

# Ab Initio Study on the Dimerization of Lignol Model Species

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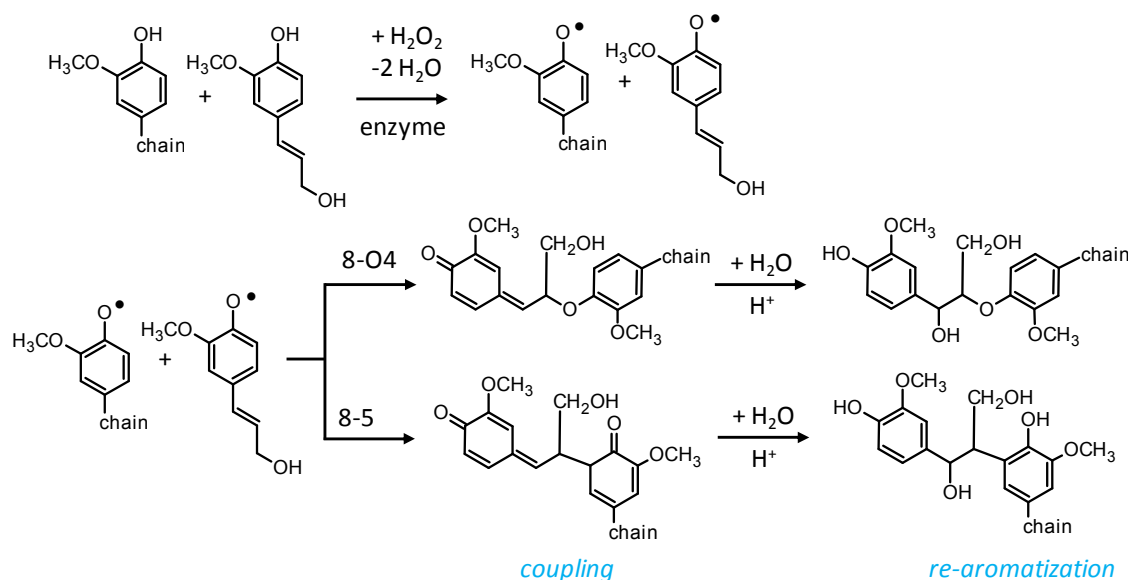
## Introduction

Lignocellulosic biomass is considered a viable alternative to fossil resources for energy and chemical production. Despite its benefits as renewable and carbon neutral resource, low crude-oil prices hamper the economic prospects of its utilization as energy carrier. In order to reduce costs of bio fuel production from lignocellulosic biomass, all its components need to be converted to valuable products. One idea in this direction is the ‘lignin-first’ bio-refining concept, in which the lignin fraction of lignocellulosic biomass is removed in such a way that mainly soluble lignin monomers and oligomers are formed, leaving the cellulosic and hemicellulosic parts undissolved behind [1][2]. The sugar part is subsequently fermented to bio-ethanol or hydro-treated and converted through steam-cracking to fuels and base chemicals, while the lignin mono- and oligomers are converted to various high-value products. Since the lignin fraction is this primary interest in this process, its composition has a significant impact on the economics. Being able to control the lignin composition would allow to generate ‘customized’ lignin mono and oligomer pools to increase profits. Hence, it is necessary to develop a thorough understanding of lignin synthesis in plants to create such engineering opportunities.

One area of current uncertainty is the lignin polymerization step. Plants produce lignin monomers (lignols) via quite well-known metabolic pathways [3][4]. Once these lignols are produced, they are transported to the cell wall and couple to an existing lignin polymer chain. The commonly considered mechanism [3][4] for this process is the radical recombination mechanism shown in Figure 1a. The phenolic groups of the lignin chain and the new lignol – shown for guaiacyl (G) units – are both enzymatically oxidized using one mole  $\text{H}_2\text{O}_2$  as oxidant. Next the phenoxy group of the chain adds to the “8” position of the resonantly stabilized lignol radical. This happens preferably in one of two ways: either the phenoxy oxygen or the carbon atom in ortho position to it (referred to as “5”) forms the bond. Finally, water is added and the aromaticity is restored. The addition step is considered to be ‘random’ to account for the variety in the lignin structure. One problem with this mechanism is the lack of justification for the restriction that lignol radical only reacts at the “8” position. A radical addition mechanism would resolve this issue, however radical polymerization schemes typical for plastics formation contain chain propagation steps that would (a) yield structures not seen in nature and (b) are in conflict with the molar consumption of  $\text{H}_2\text{O}_2$ . The proposed radical addition scheme shown in Figure 1b resolves these issues. Here only the end group of the lignin chain is oxidized, leaving the enzyme itself also in an oxidized state. Radical addition by the oxygen or ortho-carbon radical site leads to radical intermediates, which subsequently reduce the oxidized enzyme. If necessary, proton transfer reactions re-aromatize the molecule.

