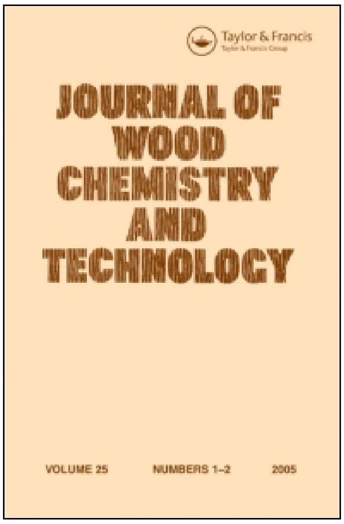

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Tomoya Yokoyama[a]; Yuji Matsumoto[a]
[a] Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo, Japan

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Revisiting the Mechanism of *β*-*O*-4 Bond Cleavage during Acidolysis of Lignin. Part 2: Detailed Reaction Mechanism of a Non-Phenolic C_6-C_2 Type Model Compound

Tomoya Yokoyama and Yuji Matsumoto
Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo, Japan

Abstract: The detailed reaction mechanism of a C_6-C_2 dimeric non-phenolic *β*-*O*-4 type lignin model compound, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (**V′G**), was examined under acidolysis conditions (mainly 0.2 mol/l HBr in 82% aqueous 1,4-dioxane at 85°C), and was suggested to be as follows. The initial elementary reaction step is protonation of the *α*-hydroxyl group, followed by the release of water to afford a benzyl cation intermediate (**BC**′). The latter step is relatively slow but reversible. The *β*-proton abstraction from **BC**′ by the solvents affords an enol ether compound, 1-(2-methoxyphenoxy)-2-(3,4-dimethoxyphenyl)ethene (**EE**′). This step is practically irreversible, and is the rate-determining step in the disappearance of **V′G**. The stereoisomers of **EE**′ are rapidly converted into each other, accompanied by protonation of the double bond. Complete protonation affords a *β*-oxymethylene cation intermediate (**OMC**′), which is also formed *via* hydride transfer from the *β*- to *α*-position of **BC**′ as a minor route. **OMC**′ preferentially undergoes the addition of water at the *β*-position, and the consequent *β*-*O*-4 bond cleavage affords 2-methoxyphenol and a Hibbert's monomer, 3,4-dimethoxyphenylacetaldehyde.

Keywords: Acidolysis, alkyl-aryl ether, kinetic, lignin, rate-determining step

INTRODUCTION

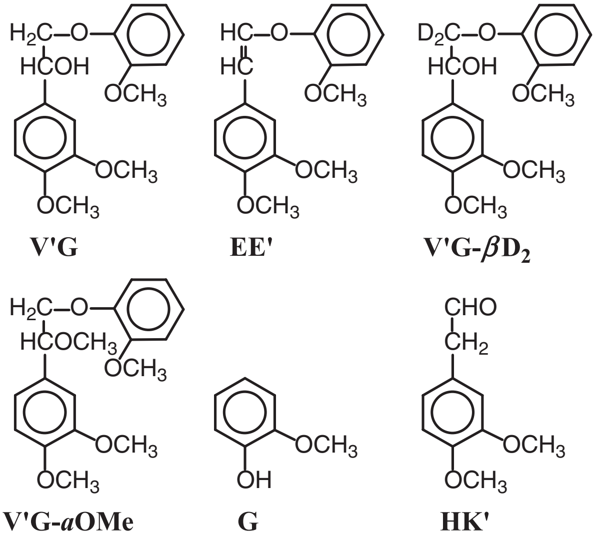
Acidolysis of wood-based biomaterials is commonly utilized in biomass conversion processes. The aim is generally to hydrolyze carbohydrates and remove lignin. The reaction conditions can be arranged to selectively remove

Address correspondence to Tomoya Yokoyama, Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan. E-mail: yokoyama@woodchem.fp.a.u-tokyo.ac.jp

lignin without serious damage to carbohydrates.[1] The most important reaction for the removal of lignin is the cleavage of *β*-*O*-4 bonds, which are the most abundant linkages between lignin monomeric units.

