

Alkyl-rhodium transition state stabilities as a tool to predict regio- and stereoselectivity in the hydroformylation of chiral substrates

Giuliano Alagona ^{*}, Caterina Ghio

CNR-IPCF, Istituto per i Processi Chimico-Fisici, Molecular Modeling Laboratory, Via Moruzzi 1, I-56124 Pisa, Italy

Received 1 December 2004; revised 21 December 2004; accepted 21 December 2004

Available online 14 April 2005

Abstract

A theoretical investigation on the stability of the alkyl rhodium transition states as the key-step determining the regio- and diastereoselective outcomes of the hydroformylation reaction with an unmodified rhodium catalyst ($\text{H-Rh}(\text{CO})_3$) has been carried out. The results obtained employing effective core potentials for Rh in the LANL2DZ valence basis set, with the other atoms described at the B3P86/6-31G* level, have been compared to those computed with B3LYP/SBK(d), using effective core potentials for Rh and main group atoms. A number of contaminations between those levels or additional basis functions have also been used. The substrates considered are three related chiral olefins, namely (1-vinyloxy-ethyl)-benzene (**1**), (1-methyl-but-3-enyl)-benzene (**2**), and (1-methyl-allyl)-benzene (**3**). The structural features of the various possible complexes, which show a second chiral center at the inner olefin carbon upon complexation, do not present major changes among the various computational descriptions for each substrate. Significant differences in relative stabilities of the lowest energy transition states can be detected in the case of the ethereal substrate (**1**), whereas for both chiral alkenes (**2** and **3**) only very small energy gaps have been computed. In the case of **1** and **2**, a quantitative agreement with available experimental results is obtained at the B3P86/6-31G* level, that should allow the prediction of regio- and stereoselectivity for chiral olefins not already screened. The B3LYP/SBK(d) values are comparable to the B3P86/6-31G* ones, although in the case of vinyloxy (**1**) the B3LYP/SBK(d) regioisomeric ratio turns out to be critical.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Regioselectivity; Diastereoselectivity; Unmodified rhodium catalysts; Theoretical investigation

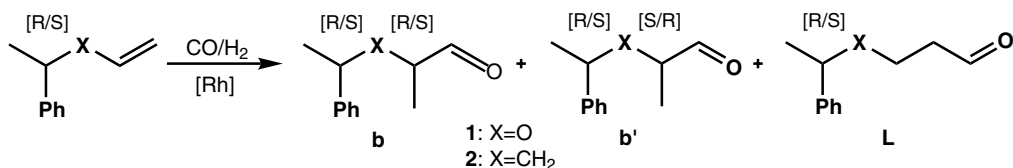
1. Introduction

Hydroformylation of alkenes, one of the largest industrial catalytic processes, is used for the production of aldehydes [1], which can conveniently be converted to alcohols [2]. Though discovered many years ago [3], this reaction is still being studied both experimentally [1,4] and theoretically [5] to elucidate its mechanism. The hydroformylation reaction makes use of a number of

homogeneous transition metal complexes as catalysts. The most common are low-valent cobalt and rhodium [2,4a,6] complexes, albeit complexes based on Pt, Ru, Ir and Pd are used in asymmetric hydroformylation [7]. Since the economical value of the final product is linked to the nature of the aldehyde (linear, L, or branched, B), it is very important to control the reaction regioselectivity. In the case of branched aldehydes with chiral centers, such as those displayed in Scheme 1, the reaction diastereoselectivity is to be considered as well. Obviously, analogous schemes can be imagined for chiral unsaturated substrates without any separator (no X group), one of them taken also into account in this investigation.

^{*} Corresponding author. Tel.: +39 050 3152450; fax: +39 050 3152442.

E-mail address: G.Alagona@ipcf.cnr.it (G. Alagona).



Scheme 1.

A reliable method to obtain an a priori estimate of the reaction regio- and diastereoselectivities, i.e., the regioisomeric (B:L, with $B = b + b'$) and diastereomeric (b:b') ratios between the aldehydes produced, would be very helpful because of the monetary value of chiral unsaturated substrate hydroformylation and might even save a good number of experimental trials.

