Journal of Organometallic Chemistry 801 (2016) 30–41

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Exploring activity differences between the hydroformylation catalysts: Insights from theory

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ARTICLE INFO

Article history:
Received 9 July 2015
Received in revised form
3 September 2015
Accepted 13 October 2015
Available online 17 October 2015

Keywords:
Hydroformylation
Rhodium
Monodentate
Density functional theory (DFT) calculations

ABSTRACT

Hydroformylation catalysis is the most important homogeneous catalysis process of the current day. The current computational investigation aims to understand the nature of the hydroformylation process when monodentate ligands are employed. The complete catalytic cycle for different monodentate ligands bound to the rhodium center has been studied with full quantum chemical calculations, with density functional theory (DFT). To the best of our knowledge, this is the first systematic investigation of the relative free energy surfaces for mono-coordinate monodentate and bi-coordinated monodentate ligands in hydroformylation catalysis. The results indicate that the barriers are lower for the mono-coordinate monodentate species in comparison to the bi-coordinate monodentate, for all the ligand cases studied, indicating higher activity for the mono-coordinate monodentate active species.

1. Introduction

Since its serendipitous discovery in 1938, hydroformylation: the “oxo process”, has become the largest homogeneously catalyzed reaction in industry. It represents an atom efficient process for the conversion of olefins to aldehydes by the addition of carbon monoxide (CO) and dihydrogen (H_2) across a carbon–carbon double bond of the olefin in the presence of the catalyst. The reason this reaction has assumed significance over time is because of the increased importance of aldehydes as precursors for drugs, solvents, fertilizers and other valuable chemicals. Annually, more than ten million tons of aldehydes are produced today by means of the hydroformylation reaction [1]. This reaction was initially done with the aid of cobalt (I) carbonyl complexes [2,3], but rhodium (I) complexes soon became the catalysts of choice [4], because of their greater efficiency and functional group tolerance in comparison to the cobalt analogues [5–8]. Over time, rhodium catalysts have evolved from having carbonyl ligands [9,10] to monodentate [7,11–23] and bidentate [24–28] phosphine ligands, as well as mixed phosphine-phosphite ligands [29–35]. It is well established [21,36,37] that the mono-phosphine ligand modified catalysts give higher activity over the diphosphine ligand modified catalysts. Moreover, diphosphine ligands are more difficult to synthesize in comparison to mono-phosphine ligands. On the other hand, diphosphine ligand modified catalysts are found to be more selective over the mono-phosphine ligand modified catalyst systems [21,37–39].

The generally accepted mechanism for the hydroformylation catalysis process is the “Heck and Breslow” mechanism, which is shown in Scheme 1, with the catalyst considered being rhodium coordinated to a monodentate ligand: $HRh(CO)_2(L)$, (where L symbolizes the modified monodentate ligand). As Scheme 1 illustrates, the catalysis process involves several steps, consisting of (i) olefin coordination to the metal center, (ii) migratory insertion of the coordinated alkene into the metal-hydride bond, (ii) coordination and insertion of CO into the metal-alkyl group to form the acyl chain, (iii) oxidative addition of dihydrogen followed by (iv) reductive elimination of the aldehyde and restoration of the active catalyst species. In addition to this, experimental [40–43] and computational studies [44] have indicated that an 18 electron trigonal bipyramidal acyl complex (**7** in Scheme 1) is formed as a dormant species during the hydroformylation process. The other important species that is not part of the catalytic cycle is the 18 electron trigonal bipyramidal pre-catalyst species (**1** in Scheme 1 below) from which the 16 electron active catalyst species is produced by the dissociation of a CO group.

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http://dx.doi.org/10.1016/j.jorganchem.2015.10.015
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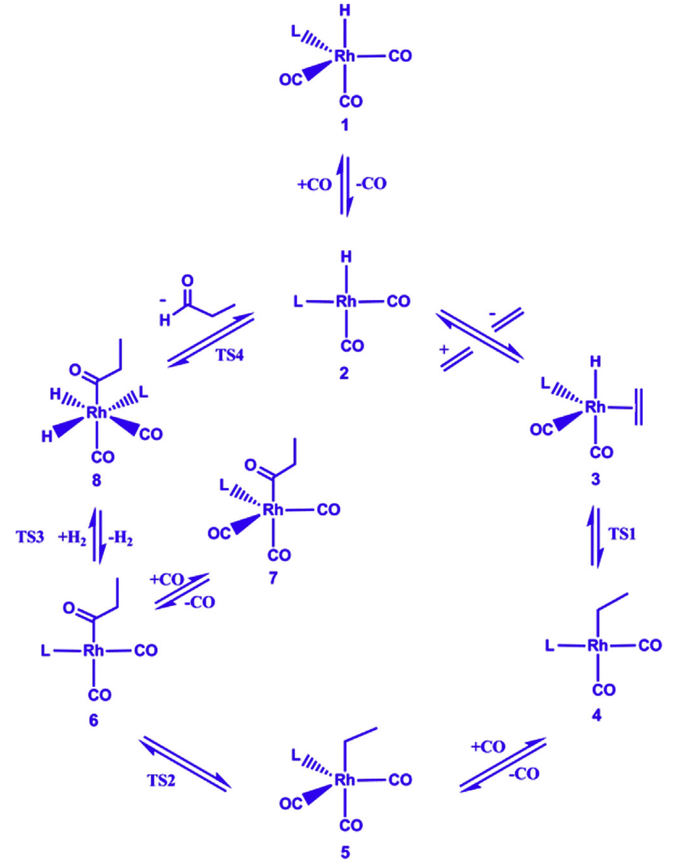

Scheme 1. The Heck–Breslow mechanism for hydroformylation; ethlyene has been considered here as the substrate; the case is for mono-coordinate monodentate ligand coordinated to the metal center.

