

# Reaction kinetics of homogeneously catalyzed dehydrogenation of 1-phenyl-1,3-propanediol-derived lignin model compound

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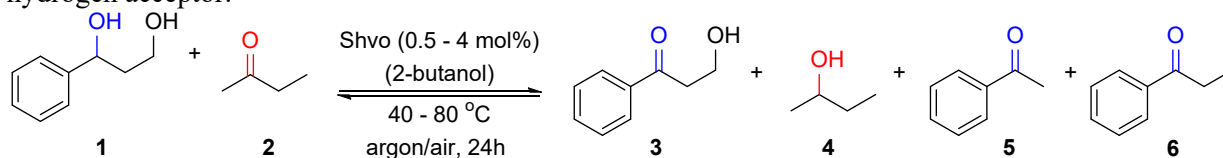
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## Highlights

- Kinetic analysis of the Shvo catalysed dehydrogenation
- Reaction order in the catalyst below unity
- Numerical data fitting and parameter estimation

## 1. Introduction

Lignin, a structural element of lignocellulosic biomass, is a potential sustainable feedstock for manufacturing fuels, fine chemicals, and different materials [1]. New functionalities can be introduced into lignin structures by oxidative dehydrogenation of the hydroxyl groups or, for example, by using hydrogen transfer from lignin hydroxyl group to an acceptor containing a keto group [2]. For hydrogen transfer reactions, various homogeneous and heterogeneous transition metal catalysts can be utilized [3]. Homogeneous ruthenium complexes have been frequently employed as catalysts for several organic transformations, including (de)hydrogenations, racemizations and reductive aminations, often displaying high selectivity and product yields [3]. Introduced in the early 1980s, the Shvo-catalyst is considered as one of the most active transition metal complexes for hydrogen transfer reactions [4]. Dissociation of the Shvo-catalyst into two different complexes allows to perform both dehydrogenation and hydrogenation steps, making it a versatile catalyst applicable for a broad range of hydrogen transfer processes [5]. Moreover, the Shvo-catalyzed transfer hydrogenation can be efficiently carried out under mild condition. Herein, the reaction kinetics of the Shvo-catalyzed dehydrogenation of 1-phenyl-1,3-propanediol (Figure 1), representing a diol fragment in lignin, was investigated using 2-butanone as the hydrogen acceptor.