The *β*-*O*-4 bond cleavage during the acidolysis of lignin has been discussed in several papers,[2–13] and the mechanism involved and the rate-determining step have been suggested.[3] However, because the hypothesized mechanism does not appear to explain the dependence of the acidolysis rate on the type of acid applied,[13,14] we reexamined the mechanism involved and published a paper on the reaction route of a C_6-C_2 dimeric non-phenolic *β*-*O*-4 type lignin model compound, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (veratrylglycol-*β*-guaiacyl ether, **V′G** in Figure 1).[14] It has been proven kinetically that **V′G** is primarily and irreversibly converted into an enol ether compound, 1-(2-methoxyphenoxy)-2-(3,4-dimethoxyphenyl)ethene (**EE′** in Figure 1), and the successive *β*-*O*-4 bond cleavage affords 2-methoxyphenol (guaiacol, **G** in Figure 1) and a Hibbert's monomer, 3,4-dimethoxyphenyl acetaldehyde (**HK′** in Figure 1).[14] However, the detailed reaction mechanism and route have not yet been clarified.

In this study, the detailed reaction mechanism and route of **V′G** were examined. We attempted to establish the elementary reaction steps and clarify the rate-determining step. For these purposes, the enol ether compound **EE′**, a deuterated compound labeled at the *β*-position of **V′G**, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)(2,2–$^2H_2$)ethanol (**V′G-*β*D₂** in Figure 1), and a



V'G **EE'** **V'G-*β*D_2**

V'G-*a*OMe **G** **HK'**

Figure 1. Chemical structures of the compounds referred to in this article.

compound with a methyl ether at the α-position of **V′G**, 1-methoxy-2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethane (**V′G-αOMe** in Figure 1), were also acidolyzed under conditions identical to those described previously.[14] The chemical structures of the compounds referred to in this paper are shown in Figure 1.

EXPERIMENTAL

Materials

Most of the chemicals used in this study were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Among the chemicals, 1,4-dioxane was refluxed with sodium and successively distilled. The other chemicals were used directly without further purification.

V′G was synthesized according to a modified version of the method of Adler et al.,[15] which was described in a previous paper.[14]

The enol ether compound **EE′** was isolated from acidolysis mixtures of **V′G** following the procedures described previously.[14] The isolated **EE′** was a mixture of *cis*- and *trans*-isomers (60/40). These isomers were separated by preparative thin layer chromatography (PTLC, Silica gel 60 F_{254} 0.5 mm, Merck Ltd., Tokyo, Japan) with a hexane/ethyl acetate mixture (10/1) as a mobile phase. The separation was performed 10 times with drying the mobile phase in the intervals. After the separation, **EE′** remained a mixture of the *cis*- and *trans*-isomers (91/9), but was used in the experiments. The structure and composition were confirmed by ^{1}H-NMR (JNM-A500, 500 MHz, JEOL Ltd., Tokyo, Japan) and GC/MS (GC-17A/QP-5000, Shimadzu Co., Kyoto, Japan).[14]

The deuterated compound **V′G-βD$_2$** was synthesized from 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanone (**Eth**), which was produced in the middle of the **V′G** synthesis. **Eth** (500 mg) was dissolved in ethan(^{2}H)ol (C_2H_5OD, 15 ml) containing potassium carbonate (60 mg) and left to stand for 30 h at 60°C. The complete conversion of **Eth** to 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)(2,2–$^2H_2$)ethanone was confirmed by GC/MS. MS m/z (rel. int.): 304 (M^+, 10), 165 (100), 153 (6), 137 (6), 122 (4), 109 (3), 92 (5), 77 (11), 51 (6). **V′G-βD$_2$** was produced from this deuterated **Eth** following the same method as that used for the **V′G** synthesis from **Eth**.[13] The mol% yield was about 89% on the basis of the amount of **Eth** used for the synthesis. The structure and purity were confirmed by ^{1}H-NMR and GC/MS. ^{1}H-NMR ($CDCl_3$): δ 3.88, 3.89, 3.90 (s, 9H, 3 -OCH_3), 5.04 (s, 1H, Cα-H), 6.84–7.04 (m, 7H, aromatic). MS m/z (rel. int.): 306 (M^+, 11), 287 (1), 182 (20), 167 (100), 153 (39), 140 (46), 139 (58), 124 (40), 109 (19), 92 (8), 77 (19), 70 (6), 52 (8).