The objective of the current study is to use ab initio methods to explore the feasibility of both mechanisms in terms of reaction enthalpies and barrier heights.

(a) radical recombination mechanism



(b) alternative radical addition mechanism

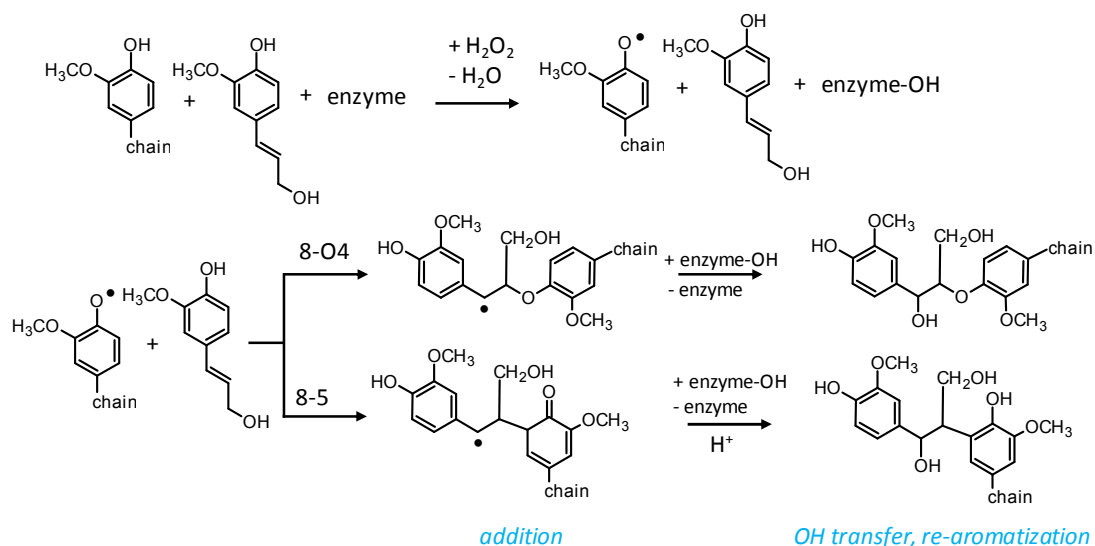


Figure 1 (a) Illustration of the commonly accepted radical recombination mechanism using G units as example. (b) proposed radical addition mechanism for the same linkages.

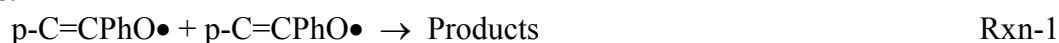
**Methodology**

Several studies have already addressed lignin formation chemistry, however these generally employed DFT based calculation methods [5]-[20]. In this study, the CBS-QB3 level of theory is used. Since CBS-QB3 calculations of large molecules are highly demanding, in particular with respect to the storage of integrals, such calculations are limited to molecules containing up to about 20 heavy atoms given the currently available facilities. Therefore only small model compounds can be used. The CBS-QB3 calculations are performed with the G09 suite of programs [21]. Geometries are optimized at the B3LYP/CBSB7 level and the same level is used for frequency calculations. Several single-point energy calculations are combined to obtain the final 0K CBS-QB3 energy, which is used without further corrections in this study. Statistical

mechanics is used to calculate thermal contributions to the enthalpy, the entropy and heat capacity values using the optimized structure of the lowest energy conformer and the harmonic frequencies as input. Internal rotations are separately treated as 1-D modes. The hindrance potentials needed for the hindered rotor treatments also help with the identification of the lowest energy conformer. Transition states are identified as structures with a single imaginary frequency which resembles the expected reacting mode. More calculation details can be found in [22].

