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Revisiting the mechanism of β -O-4 bond cleavage during acidolysis of lignin IV: dependence of acidolysis reaction on the type of acid

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Abstract The dependence of the acidolysis reaction of a C₆-C₃ dimeric nonphenolic β -O-4 type lignin model compound, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (veratrylglycerol- β -guaiacyl ether, VG), on the type of acid applied was examined using three different acids [0.2 mol/l HCl, 0.2 mol/l HBr, and 0.1 mol/l (0.2 N) H₂SO₄ in 82% aqueous 1,4-dioxane at 85°C]. In the HCl system, the major reaction modes of the corresponding benzyl cation-type intermediate (BC), which is produced by protonation of the α -hydroxyl group of VG and successive release of the water molecule, are the abstraction of the β -proton and hydride transfer from the β - to the α -position. The liberation of formaldehyde from the γ -hydroxymethyl group of BC is the predominant reaction mode in the H₂SO₄ system. Apparently, an unknown reaction mode or modes is operative in the early stage of the HBr system that causes rapid disappearance of VG accompanied by the quantitative formation of 2-methoxyphenol without affording the common counterpart of a Hibbert's ketone, 1-hydroxy-3-(3,4-dimethoxyphenyl)propan-2-one. The reaction mode in the HBr system changes with the progress of the reaction and is the same as that in the HCl system after the early stage.

Key words Alkyl-aryl ether · HCl · H₂SO₄ · HBr · Lignin

Introduction

β -O-4 bond cleavage during the acidolysis of lignin has been discussed in several articles,^{1–13} and the mechanism

involved and the rate-determining step have been suggested.⁴ However, because the hypothesized mechanism does not appear to explain the dependence of the acidolysis rate on the type of acid applied,¹⁴ we have reexamined the mechanism involved and published articles in which we studied a C₆-C₂ dimeric nonphenolic β -O-4 type lignin model compound, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (veratrylglycol- β -guaiacyl ether, V'G in Fig. 1) and a C₆-C₃ type analog, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (veratrylglycerol- β -guaiacyl ether, VG in Fig. 1), under acidolysis conditions (0.2 mol/l HBr in 82% aqueous 1,4-dioxane (v/v) at 85°C).^{14–16}

In the acidolysis of V'G using HBr, the disappearance of V'G and formation of the corresponding enol ether compound, 1-(2-methoxyphenoxy)-2-(3,4-dimethoxyphenyl)ethene (EE' in Fig. 1), and two characteristic reaction products, 2-methoxyphenol (guaiacol, G in Fig. 1) and a Hibbert's monomer, 3,4-dimethoxyphenylacetaldehyde (HK' in Fig. 1), were examined.¹⁴ It was kinetically proven that EE' is primarily formed from V'G, and then the β -O-4 bond is cleaved affording quantifiable amounts of G and HK'.¹⁴ It was also indicated that the scission of a carbon–hydrogen bond at the β -position of the corresponding benzyl cation-type intermediate, which is produced by protonation of the α -hydroxyl group of V'G and successive water liberation, is the rate-determining step and that a hydride certainly transfers from the β - to α -position of the cation as a minor reaction.¹⁵ In a similar way to the acidolysis of V'G, it was confirmed in the acidolysis of VG using HBr that the corresponding carbon–hydrogen bond scission is also the rate-determining step and the corresponding hydride transfer certainly occurs.¹⁶ The frequency of this hydride transfer seems to be higher than has generally been considered.¹⁶ A trace amount of the corresponding enol ether, 2-(2-methoxyphenoxy)-3-(3,4-dimethoxyphenyl)prop-2-en-1-ol (EE in Fig. 1), was first detected in the acidolysis of VG when a heavy solvent system (DBr/D₂O) was applied under the same conditions,¹⁶ although EE is known to be significantly labile under acidolysis conditions.⁴ The detection of EE confirmed β -proton abstraction from the corresponding benzyl cation-type intermediate.