The compound with α-methyl ether **V′G-αOMe** was synthesized from **V′G**. **V′G** (400 mg) was dissolved in 50 ml of methanol containing 500 mg of sulfuric acid, and allowed to react for 5 h at 45°C. This methanol solution was mixed with 50 ml of chloroform and 30 ml of water, and extracted. The mixture was further extracted with 30 ml of chloroform 3 times, and the combined organic layer was washed with water and brine, and dried over anhydrous sodium sulfate. Then, the solvent was removed using a rotary evaporator at 35°C, and the obtained crystals were recrystallized from methanol. The mol% yield was about 91% on the basis of the amount of **V′G** used for the synthesis. The structure and purity were confirmed by GC/MS. MS m/z (rel. int.): 318 (M^+, 4), 194 (3), 181 (100), 166 (8), 151(6), 135 (2), 121 (2), 107 (1), 91 (4), 77(9), 52 (4).

Acidolysis and Quantification of the Model Compounds

All the acidolyses were conducted in a three-necked bottom-round glass flask (50 ml) equipped with a condenser, thermometer, and magnetic stirrer. The air in the flask was primarily replaced with nitrogen. **V′G** (50 mg) was allowed to react for 6 h at 85°C in 82% aqueous 1,4-dioxane (30 ml, v/v) containing any one of 0.2 mol/l HBr, 0.2 mol/l HBr + 0.1 mol/l $(CH_3)_4N^+Br^-$, and 0.2 mol/l DBr. When the applied acid was DBr, the solvents were D_2O and 1,4-dioxane. Each one of **EE′**, **V′G-βD$_2$**, and **V′G-αOMe** was also acidolyzed under the same conditions. The procedures used were exactly the same as those described previously.[14] The concentrations of the starting compounds and the reaction product **G** showing cleavage of the β-*O*-4 bond were determined following a method described previously.[14] The concentration of another reaction product **HK′** was quantified only when **V′G** was the starting compound.

RESULTS AND DISCUSSION

The utilized model compound **V′G** is advantageous for examining the detailed mechanism of β-*O*-4 bond cleavage during acidolysis, although the side chain component consists of two carbons and does not completely resemble native lignin, which has three carbons in the side chain. **V′G** is primarily and irreversibly converted into relatively stable **EE′**.[14] The rate constants of the disappearances of **V′G** and **EE′** are similar (Table 1). Because of this, the reaction process from **V′G** to **G** and **HK′** can kinetically be divided into first and second halves, each of which consists of fewer elementary reaction steps than the whole process. Kinetic parameters must differ between the halves, and hence, the parameters can be examined individually for the disappearances of **V′G** and **EE′** (the formation of **G** and **HK′**).

Table 1. List of the observed pseudo-first-order reaction rate constants

Rate constants ($\times 10^{-3}$ min^{-1})			
$k_{\mathrm{V'G}}$	8.54	$k_{\mathbf{V'G}\text{-}\alpha\mathbf{OMe}}$	33.0
$k_{\mathbf{V'G}\text{-}\beta\mathbf{D2}}$	2.19	$k_{\mathbf{EE'}}$	8.25
$k_{\mathbf{V'G}\text{-Br–}}$	7.02	$k_{\mathbf{EE'}\text{-}cis91}$	8.11
$k_{\mathbf{V'G}\text{-DBr}}$	21.5	$k_{\mathbf{EE'}\text{-DBr}}$	7.48

The elementary reaction steps in the β-*O*-4 bond cleavage of **V′G** during acidolysis can reasonably be assumed on the basis of the contents of earlier papers,[2–14] and the steps are shown in Figure 2. The initial step is protonation of the α-hydroxyl group (step I) followed by the release of water affording a benzyl cation-type intermediate (**BC′** in Figure 2, step II). The abstraction of a β-proton by a base converts it into the enol ether **EE′** (step III). Protonation of the double bond affords a β-oxymethylene cation intermediate (**OMC′** in Figure 2, step IV). **OMC′** can also be formed directly from **BC′** *via* hydride transfer from the β- to α-position (step V). The addition of water at the β-position (step VI) and the consecutive β-*O*-4 bond cleavage afford **G** and **HK′**. On the basis of the results obtained in this study, the mechanism and validity of each step are discussed. It has to be noted that **BC′** is assumed to be formed although this is yet to be confirmed. We plan to demonstrate the formation of benzyl cation type-intermediates in the acidolyses of β-*O*-4 type model compounds under various conditions.