## Results

The following reactions have been considered as models for the lignin formation mechanisms:



Rxn-1 represents the radical recombination reaction and Rxn-2 the crucial step of the radical recombination sequence. The re-aromatization step is assumed to be not rate limiting.

Reaction Rxn-1 has ten possible channels shown in Figure 2. Except for the peroxide, all channels are exothermic. Furthermore, most barriers are submerged (lower in enthalpy than the reactants) or only slightly above the entrance channel. This suggest that all pathways

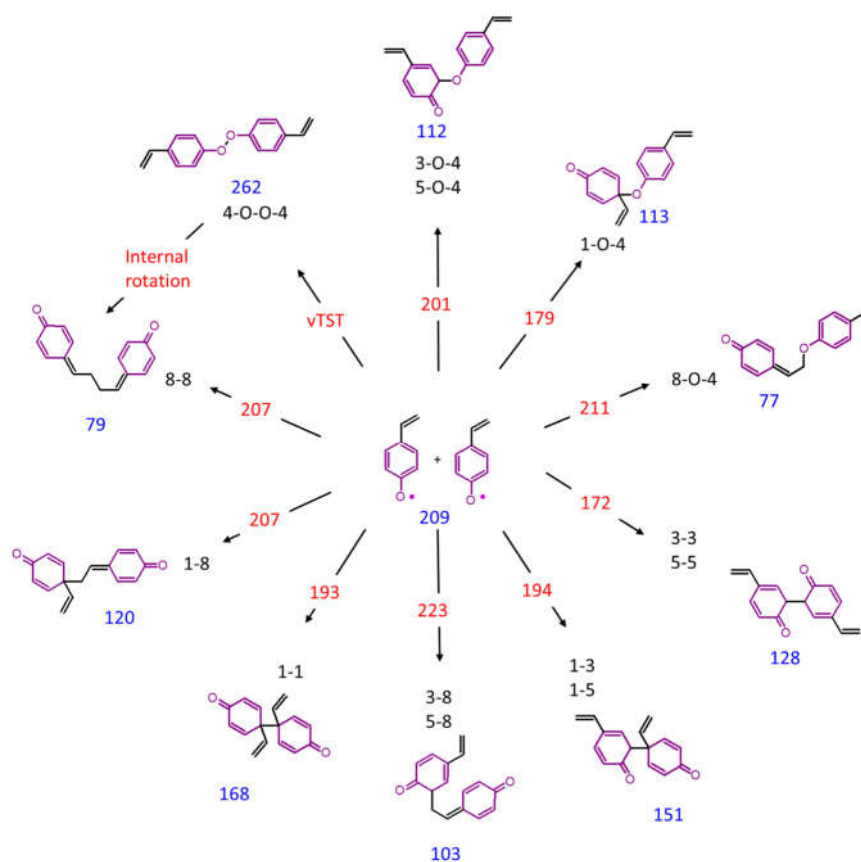


Figure 2 Exploration of all possible radical recombination pathways of *p*-vinyl phenoxy radicals. Blue:  $\Delta H^{298}$  of the products in kJ/mol; red:  $\Delta H^{298}$  of the transition states in kJ/mol. The black labels indicate the linkage type.

should be accessible. Given that experiments only found products arising from addition to the “8” position, it is clear that a kinetically controlled radical recombination mechanism does not lead to the correct product distribution. One encouraging result, though, is that the most stable products are those originating from 8-O4, 8-8 and 8-5 (or 5-8) linking in agreement with the observations in laboratory lignin dimerization experiments [23][24].