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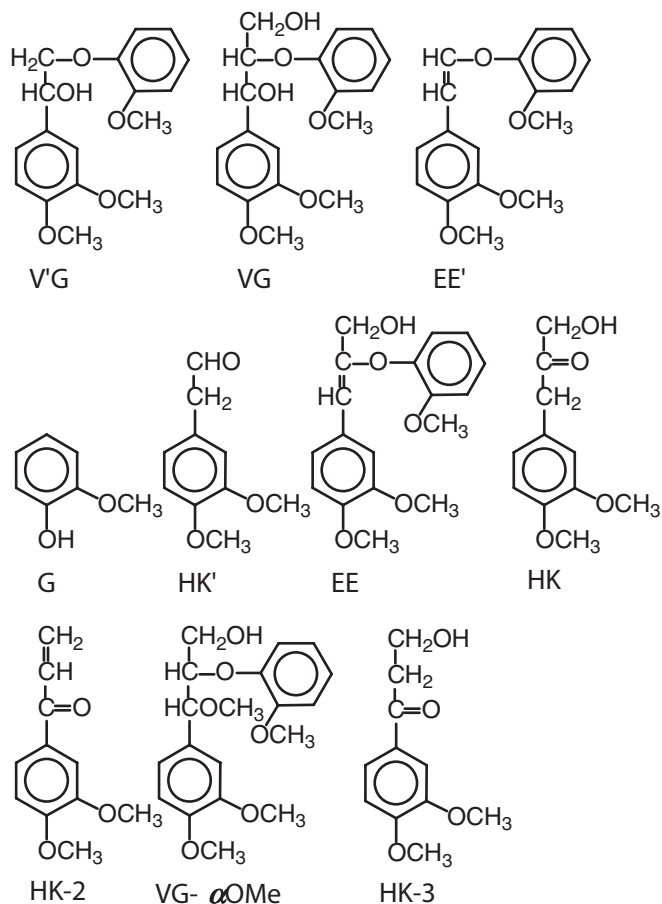


Fig. 1. Chemical structures of the compounds referred to in this article. The stereo structure of the side chain is not taken into consideration

It has been reported that the rate and route of β -O-4 bond cleavage are dependent on the type of acid applied.^{12,13} In this study, the dependence of the acidolysis reaction of VG on the type of acid applied was examined under conditions similar to those employed in our previous studies: 0.2 mol/l HCl, 0.2 mol/l HBr, or 0.1 mol/l (0.2 N) H₂SO₄ in 82% aqueous 1,4-dioxane (v/v) at 85°C.¹⁴⁻¹⁶ The disappearance and formation of VG, G, EE', HK', and a Hibbert's ketone-type compound, 1-hydroxy-3-(3,4-dimethoxyphenyl)propan-2-one (HK in Fig. 1), were quantitatively and kinetically examined. The chemical structures of the compounds referred to in this article are shown in Fig. 1.

Materials and methods

Materials

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

VG was synthesized in accordance with the method of Adler et al.¹⁷ HK, EE', and HK' were synthesized in accor-

dance with the method described in our previous articles¹⁴⁻¹⁶ and applied as authentic compounds. A monomeric reaction product, 1-(3,4-dimethoxyphenyl)prop-2-en-1-one (HK-2 in Fig. 1), was identified by ¹H-NMR and GC/MS to be a Hibbert's ketone-type compound. ¹H-NMR (500 MHz, sol.: CDCl₃): δ 3.95–3.99 (3.96, 3.97) (6H, s, Ar-OCH₃), 5.89 (1H, dd, $J = 1.5, J = 10.5$, C γ -H_a), 6.50 (1H, dd, $J = 1.5, J = 17.0$, C γ -H_b), 6.92 (1H, d, $J = 9.0$, ArC5-H), 7.21 (1H, dd, $J = 10.5, J = 17.0$, C β -H), 7.58 (1H, d, $J = 2.0$, ArC2-H), 7.61 (1H, dd, $J = 2.0, J = 8.5$, ArC6-H). MS m/z (rel. int.): 192 (M⁺, 62), 165 (100), 163 (19), 137 (21), 122 (10), 91 (11), 77 (29), 55 (30).

