

DFT STUDIES ON THE MECHANISM OF THE Ru-MACHO-CATALYZED GUERBET REACTION OF ETHANOL TO BUTANOL

XXIV International Conference on Chemical Reactors CHEMREACTOR-24

September 12 - 17, 2021



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Introduction

The aim of the Carbon2Chem® project is the utilization of steel mill flue gases as a resource for the synthesis of fine and base chemicals. As part of the SynAlk subproject CO and CO₂ are used to produce C₂₊-alcohols. [1] As part of this project the formation of higher alcohols out of ethanol via the Guerbet-reaction is investigated with the aim of a direct continuous conversion of ethanol to butanol. Butanol has a higher energy density (90% that of gasoline) than Ethanol (70% that of gasoline) and other than ethanol is immiscible with water (no corrosive effects on combustion engines). [2] It is therefore an ideal fuel additive. For this reason the conversion of bioethanol to butanol is of high interest on behalf of more sustainable fuels.

Previous work showed, that the Ru-MACHO-catalyst is active for the guerbet-reaction from ethanol to butanol and that the reaction leads to 1-butanol as well as 2-butanol as products. The reaction can be described as a ball in a maze game, where tilting the game in different direction equals the variation of reaction

Parameters, leading to different products and side products. [3]

To obtain further information on the mechanism DFT calculations are carried out.



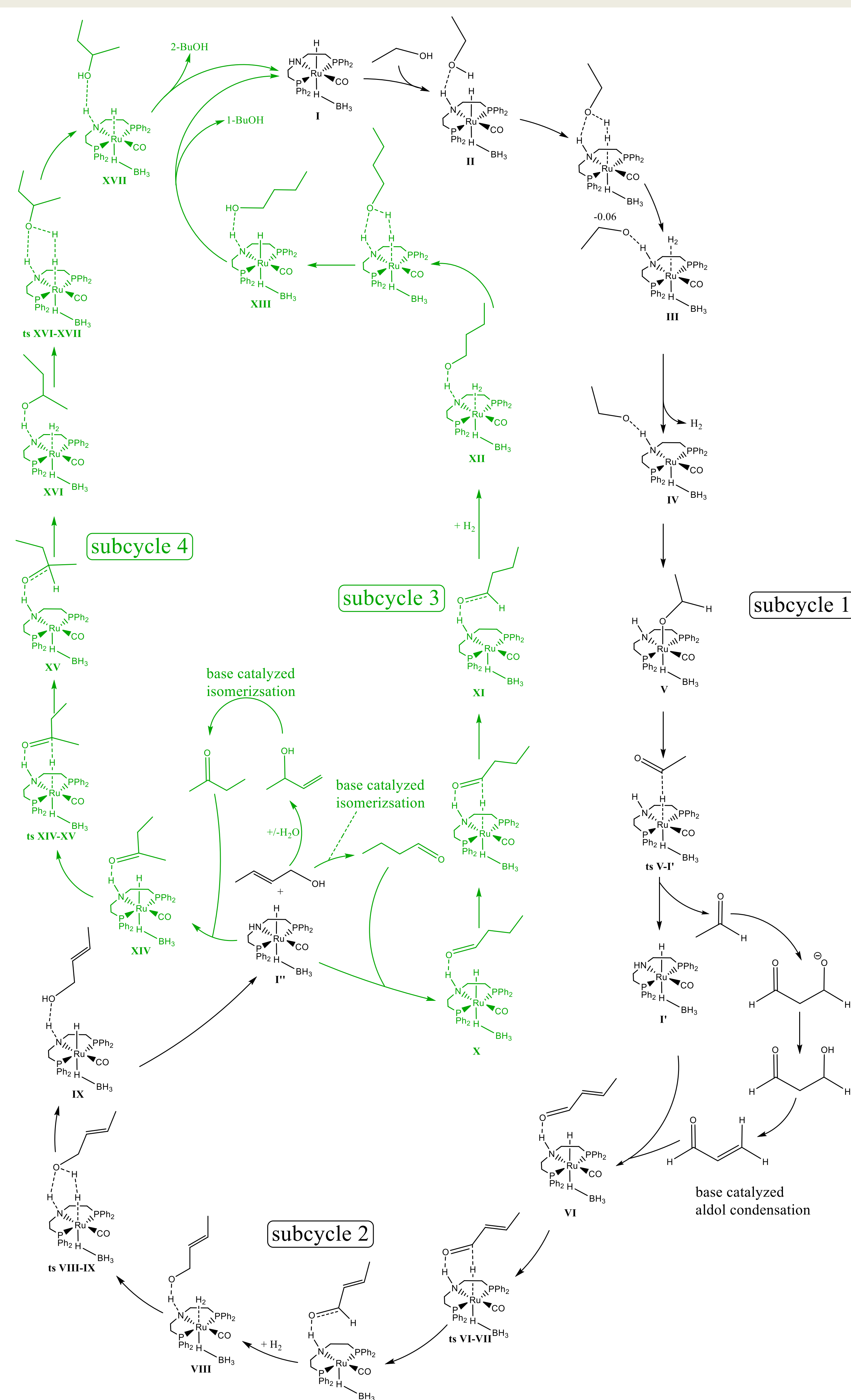
The Guerbet reaction as a ball-in-a-maze. [3]

