

Kinetics and Selectivity in Hydroformylation of Propene

EWA N. SZLAPA¹ and JEREMY N. HARVEY¹

¹ KU Leuven, Quantum Chemistry and Physical Chemistry Celestijnenlaan 200f, 3001 Heverlee, Belgium.

Homogenously catalysed hydroformylation, used in industrial synthesis of aldehydes from alkenes and syngas (hydrogen and carbon monoxide), is one of the most extensively studied reaction both experimentally and theoretically [1-2]. One of the crucial aspects of the reaction is the selectivity of the catalyst towards the desired product. In this studies we employ the computational approach in order to investigate the kinetics and selectivity of unmodified cobalt-catalysed propene hydroformylation. In this chemical process a propene substrate reacts at a high temperature with hydrogen and carbon monoxide producing two aldehyde isomers: linear n-butylaldehyde and branched iso-butylaldehyde. The product ratio depends on the reaction conditions (temperature, initial catalyst and propene concentrations and pressure of gases). Density functional theory and explicitly correlated coupled-cluster methods are used to accurately compute potential energy surfaces of the catalysis leading to both products. Coupling the computationally resolved mechanism with kinetic modelling gives an important insight into the detailed mechanism of the investigated reaction. The proper designation of symmetry numbers [3] is essential in order to reproduce the experimental selectivity [4-5].

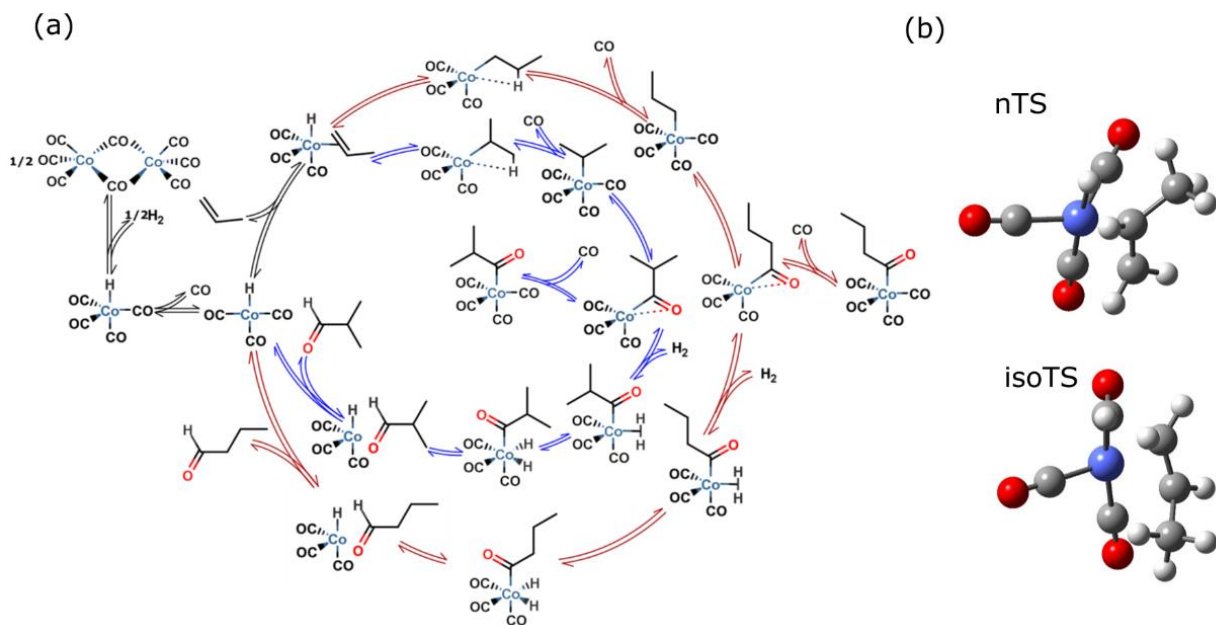


Figure 1 (a) Catalytic cycle of propene hydroformylation reaction indicating elementary steps and pathways leading to two distinct products. The red cycle leads to formation of linear n-butylaldehyde, while a blue cycle leads to branched iso-butylaldehyde. (b) The pathway separates at bifurcation step and depends on the orientation of propene while it is inserted into Co-H bond

[1] T. Kégl, *RSC Adv.* 5, 4304 (2015).

[2] L. E. Rush, P. G. Pringle, J. N. Harvey, *Angew. Chem. Int. Ed.* 53, 8672 (2014).

[3] A. Fernández-Ramos, B. A. Ellingson, R. Meana-Pañeda, J. M. C. Marques, D. G. Truhlar, *Theor Chem Account* 118, 813 (2007).

[4] R. V. Gholap, O. M. Kutz, J. R. Bourne, *Ind. Eng. Chem. Res.* 31, 1597 (1992).

[5] R. V. Gholap, O. M. Kutz, J. R. Bourne, *Ind. Eng. Chem. Res.* 31, 2446 (1992).