Acidolysis conditions and quantification

All the acidolyses were conducted in a three-necked round-bottomed glass flask (50 ml) equipped with a condenser, thermometer, and magnetic stirrer. The air in the flask was initially replaced with nitrogen. VG (50 mg) was reacted at 85°C in 82% aqueous 1,4-dioxane (1,4-dioxane/water = 82/18, v/v, 30 ml) containing 0.2 mol/l HBr, 0.2 mol/l HCl, or 0.1 mol/l (0.2 N) H₂SO₄. The acidolysis run was repeated in each system five, five, and three times, respectively, to confirm the reproducibility. The initial concentration of VG was 5.0 mmol/l. The concentrations of residual VG and reaction products G, HK, EE', and HK' were determined at prescribed reaction times.

The work-up and analytical procedures were exactly the same as those employed in our previous article.¹⁶ GC and HPLC were used for the quantification of the monomers (G, HK, and HK') and the dimers (VG and EE'), respectively.

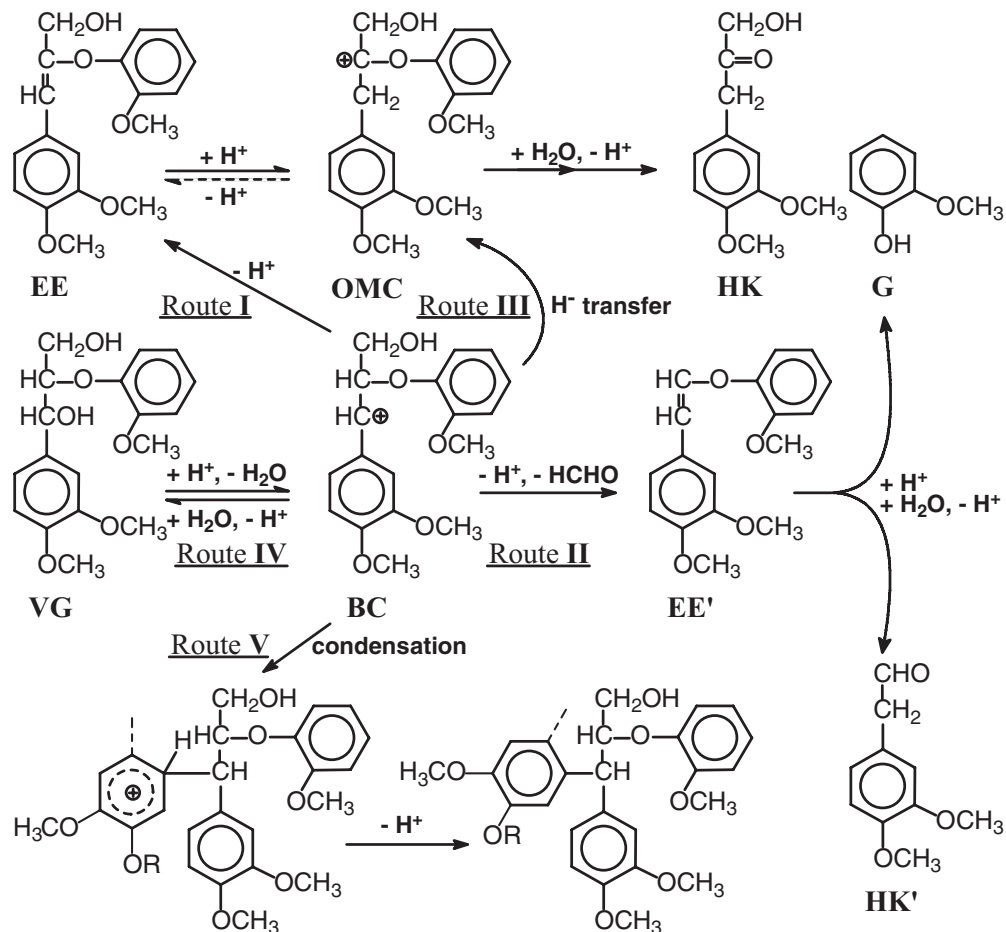
Results and discussion

Primary and comprehensive considerations on the reaction route of VG

The reaction route of VG can be considered on the basis of the contents of earlier articles¹⁻¹⁶ and is shown in Fig. 2, although many of the elementary reaction steps are not confirmed to be operative. It is generally believed that the benzyl cation-type intermediate (BC in Fig. 2) is primarily formed in acidolysis of VG, although the formation of BC has not yet been proven. BC is assumed to be primarily formed in this article.

The reaction route of BC is decisive for the whole degradation process of VG. Five reaction modes are currently proposed for BC (Fig. 2). Route I is the abstraction of the β -proton by a certain base to afford significantly acid labile EE, which cannot be detected under general acidolysis conditions. EE is consecutively acid hydrolyzed at the β -O-4 bond to give G and HK. It is reasonable to assume that the amounts of G and HK produced via route I are the same. The existence of route I was confirmed in our previous article.¹⁶ In route II, the proton of the γ -hydroxyl group is abstracted by a certain base and formaldehyde is released, affording EE'. EE' is more stable than EE under acidic

Fig. 2. Assumed reaction routes (I–V) of VG acidolysis (R = H or CH₃)