The twelve channels for Rxn-2 are shown in Figure 3. Only 2 pathways are exothermic (8-8, and 8-O4), which are the dominant ones in dimerization experiments [23][24]. The 3-8 (same as 8-5) is slightly endothermic, while all others are stronger endothermic. All reactions proceed through barriers that are clearly above the energy of the reactants. The reactions forming the 8-8, 8-O4 and 3-8 linkages shown in Figure 3 have the lowest barriers. Hence, the radical addition step offers a natural explanation why lignin growth involves preferentially the “8” position and why only a few products are formed.

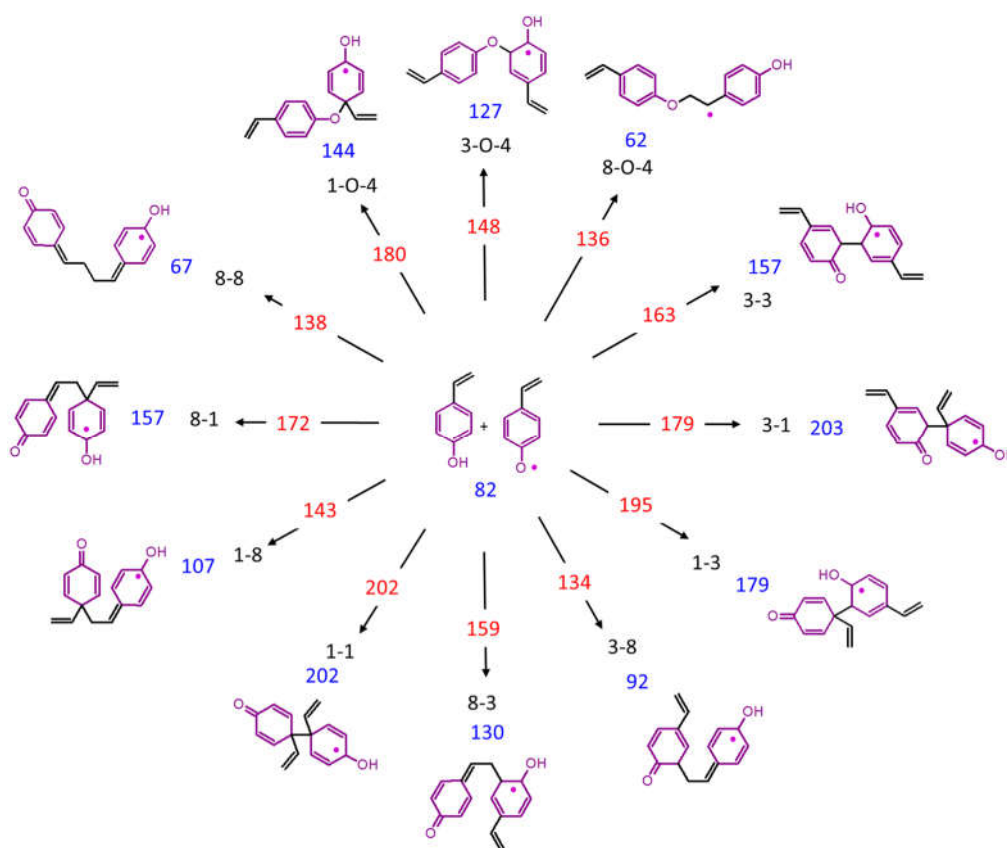


Figure 3 Exploration of all possible pathways for *p*-vinyl phenoxy radical adding to *p*-vinyl phenol. See the caption of Figure 2 for explanations of the color code.

Similar calculations using *p*-coumarylalcohol, *p*-HOPhCH=CHCH<sub>2</sub>OH, instead of *p*-vinylphenol lead to the same conclusions. Additional calculations with model compounds resembling the G and S units in lignin are in progress and will be presented at the meeting.

## Conclusions

The CBS-QB3 method has successfully been applied to investigate the dimerization of model compounds that resemble the lignin dimerization process. Based on the stability of products and the barrier heights obtained, the radical addition mechanism is able to correctly predict the experimentally observed linkages. In contrast, the radical recombination reaction predicts a wealth of products not seen in nature. Extension of the current study towards G and S units is needed to test if the known reactivity differences between the different lignols can also be predicted with the new radical addition model. Such calculations are in progress.

## Acknowledgments

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