The disappearances of the starting compounds, **V′G**, **EE′**, **V′G-βD$_2$**, and **V′G-αOMe**, followed the pseudo-first-order reaction rate law quite well. All the observed rate constants are shown in Table 1. All the reactions were almost quantitative, and only trace amounts of unidentified products were detected. All of these phenomena are similar to those observed previously.[14]

Search for the Rate-Determining Step in the Disappearance of V′G

When the disappearance rates of **V′G** and **V′G-βD$_2$** are compared in the HBr/H$_2$O system, the former is much greater than the latter (Table 1). The ratio of the rate constants ($k_{\mathrm{V'G}}/k_{\mathrm{V'G}\text{-}\beta\mathrm{D2}}$) is 3.9, which shows that a primary kinetic isotope effect is clearly observed. It has been confirmed that the carbon-hydrogen bond at the β-position breaks in the rate-determining step. Two possible mechanisms are presented: a proton is abstracted by a base at the β-position of **BC′** affording **EE′** (step III), and a hydride transfers from the β- to α-position of **BC′** converting it into **OMC′** (step V). It was reported that the ratio of rate constants between a compound and the corresponding appropriately deuterium-labeled compound is not large ($1 < k_{\mathrm{H}}/k_{\mathrm{D}} <$ around 2.3) in a reaction where a 1,2-hydride shift is the rate-determining step.[16] Because the

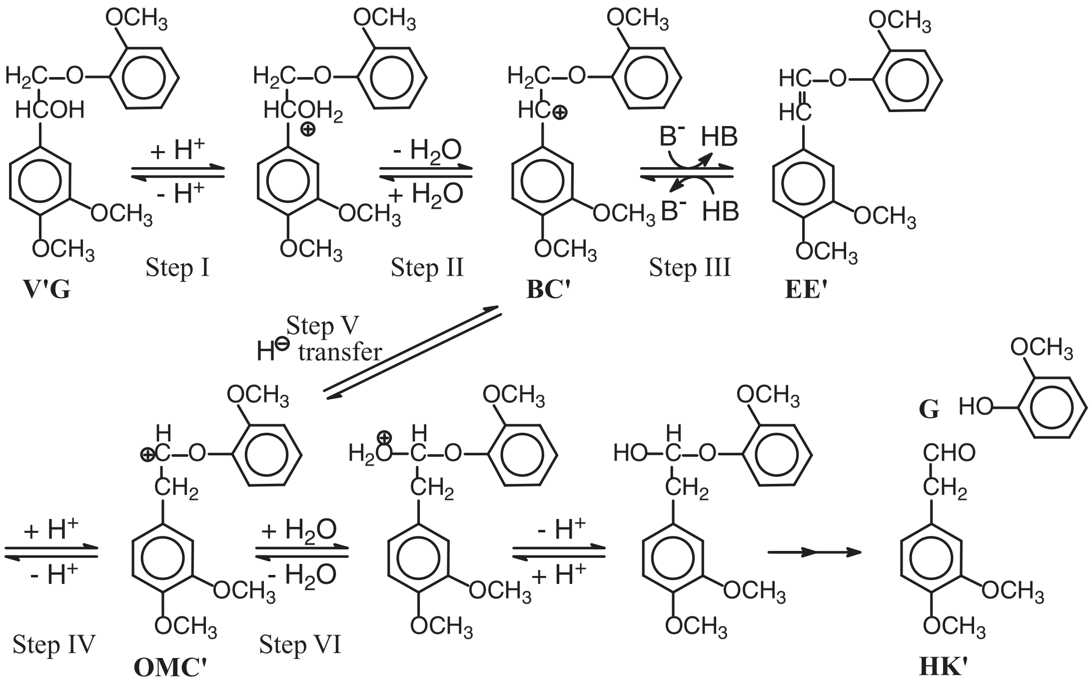


Figure 2. Presumed elementary reaction steps of **V′G** during the acidolysis on the basis of the contents of earlier papers.[2–13]

ratio is 3.9 in this study, step III is probably the major route. Further discussion of the predominance of step III over step V is as follows.