conditions and can be detected in acidolysis experiments.¹¹ EE' is also acid hydrolyzed at the β -O-4 bond to give G and HK'. It is also reasonable to assume that the amounts of G and HK' produced via route II are the same. The existence of route II has already been confirmed in earlier articles.^{3,4,7,11,13} In route III, the hydride transfers from the β - to the α -position to give the β -oxymethyne cation (OMC in Fig. 2), which is instantaneously hydrolyzed to afford G and HK. Similarly to route I, the amounts of G and HK produced via route III are the same. The existence of route III was confirmed in our previous article.¹⁶ Route IV is the reformation of VG by the addition of a water molecule. It is considered that both *erythro* and *threo* stereoisomers are formed by the addition. The existence of route IV was confirmed in a preliminary experiment in which a methyl derivative of VG, 3-methoxy-2-(2-methoxyphenoxy)-3-(3,4-dimethoxyphenyl)propan-1-ol (VG- α OMe in Fig. 1), was acidolyzed in the HBr system. Large amounts of VG were detected in the experiment, which indicates that a water molecule is added to the α -position of BC. The primary reaction of VG- α OMe can reasonably be assumed to be protonation of the α -methoxyl group and successive liberation of the methanol molecule affording BC. Route IV is not referred to in the following text. It is a topic of our further research to quantitatively examine route IV. Route V is a condensation reaction with an aromatic structure to

give a trimer. Route V is not examined in this study because the initial concentration of VG is low (5.0 mmol/l), and hence, condensation reactions do not frequently occur.

The stability of HK was primarily examined by subjecting it to the HBr acidolysis system because it has been shown that HK is converted to its isomers and disproportionation products under acidolysis conditions.¹⁸ The recovery of HK was 91% at a reaction time of 6 h, which indicates that its stability is high, and, consequently, the conversion reaction of HK to its isomers and others is not important in this study.

It should be emphasized that there may be unknown reaction modes that have not yet been observed or proposed. The possibility of unknown reaction modes is discussed in the following sections.

On acidolysis using HCl

The changes in the yields of VG, G, and HK when VG was acidolyzed in the HCl system are illustrated in Fig. 3 on the basis of the initial amount of VG. The lines in Fig. 3 are drawn as the best-fit curves. The yields of other minor reaction products EE' and HK' are shown in Fig. 4.