Of course, there are several factors affecting the reaction outcome. Among them, substrate structure and properties, reaction parameters (P, T, concentration), and nature of the catalyst (unmodified, or modified with phosphorous ligands) are those playing the most important role. The presence of phosphine ligands, mainly because of steric hindrance [5d], somewhat inhibits the activity of the catalyst imposing severe reaction conditions without a generalized improvement in selectivity, although unmodified catalysts are sometimes charged with low selectivity [1c]. However, this is not always true, as clearly shown in the case of styrene [8]. Conversely, with unmodified catalysts, such as those employed in this study, the reaction occurs under mild conditions, where other typical side processes are negligible. This allows a consistent comparison between theoretical and experimental (obtained using $[\text{Rh}_4(\text{CO})_{12}]$ as a catalyst precursor) results, without any interference from phosphine ligands. Additionally, as much simpler models than modified catalysts, they have a heuristic function, since the hydroformylation mechanism is far from being well understood [1c]. Last, but not least, the computational complexity of the system is significantly lower.

As far as the particular reactions reported in Scheme 1 are concerned, branched aldehydes decidedly prevail over linear regioisomers when $X = \text{O}$ and, between the possible pairs of diastereomers of the branched aldehyde, the (R,R) or (S,S) pair, i.e., b, prevails over the (R,S) or (S,R) one, i.e., b'. In contrast, when $X = \text{CH}_2$, the prevalence of one species over the other is very limited or vanishingly small [9]. Of course, different results can be obtained in the case of a diverse substrate, even in analogous experimental conditions.

The hypothesis that the regio- and diastereoselectivity of the hydroformylation reaction originate at the alkyl formation step was confirmed in our previous theoretical investigations [10] by comparison with experiments employing unmodified rhodium catalysts in mild conditions. It is worth noting that an experimental determination of the relative concentrations of isomeric alkyl

rhodium intermediates (not to mention transition states) is not allowed, since they are very reactive under typical hydroformylation conditions. The experimental evidence is thus confined to the aldehyde products.

In the present investigation, the stability of the alkyl rhodium transition states for three chiral substrates at various computational levels is considered. Aim of this study is not just of assessing which of them is adequate and affordable to eventually predict the outcome of hydroformylation reactions with different olefins as substrates, but also of evaluating and analyzing their behavior. In addition the computational strategy is discussed, because even sophisticated computational descriptions miserably fail without an accurate and careful conformational analysis within each configuration.

2. Computational details

All the calculations have been carried out with the Gaussian98 system of programs [11] in the density functional theory (DFT) framework. Gradient-corrected Becke's three parameter hybrid exchange [12] and Perdew's P86 gradient-corrected correlation [13] functionals, B3P86, at the 3-21G [14] and 6-31G* [15] levels for C, O and H have been used, coupled for Rh to effective core potentials (which implicitly include some relativistic effects for the electrons near the nucleus) in the LANL2DZ [16] corresponding valence basis set. In what follows, for the sake of simplifying the notation, reference to 3-21G and 6-31G* basis sets stand for 3-21G/LANL2DZ and 6-31G*/LANL2DZ, i.e., both names include also the aforementioned Rh description without any need of mentioning it again. The 3-21G results are reported in Supplementary Material (Tables S1–S3).

Another set of calculations has been carried out using B3LYP/SBK(d), that is the gradient-corrected Becke's three parameter hybrid exchange functional, as above, and the Lee, Yang, Parr's correlation [17] functional. SBK(d) denotes the effective core potential basis set of Stevens et al. [18] (named CEP-31G in Gaussian), employed for Rh and the main group atoms, with CEP replacing, respectively, the 14 innermost core orbitals only and the *1s* orbitals, but augmented with a *d* polarization function [19]. Thus, 17 electrons for Rh are included in the valence space and treated explicitly; the associated Rh valence basis set is of quadruple and triple ζ quality for the *sp* and *d* shells, respectively, with a

Download English Version:

<https://daneshyari.com/en/article/1327934>

Download Persian Version:

<https://daneshyari.com/article/1327934>

[Daneshyari.com](https://daneshyari.com)