When **V′G-βD$_2$** is acidolyzed in the HBr/H_2O system, a degradation product **HK′** should have either one or two deuteriums depending on its reaction route. When the route involves steps III and IV, **HK′** has only one deuterium in the formyl group. If the route involves step V, **HK′** also has the other deuterium at the α-position. **V′G-βD$_2$** was acidolyzed in the HBr/H_2O system for 4 h, and **HK′** was analyzed by GC/MS. The mass chromatogram (MC) of m/z 182 (the molecular ion peak of **HK′** with two deuteriums) showed a peak that was on top of the **HK′** peak in the total ion chromatogram (TIC). However, the MC peak of m/z 182 was much smaller than that of m/z 181 (the molecular ion peak of **HK′** with one deuterium), which was also on top of the **HK′** peak in the TIC. The deuterium at the α-position would have been lost by tautomerization between **HK′** and the corresponding enol form, so the amount of **HK′** with two deuteriums may initially be larger than that expected from the MC. These results indicate that step V certainly exists, although it is not the major route. When **V′G** is acidolyzed in the DBr/D_2O system, the detection of **HK′** without deuterium shows the existence of step V as a reaction route. As expected, the MC of m/z 180 (the molecular ion peak of **HK′** without deuterium) showed a peak located on top of the TIC peak of **HK′**. The peak of m/z 180 was much smaller than that of m/z 181. Similarly, the protiums at the α-position may be lost by the tautomerization. Further discussion of the predominance of step III over step V is presented in the following section.

Analysis of the Rate-Determining Step in the Disappearance of V′G

When **V′G** was acidolyzed in the 0.2 mol/l HBr/H_2O system containing 0.1 mol/l $(CH_3)_4N^+Br^-$ (total concentration of Br^-: 0.3 mol/l), the disappearance of **V′G** was slightly slower than in the 0.2 mol/l HBr/H_2O system without the salt ($k_{\mathbf{V'G}\text{-Br}^-}$ and $k_{\mathbf{V'G}}$ in Table 1). If the bromide anion abstracted a β-proton from **BC′** in the rate-determining step (step III), the disappearance of **V′G** should have been faster in the system with the salt. The obtained result indicates that it is not the bromide anion, but rather the solvents, water and/or 1,4-dioxane, that abstract a β-proton in the rate-determining step, although counter anions of acids were previously suggested to abstract the proton.[11] It has been reported that bromide anion strongly affects the β-proton abstraction from a benzyl cation type intermediate in 90% aqueous dioxane while the influence is much smaller in 80% aqueous dioxane when derivatives of 1,2-diphenylethane-1,2-diol are acidolyzed in these systems.[12] A possible explanation for the slower disappearance of **V′G** in the system with the salt is that the proton activity is probably lower than in the system without the salt. The presence of the excess bromide anion would decrease the concentration of protons free from the electrostatic attractive force from the bromide, as the solvent system is 82% aqueous 1,4-dioxane in which protons and bromide would not be sufficiently solvated. The fact that the solvents abstract a β-proton in the rate-determining step suggests that the rate of step III itself is not directly dependent on the concentration of acid, although it certainly influences the rate of β-O-4 bond cleavage during acidolysis.[13] There could be an additional rate-determining step besides step III, where the concentration of acid influences the rate. Alternatively, the concentration of acid may indirectly affect the rate of the rate-determining step. The effect of acid concentration is discussed further in the following section.

On the Reversibility of Steps II and III, and the Fate of BC′

It has been reported that **V′G** is not detected at all in the acidolysis of **EE′** under conditions identical to those used in this study.[14] This result indicates that one of the following two phenomena is operative: protonation of the double bond of **EE′** does not afford **BC′** but only affords **OMC′** (step III is irreversible), or water is not added to **BC′** even though **BC′** is produced by protonation of the double bond (step II is irreversible). To examine these possibilities, **V′G-αOMe** was acidolyzed in the HBr/H_2O system. As shown in Figure 3, the disappearance of **V′G-αOMe** occurred rapidly ($k_{\mathbf{V'G\text{-}\alpha OMe}}$ in Table 1), and both **V′G** and **EE′** were formed. The initial elementary reaction of **V′G-αOMe** must be protonation of the α-methoxyl group, and the successive release of methanol affords **BC′**. It can be concluded from this result that water certainly adds to