Results

For the investigation of the mechanism the BP86/def2-SVP method including Grimme dispersion and Becke-Johnson damping via GD3BJ is used. Structures in black have already been calculated, structures in green still need to be validated by calculations with the chosen method.

The mechanism for the formation of 1-butanol and 2-butanol can be divided into 4 different subcycles:

- **Subcycle 1** - Dehydrogenation of the ethanol: Ethanol coordinates to the hydrogen bound to the Nitrogen on the catalysts backbone via its oxygen atom (II). The oxygen is then dehydrogenated under the formation of H₂ (III). The Hydrogen-molecule splits of and leaves a free coordination site at the ruthenium-center of the catalyst (IV), where the ethanolate recoordinates via its oxygen atom (V). By transferring a proton to the ruthenium-center acetaldehyde is formed.
- **Subcycle 2** - Hydrogenation of the aldehydes CO-Bond: Crotonaldehyde, which is formed by the aldolcondensation of two acetaldehyde-molecules coordinates to the hydrogen-atom on the N-H-Bond of the backbone (VI). The hydrogen Atom coordinated to the Ruthenium-atom is transferred to the Carbon Atom of the CO-double-bond of the aldehyde, which leads to a free coordination site on the central atom (VII). H₂ coordinates to the free coordination site (VIII), and one of its Hydrogen atoms is transferred to the oxygen-Atom in the following (IX). Crotyl alcohol is formed.
- **Subcycle 3** - Hydrogenation of the CC-Bond: A base catalyzed isomerization of Crotyl alcohol leads to butanal, which then can be hydrogenated to 1-butanol in a mechanism similar to subcycle 2 (structures X to XIII).
- **Subcycle 4** - Hydrogenation of the CC-Bond: The Crotyl alcohol can be rearranged to but-3-en-2-ol using water. The formed alcohol can then be isomerized to 2-butanone, which can be hydrogenated in the same manner as in subcycles 2 and 3 (structures XIV to XVII).



Reaction mechanism of the formation of 1-butanol and 2-butanol via the Ru-MACHO-catalyzed guerbet reaction

[1] M. Oles, W. Lüke, R. Kleinschmidt, K. Büker, H. J. Weddige, P. Schmöle, R. Achatz, Chem. Ing. Tech. 2018, 90, 169 – 178.

[2] H. Aitchison, R. L. Wingad, D. F. Wass, ACS Catalysis, 2016, 6, 7125-7132.

[3] Ohligschläger, Andreas; Staalduinen, Nils; Cormann, Carsten; Mühlhans, Jan; Wurm, Jan; Liauw, Marcel A., Chemistry - Methods, 2021, 4, 181-191

Conclusion and Outlook

- Subcycle 1 and 2 could already be calculated. Subcycle 3 and 4 are still under investigation.
- It could be shown, that the CO-double-bond of the crotonaldehyde has to be hydrogenated first, and the formed crotyl alcohol isomerized to crotonaldehyde to be hydrogenated to butanol. A direct route for the hydrogenation of the CC-double-bond could not be found.
- Side reactions still need to be investigated.

We gratefully appreciate the support received from the Federal Ministry of Education and Research of the Federal Republic of Germany (Bundesministerium für Bildung und Forschung, BMBF, 03EK3041D, Verbundvorhaben Carbon2Chem-L4: SynAlk – Teilprojekt 'Herstellung von C₂₊-Alkoholen auf Basis von H₂, CO und CO₂ aus Kuppelgasen').