Since the mechanism consists of many steps, with barriers of comparable heights [45], pinpointing the slowest step in the reaction pathway has proved to be somewhat contentious [11,12,46,47]. Oxidative addition of H_2 to the rhodium center was initially considered the slowest step [48,49], but later studies have muddled the waters somewhat [11,45–47,50]. Calculations of the free energy surface of hydroformylation with $HRh(CO)_3PH_3$ and $HRh(CO)_2(PH_3)_2$ as models for phosphine-substituted rhodium catalysts suggested that the CO insertion step would have the highest barrier [51–53], a result that was altered if solvent effects were taken into account, then giving the oxidative addition of H_2 as the rate determining step [48,51–54]. On the other hand, Gleich and Hutter [55] concluded that the association of alkene to the active species **2** might be playing a key role in enhancing the activity with the more basic systems. Later studies have modeled real systems. Erik Zuidema et al. [56] have done calculations for ethylene hydroformylation with the xantphos modified catalyst system. By focusing specifically on the alkene coordination and hydride insertion steps, they concluded that the rate of the reaction collectively depended on the initial three steps of the catalytic cycle: CO dissociation, alkene coordination to the metal center, and hydride insertion. Jensen's group [44] has investigated the entire hydroformylation cycle for a set of different catalyst systems and concluded that the slowest step of the reaction is either (a) the alkene coordination step followed by migratory insertion of the hydride, or (b) the hydrogenolysis step followed by reductive elimination. They stated that whether the slowest step is (a) or (b) depended on whether the coordinating ligands were electron withdrawing or electron donating respectively. Overall, their results suggested that increasing the electron withdrawing, or the π accepting ability of the ligands, would lead to improvement in catalytic effectiveness. Computational papers subsequent to that [57] have focused on investigating the migratory insertion first step of the hydroformylation process, studying in particular the size and electron withdrawing effects on the rate influencing steps of the hydroformylation process.

It is interesting to note that the previous computational investigations on monodentate ligand systems since the work of Jensen and coworkers [44] has focused on the complex $HRh(CO)_2L$ as the 16 electron species (**2** in Scheme 1 above). However, there is an alternative 16 electron species that is possible along the cycle: the species $HRh(CO)L_2$, i.e. the bi-coordinate monodentate ligand modified rhodium complex. Indeed, there have been experimental reports that suggest that bi-coordination of monodentate ligands might be an important active species during the hydroformylation. Ziolkowski et al. found from IR studies that the 18 electron precatalyst species **1** had three monodentate ligands coordinated to the metal center [58]: a species that would give rise to the bi-coordinate 16 electron complex **2**. Similar findings have been reported by Jes Hjortkjaer [59],A.M. Trzeciak [60]Ziółkowski et al. [61] and Pakkanen et al. [62].

Hence, since both mono-coordinate monodentate ligand coordination, as well as bi-coordination of monodentate ligands is possible, an interesting question that can be asked is: which of the two species is likely to be the more active during the hydroformylation catalysis? Knowing this will provide important insights into the hydroformylation catalysis process. This is the focus of the current computational investigation. We have based the investigation on a recent experimental report by van Leeuwen and coworkers [21], where they have shown that there is a marked difference in activity (of about a thirteen-fold) when the monodentate ligands employed are altered from $L = PPh_3$ to $L = PPy_3$ (where Py_3 is the pyrrolyl ligand). Keeping the experimental evidence in mind, the complete reaction cycle for the two possible species: $HRh(CO)_2L$ or $HRh(CO)L_2$, has been carefully investigated with full quantum chemical calculations, employing density functional theory (DFT). The entire catalytic cycle has been investigated for three different monodentate ligand cases: PPh_3 (tri-phenyl phosphine), $PPhPy_2$ (phenyl dipyrrolyl phosphine) and PPy_3 (tripyrrolyl phosphine) (see Fig. 1 below). Though previous computational studies have tended to focus on a part of the catalytic cycle, it is necessary to investigate the complete catalytic cycle, in order to get a comprehensive idea as to the rate influencing steps of the reaction. The results, which will be discussed below, provide insights about which of the two species: $HRh(CO)_2L$ or $HRh(CO)L_2$, is the more active, and also indicates that common features indeed exist in the nature of the catalytic cycles for the cases studied.

2. Computational details

All the DFT calculations were carried out using the Turbomole 6.0 suite of programs [63]. Geometry optimizations were performed using the Perdew, Burke, and Erzenhof density functional (PBE) [64]. The electronic configuration of the atoms was described by a triple-ζ basis set augmented by a polarization function (Turbomole basis set TZVP) [65]. The resolution of identity (ri) [66], along with the multipole accelerated resolution of identity (marij) [67] approximations were employed for an accurate and efficient treatment of the electronic Coulomb term in the density functional calculations. Care was taken to ensure that the obtained transition state structures possessed only one imaginary frequency corresponding to the correct normal mode. Single point calculations were then done with the hybrid B3-LYP functional [68,69] on all the