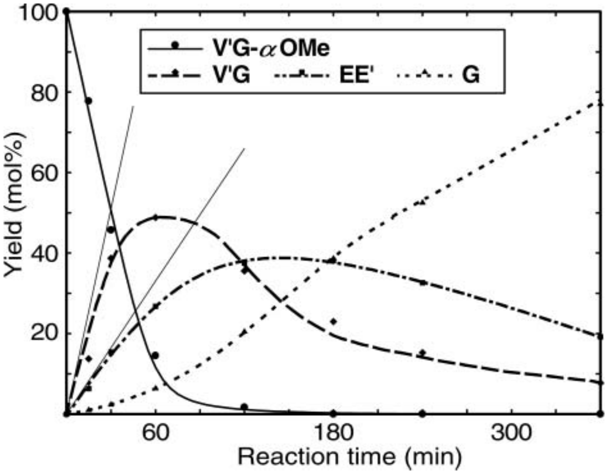


Figure 3. Change in the yields of **V′G-αOMe**, **V′G**, **EE′**, and **G** during the acidolysis of **V′G-αOMe**.

BC′ (step II is reversible), and hence, the formation of **EE′** from **BC′**, step III, is irreversible.

The ratio of the initial formation rates between **V′G** and **EE′** in the acidolysis of **V′G-αOMe** can be estimated from the initial slopes of their formation curves in Figure 3. The ratio (**V′G/EE′**) is about 3, which suggests that the addition of water at the α-position of **BC′** occurs at least 3 times more rapidly than the abstraction of a β-proton from **BC′**. The other solvent, 1,4-dioxane, can also abstract a β-proton from **BC′**, so the addition occurs more than 3 times as rapidly when the abstraction by dioxane is taken into consideration.

On the Effect of Acid Concentration

The rate constants for the disappearances of **V′G** in the 0.2 mol/l HBr and DBr systems ($k_{\mathbf{V'G}}$ and $k_{\mathbf{V'G}\text{-DBr}}$) were 0.00854 and 0.0215, respectively (Table 1). The ratio ($k_{\mathbf{V'G}}/k_{\mathbf{V'G}\text{-DBr}}$) is 0.40, which is less than unity and indicates that the disappearance of **V′G** is a reaction of specific acid catalysis.[17] In this kind of reaction, an acid dissociation equilibrium is rapidly established before the rate-determining step, and not the concentration of a starting compound, but rather that of its discrete conjugate acid, determines the rate of the rate-determining step. Because the concentration of the discrete conjugate acid of **V′G** is lower and a smaller amount of **BC′** is consequently produced in the HBr/H_2O system than in the DBr/D_2O system, the disappearance rate of **V′G** is slower in the former than in the latter system. It is reasonable to suggest that step I represents this type of equilibrium in the acidolysis of **V′G**. However, the disappearance of **V′G** must involve specific acid catalysis even when step II is sufficiently rapid to establish the equilibrium between **V′G** and **BC′**. As mentioned in the previous section, the rate ratio of the reverse of step II to step III is about 3, which suggests that the difference in the activation energies between the reverse of step II and step III cannot be sufficiently large. It is reasonable to assume that the activation energy of step II is not sufficiently low to rapidly establish equilibrium between **V′G** and **BC′**. Therefore, it is considered that step I represents a rapidly established equilibrium followed by a relatively slow step II. An effect of a high concentration of acid on the disappearance rate of **V′G** is that a higher concentration of the conjugate acid of **V′G** is formed, and consequently, the concentration of **BC′** is higher.

Detailed Mechanism of the Disappearance of EE′

The enol ether compound **EE′** consists of two stereoisomers, the *cis*- and *trans*-forms. When **V′G** was acidolyzed in the HBr/H_2O system, **EE′** was primarily formed and the concentration of the *cis*-form was about 70% in the initial phase. The concentration decreased to about 53% at a reaction time of 360

