. The preference for axial hydride and equatorial olefin can be attributed to the presence of a vacant axial d orbital ($dz^2$) suitable for the σ bonding with the 1 s orbital of the hydride and the occupied equatorial d orbitals ($dx^2-y^2$, dxy) appropriate for the back-donation to the π* orbital of 1-butylene. The bond between 1-butylene and the Rh center atom is formed by the σ donation of the π orbital of 1-butylene to an unoccupied d orbital of rhodium and the back-donation of an occupied d orbital of the metal to the π* orbital of 1-butylene.

For the different orientations of ethyl in 1-butylene and the different positions of ligands relative to rhodium, there are four possible isomers for the intermediates **2** such as **2a1**, **2a2**, **2b1** and **2b2**. These isomers have similar energies and **2a1** is a little favored of them. For example, the difference between **2b1** of the highest and **2a1** of the lowest is only 7.09 kJ/mol.

The calculated bond lengths of the Rh-H bonds in **2** are slightly shorter than those in the complex **1** because of the decrease in the occupancy of the anti-bond σ* of the Rh-H bonds. The increased values of the Rh-H bond lengths in **2a1** and **2a2** (to 0.1603 and 0.1597 nm) are more than those in **2b1** and **2b2** (to 0.1566 and 0.1565 nm). The lengths of the C1–C2 bonds in the complexes **2** are approximately 0.1406 nm, whereas the C1–C2 bond in **Re** is 0.1333 nm. It is clear that the C1–C2 double bond is activated via the coordination of 1-butylene to the active catalyst **1**. The change in the Wiberg bond indexes and the Mulliken overlap populations in this step are in agreement with the change in structure. Boys[24] localized Kohn-Sham orbitals of **2a1** shown in Fig. 4 make clear that the C-C double is activated by d orbital of Rh atom.

Subsequently, the C1=C2 bonds in **2** insert into the Rh-H bonds to generate four-coordinated unsaturated Rh-alkyl complexes **3** via transition states **TS 1** which have