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Ab Initio Study on the Dimerization of Lignol Model Species

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Motivation



- Ecology friendly
 Sustainability
 CO₂ neutrality: climate change
 Wild fire protection
- Economics is challenging
 - Low price for fossil resources
 - Low heating value
 - Costly post-processing



Lignin structure

H₃CO

VIB model:

- Linear polymer
- Saturated C3 units
- OH in "7"(α) position
- Random S,G distribution
- Random linkage distribution
- 8-8 pinoresinol is proposed as initial lignol dimer
- In trees: few H units present
- => Structure implies

non-enzymatic radical coupling





Lignol Metabolism Well Known

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Currently accepted model: Radical Recombination



Polymer chemistry model: Radical Addition



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except for start structure

- Explains involvement of "8" position
- Initial link is okay

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- Yields long chains, no recombination dimers/oligomers
- Propagation leads to wrong structure •
- Molar consumption of H_2O_2 not explained

QM calculations performed to address the following questions:

- > Is radical recombination more selective than expected ?
- Can initial radical addition step explain the preference of linkages observed?
- Ideas for new model ?

A few words on the calculations

Previous studies

- DFT based calculations
 - Minnesota functionals as best level
 - thermodynamic control of overall process
 - Spin densities and orbital polarizations
 - Able to study *large* molecules
- > so far not very convincing results on selectivity questions

Our study (in progress)

- post-HF based calculations
 - CBS-QB3 level of theory is well-established
 - reliable, low risk for no artificial results
 - Looking at TS and intermediates
- Restricted to small model compounds





Large No of products expected from Recombination

Observations

- No significant energy barriers
- All products but peroxide are **exothermic**
 - 8-O-4 product most stable
 - Dominantly formed 8-8 product only second most stable
 - High exothermicity does not allow reverse rxn at room temperature
- No foundation found for "8" rule
 - Large product spectrum expected in DHP experiments





linkage	2x p-C=CPhO∙	p-C=CPhO∙ + p-t-HOCC=CPhO∙	
8-8	-130	-131	N/A
8-1	-90	-87	N/A
8-3	-107	-106	-101
8-0-4	-133	-150	-131
3-3	-82	-79	N/A
3-0-4	-97	-96	-93

- results for larger model compound confirm those obtained for vinyl phenoxy radicals
- exception: 8-O-4 bond formation is more favorable due to H bond formation

More complex Model compounds support conclusion



- Use of larger model species
 Increases complexity
- ... but does not change the basic conclusions: too many plausible product channels





Addition mech: Thermodynamic control of pathways

Observations

- Substantial energy barriers
 - Lowest barriers for 8-3, 8-O-4 and 8-8
 - Explains involvement of "8" site
- Most products are endothermic
 - 8-O-4 and 8-8 product are exceptions (exothermic)
- Only a small spectrum of products expected in DHP experiments
- Reversibility + (lack of) aromatization explains formation of few linkages





Conclusion: new proposal for coupling mechanism

Calculation results show

- Recombination mech. not supported no differentiation between pathways
 - Highly exothermic products
 => no reversibility
- Addition mech. Is okay thermodynamic + kinetic control => correct linkages if no propagation
- HRP involvement could lead to valid mechanism
- ¹⁸O labeling could help to clarify where the OH groups of H₂O₂ go.

Bioengineering should focus on coupling step



Radical addition with involvement of HRP (horseradish peroxidase)



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Thank you for your attention



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GLOSSARY

Dehydrogenation polymer (DHP): oxidative coupling of phenolic compounds, e.g. lignols, to dimers or oligomers; expression used by plant biologists

Metabolism: chemical reaction sequences in biologic systems

Metabolomics: systematic scientific studies of intermediates and products (metabolites) formed in cells; sum of metabolites: metabolome

Horseradish peroxidase (HRP): group of enzymes using H_2O_2 as oxidizing agent protein which binds <u>heme</u> as redox cofactor



Enzymes in Lignol Metabolism

C3H = coumarate 3-hydroxylase

- C4H = cinnamate 4-hydroxylase
- **4CL** = 4-coumarate:CoA ligase
- **CCR** = Cinnamoyl CoA reductase
- **CAD** = Cinnamoyl Alcohol Dehydrogenase
- **CSE** = caffeoyl shikimate esterase
- **COMT** = caffeine acid O-methyltransferase
- **CCoAOMT** = caffeoyl-CoA O-methyltransferase
- **F5H** = ferulate 5-hydroxylase
- **HCT** = hydroxycinnamoyl transferase
- CoA = coenzyme A



Important Molecular Structures and Trivial Names