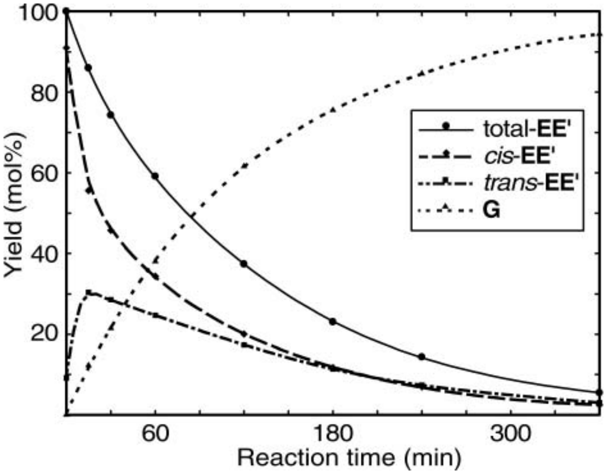


Figure 4. Change in the yields of total-**EE**′, *cis*-**EE**′, *trans*-**EE**′, and **G** during the acidolysis of **EE**′ when the initial composition of *cis*-**EE**′ was 91%.

min. The rate constant of the disappearance of **EE**′ ($k_{\mathbf{EE}'}$) was 0.00825 in the acidolysis of **EE**′ when the initial *cis*-form concentration was 60% (Table 1). The same kind of rate constant ($k_{\mathrm{EE}'\text{-}cis91}$) was 0.00811 when the initial *cis*-form concentration was 91% (Table 1, Figure 4). The rate constants seem to be independent of the composition. Conversion between the stereoisomers occurred, and the concentration of the trans-form increased rapidly in the initial phase; finally, the trans-form was slightly more prevalent than the cis-form at a reaction time of 360 min (Figure 4). These results suggest that the *trans*-form is thermodynamically more stable and that protonation of the double bond (step IV) is reversible and does not feature in the rate-determining step of the disappearance of **EE**′. If protonation featured in the rate-determining step, the transition state structures produced from both stereoisomers would be different, and hence, the rate constant would depend on the initial ratio of the isomers. In this case, conversion between the isomers would not occur. These considerations are in accordance with the disappearance of **EE**′ being a reaction of specific acid catalysis. Step IV involves rapidly established equilibrium, and the addition of water to the discrete **OMC**′ (step VI) is the rate-determining step. However, because hydrolyses of enol ethers are known as representatives of general acid catalysis,[18,19] it is necessary to discuss steps IV and VI further.

When **EE**′ (initial *cis*-form concentration: 60%) was acidolyzed in the DBr/D_2O system, the rate constant of the disappearance ($k_{\mathbf{EE}'\text{-DBr}}$) was 0.00748 (Table 1). The ratio of the rate constants ($k_{\mathbf{EE}'}/k_{\mathbf{EE}'\text{-DBr}}$) is 1.1. This result does not agree well with the above suggestion that the disappearance of **EE**′ is a reaction of specific acid catalysis. Table 2 lists the relative intensities of the

Table 2. Change in the relative intensities of the mass peaks of **EE**′ at m/z 286 and 287

		Relative intensity	
Reaction time	Isomer	286	287
0 min	*cis*	85	15
	trans	92	19
60 min	*cis*	75	27
	trans	89	39
120 min	*cis*	60	30
	trans	70	62
240 min	*cis*	83	100
	trans	75	90

m/z 286 and 287 peaks (molecular weight of **EE**′: 286) in the mass spectra of **EE**′, when **EE**′ was acidolyzed in the DBr/D_2O system. The exchange of the α-proton for a deuteron seems to be slower than that expected given that the *cis*-form rapidly converts to the *trans*-form in the initial phase (Figure 4). This suggests that the conversion between the stereoisomers is attained without formation of the discrete **OMC**′. The double bond of **EE**′ must rotate freely when the new carbon-hydrogen σ-bond at the α-position (**OMC**′) has yet to be formed. An intermediate must exist between **EE**′ and **OMC**′, which indicates that step IV can be divided into two elementary steps. The structure of the intermediate is not well defined but must be close to the π-complex between a deuteron (proton) and the double bond. It is generally understood that a π-complex is not an intermediate but a transition state structure. Therefore, the above presumed intermediate is not the π-complex but rather a poorly defined structure that is close to the π-complex. Because the proton of **EE**′ is gradually exchanged with a deuteron in a relatively slow reaction, the discrete **OMC**′ certainly forms and **EE**′ reforms from the discrete **OMC**′. However, once the discrete **OMC**′ forms, it must predominantly undergo step VI rather than the reformation of **EE**′ (step IV). Thus, step IV may be divided into the former and latter halves. However, there is another possibility as to step IV. The isomerization process is not the former half of step IV but an isolated process without proceeding to the formation of **OMC**′. If the isomerization process is the former half of step IV, the process is the rapidly established equilibrium before the rate-determining step of the disappearance of **EE**′, which must be the formation of **OMC**′. In this case, the disappearance of **EE**′ should have a character of specific acid catalysis, and hence, the above mentioned ratio between two rate constants ($k_{\mathrm{EE}'}/k_{\mathrm{EE}'\text{-DBr}}$) shows a value smaller than unity. However, because the value is 1.1, it must be more plausible to presume that the isomerization is an isolated process (step IV′) rather than the former half

