**Dependence of the formation rate of the benzyl cation intermediate on the type of aromatic nucleus in acidic reactions of lignin**

Kyoko S. Katsumata1, Takuya Akiyama2, Tomoya Yokoyama1\*, and Yuji Matsumoto1

1 Laboratory of Wood Chemistry, Department of Biomaterial Sciences, The University of Tokyo, Tokyo, Japan

2 Laboratory of Wood Chemistry, Forestry and Forest Products Research Institute (FFPRI), Tsukuba, Japan

\* Corresponding author’s e-mail address:

*yokoyama@woodchem.fp.a.u-tokyo.ac.jp*

*(NOTES: Please replace the above title, author names, affiliations, and corresponding author’s e-mail address with yours. Presenter’s name should be underlined. Please delete here (these lines with these red letters) when you will have completed to prepare your extended abstract.)*

**ABSTRACT**

We examined the dependence of the formation rate of the benzyl cation intermediate on the type of aromatic nucleus. On the basis of the observed pseudo-first-order reaction rate constants in the disappearance behavior of employed lignin model compounds, it was shown that the formation rate is in the order of: the lignin model compound with H nucleus > G nucleus > S nucleus regardless of being phenolic or non-phenolic. Phenolic lignin model compounds afforded the corresponding benzyl cation intermediate much more rapid than non-phenolic counterparts. These orders can be rationally explained by the electronic effects of the hydroxy and methoxy groups of the lignin model compounds on the benzylic cationic reaction center.

**INTRODUCTION**

Benzyl cation intermediate is believed to form as the primary intermediate in various chemical reactions of lignin under acidic conditions aiming for the utilization, degradation, and structural analysis.[1] Benzyl cation intermediate is the most important structure in reactions of lignin under acidic conditions, because its reaction route determines which of degradation or condensation lignin undergoes and what reaction products are afforded in the degradation.[2] In spite of these importance, the formation and reaction of benzyl cation intermediate have not yet been examined in detail.

**EXPERIMENTAL**

**Materials**

Lignin model compounds shown in Fig. 1 were synthesized from the corresponding benzaldehyde derivatives.



Fig. 1 Chemical structure of the lignin model compounds used in this study

All other chemicals were purchased from FUJIFILM Wako Pure Chemical Co. (Osaka, Japan), Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), and Sigma-Aldrich Japan K. K. (Tokyo, Japan), and used without further purification.

**Acidolysis reaction**

A bottom-round glass flask (50 mL) containing a 2/9 mol/L HClO4 solution (27 mL) was kept at 50°C in a water bath with stirring. To the flask was added another solution containing a lignin model compound (10 mmol/L, 3.0 mL) to initiate the reaction. At prescribed reaction times, the lignin model compound were quantified by HPLC after neutralization, addition of an internal standard compound, and filtration.

**RESULTS AND DISCUSSION**

When any lignin model compound was treated, the corresponding benzyl alcohol derivative was the only reaction product and always produced quantitatively based on the disappearing lignin model compound. Because of these and the general knowledge, the most typical reaction is considered to be the A1 mechanism for the formation of the benzyl alcohol derivative from a lignin model compound.

**Kinetic analysis**

The disappearance of all the lignin model compounds followed the pseudo-first-order reaction rate law. Table 1 lists the observed pseudo-first-order reaction rate constants (*k*obs).

Table 1 List of the *k*obs values of the lignin model compounds observed in this study.

|  |  |
| --- | --- |
| LMS*a* | *k*obs (× 10-3 min)*b* |
| **HP** | 73.8 (1.3) |
| **HN** | 17.1 (0.9) |
| **GP** | 60.7 (3.4) |
| **GN** | 10.2 (0.6) |
| **SP** | 30.5 (1.0) |
| **SN** | 00.151 (0.014) |

*a* LMS: Lignin model compound

*b* The values in the parentheses are standard deviations.

The disappearance rate of the lignin model compounds was in the order of: **HP** > **GP** > **SP** > **HN** > **GN** > **SN**. On the basis of the comparison between **HP**, **GP**, and **SP** or between **HN**, **GN**, and **SN**, it can be discussed how **H**, **G**, and **S** nucleus of the lignin model compounds affect the formation rates of the benzyl cations.

**CONCLUSIONS**

The formation rate of the benzyl cation structure is dependent on the type of aromatic nucleus of lignin model compound. It is in the order of: *p*-hyroxyphenyl > guaiacyl > syringyl regardless of being phenolic or non-phenolic.

**acknowledgements**

This study was supported by the Japan Society of the Promotion of Science.

**REFERENCES**

[1] Shioya, T., Akiyama, T, Yokoyama, T., Matsumoto, Y., “Formation rate of benzyl cation intermediate from *p*-hydroxyphenyl, guaiacyl, or syringyl nucleus in acidolysis of lignin”, *J. Wood Chem. Technol.*, **37** (2), 75-86 (2017)

[2] Yokoyama, T., “Revisiting the mechanism of *β*-*O*-4 bond cleavage during acidolysis of lignin. Part 6: A review”, *J. Wood Chem. Technol.*, **35** (1), 27-42 (2015)

*(NOTES: Please replace the above contents with yours. You should describe at least the sections of ABSTRACT, INTDODUCTION, EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS, AND REFERENCES. You can appropriately use your favorite formats for figures and tables. Please delete these notes when you will have completed to prepare your extended abstract.)*

**NOTICES:**

**\*Extended abstract must be submitted by 24:00, August 10 (JST).**

**\*Extended abstract should be no shorter than 4 pages and no longer than 8 pages.**

**\* Please send your extended abstract as a docx file to ISWFPC@woodchem.fp.a.u-tokyo.ac.jp.**

**\* All collected extended abstracts will be distributed to attendances as an electric file in the 20th ISWFPC.**

**\* Please delete these notices when you will have completed to prepare your extended abstract.**