**Figure 1.** Shvo-catalyzed dehydrogenation of 1-phenyl-1,2,3-propanediol.

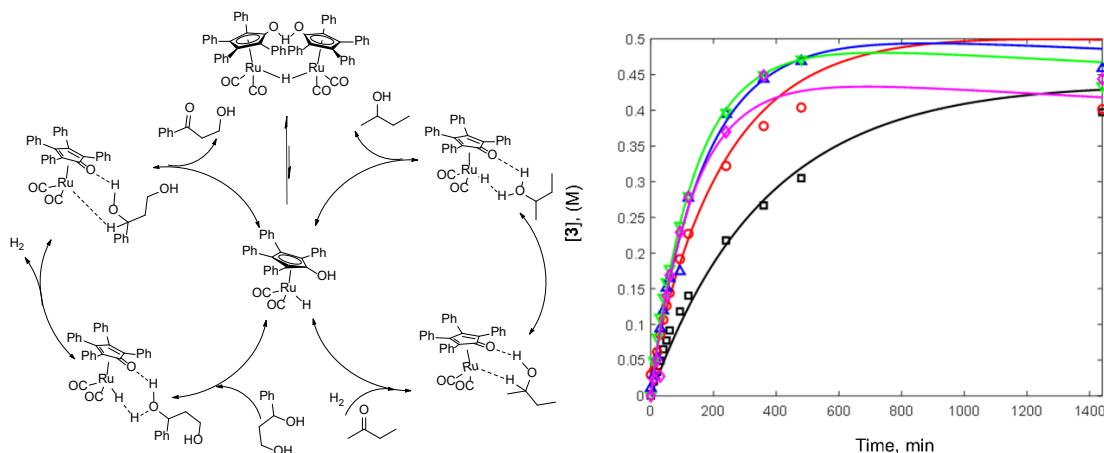
## 2. Methods

All chemicals were purchased from TCI, ABCR or Sigma-Aldrich and used without further purification (purity  $\geq 98\%$ ), unless otherwise indicated. Concentrations of the reactants and products were monitored by a gas chromatograph (GC) equipped with flame ionization detector (FID) and an HP-1 column (30 m  $\times$  320  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$ ). To investigate the influence of the catalyst concentration experiments were carried out at Shvo catalyst loadings of 0.005 mmol- 0.04 mmol with 1 mmol of solid 1-phenyl-1,3-propanediol 1 and 2 mL of the tetradecane solution (0.005 M) in 2-butanone at 60 °C. Temperature dependence was studied at 2 mol% catalyst loading between 40 and 80°C. The reaction was monitored for 24 h withdrawing periodically samples from the reaction mixture. Finally, the reaction was carried out at different ratios of 2-butanol to 2-butanone to evaluate how the presence of 2-butanol formed in the reaction mixture affects the reaction rate. The total volume of the reaction mixture was equal to 2 mL, thus the concentration of 1-phenyl-1,3-propanediol and tetradecane in the final solution remained constant in each experiment.

The rate equations have been derived based on the mechanistic model presented below. The parameter estimation was carried out with the software ModEst using as the objective function the squared difference between the experimental and calculated values of the reactant concentrations. This difference was minimized by using the hybrid simplex and Levenberg-Marquardt algorithms.

### 3. Results and discussion

The developed kinetic model was based on the outer sphere reaction mechanism involving two catalytic cycles and a common vertex (Figure 2).



**Figure 2.** a) Outer sphere mechanism, b) Concentrations profiles of 3-hydroxypropiophenone formed in the dehydrogenation of 1-phenyl-1,3-propanediol at different catalyst concentrations.

The kinetic model based on this reaction mechanism incorporated besides dissociation of the dimer catalyst, also additional features such as the limited monomer catalyst solubility in butanol compared to butanone, reversibility of hydrogen transfer from 1-phenyl-1,3-propanediol to 2-butanone and deactivation of the Shvo-catalyst, leading to the following rate expression for the main reaction

$$r_{1 \rightarrow 3} = (k'_{+2,0} K'_1 C_1 C_2 - k'_{-2,0} (K_3^{-1})' C_3 C_4) \sqrt{\frac{\gamma \lambda C_{\text{catalyst}}}{1 + K_S C_{\text{catalyst}}}} \exp(-k_d * \text{conversion}) e^{-\frac{E_{\text{act},1}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ave}}} \right)} \quad (1)$$

The parameter estimation was done for all experimental data combined giving a very good description of the data. The Markov Chain Monte Carlo analysis was performed to determine the parameters, which could not be reliably identified during the data fitting,

### 4. Conclusions

The reaction kinetics of the Shvo-catalyzed dehydrogenation of 1-phenyl-1,3-propanediol, representing a diol fragment in lignin, using 2-butanone as the hydrogen acceptor, is thoroughly analyzed, and addressed. Several new from the methodological viewpoint features of the reaction kinetics, which were not discussed in the literature, have been identified and incorporated into mathematical modelling in a rigorous way. Namely reversibility of the reaction was included in the kinetic expression. Predominance of noncatalytic dimeric species over catalytically active monomeric ones results in the reaction order below unity. The catalyst has a limited solubility in a particular solvent giving a curve with saturation, which was taken into account along with catalyst deactivation. Finally, a significant rate retardation upon elevation of butanol concentration was explained by substantially different solubility of the catalyst in butanone and butanol, which was treated using the Jouyban-Acree model for solute solubility in binary mixtures of solvents.

### References

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### Keywords

Shvo-catalyst, dehydrogenation, reaction kinetics, lignin,