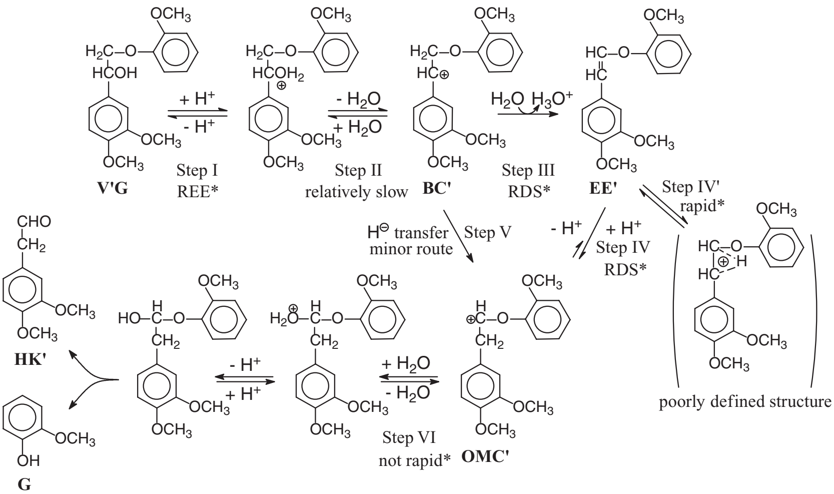


Figure 5. Proposed elementary reaction steps in the acidolysis of **V′G** on the basis of the findings in this study . (* REE: rapidly established equilibrium, RDS (Step III): rate-determining step in the disappearance of **V′G**, rapid (Step IV'): rapid isomerization, RDS (Step IV): rate-determining step in the disappearance of **EE′**, not rapid (Step VI): not rapid to make Step IV reversible).

of step IV. On the basis of these considerations, it can be stated that the two stereoisomers of **EE′** are rapidly converted into each other thus undergoing the forward and reverse variants of step IV′. The formation of **OMC′** from **EE′** (step IV), the rate-determining step of the disappearance of **EE′**, is slow but reversible. Step VI is slow enough to make step IV reversible.

The preference of step VI over the reverse of step IV ensures that not step V, but rather step III, is the main route for **BC′**, because it was proven that **V′G** is primarily converted into **EE′** and that the successive β-*O*-4 bond cleavage affords **G** and **HK′** under conditions identical to those employed in this study.[14] Step V certainly exists, but cannot be more than a very minor route.

CONCLUSIONS

The detailed reaction mechanism of **V′G** was examined under acidolysis conditions and is suggested to be as follows. Step I involves a rapidly established equilibrium between protonation and deprotonation of the α-hydroxyl group, followed by the release of water affording **BC′** (step II). StepvII is relatively slow but reversible. **BC′** is converted into **EE′** *via* the abstraction of a β-proton by the solvents (step III). Step III is irreversible and the rate-determining step for the disappearance of **V′G**. Conversion between the stereoisomers of **EE′** exists as an isolated process (step IV′) and occurs at a relatively rapid rate probably *via* a poorly defined structure that is close to the π-complex between a proton and the double bond of **EE′**. The complete protonation to the double bond of **EE′** reversibly affords **OMC′** (step IV), which must be the rate-determining step for the disappearance of **EE′**. **OMC′** is also formed *via* hydride transfer from the β- to α-position of **BC′** (step V), although this is not more than a minor reaction route. **OMC′** preferentially undergoes the addition of water at the β-position (step VI), and the consequent β-*O*-4 bond cleavage affords **G** and **HK′**. The results and findings in this study are summarized in Figure 5

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