The disappearance of VG was accompanied by the approximately quantitative formation of G and HK. The

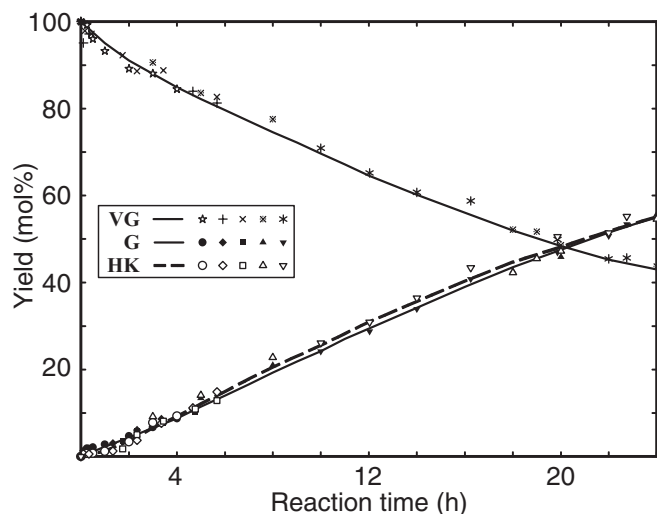


Fig. 3. Change in the yields of VG, G, and HK in the HCl system on the basis of the initial amount of VG. The data were obtained in five different runs

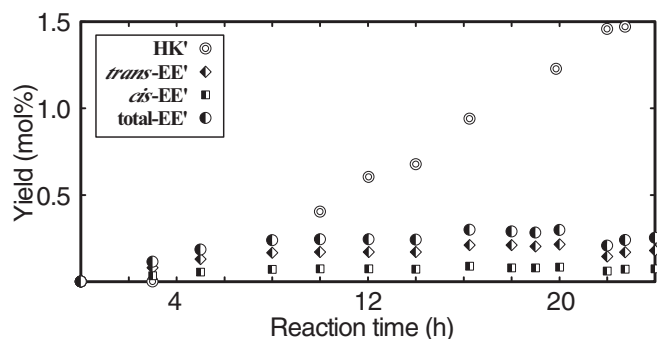


Fig. 4. Change in the yields of HK' and EE' in the HCl system on the basis of the initial amount of VG

amounts of G and HK detected were almost the same at all reaction times. Small amounts of EE' and HK' were observed. No condensation products were detected. These results indicate that BC mostly follows routes I and III in the HCl system. It is impossible to examine which route, I or III, contributes most to the disappearance of VG. Route II is a minor mode in the HCl system. All observed phenomena are in good accordance with earlier articles,^{12,13} although the possibility of hydride transfer (route III) was not considered in these articles.

The amount of the *trans* form of EE' detected was greater than that of its *cis* counterpart, although the total amounts were small. This is in contrast to the results obtained in the acidolysis of V'G, in which more of the *cis* form is produced than its *trans* counterpart.¹⁵

On acidolysis using H₂SO₄

The changes in the yields of VG, G, HK, and HK' when VG was acidolyzed in the H₂SO₄ system are illustrated in Fig. 5

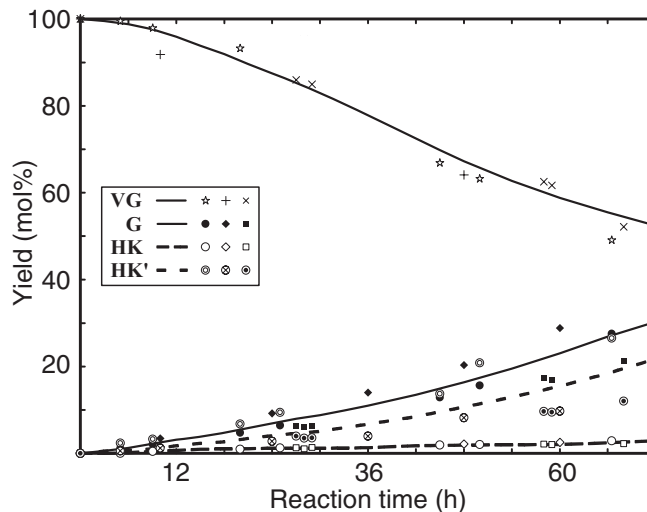


Fig. 5. Change in the yields of VG, G, HK, and HK' in the H₂SO₄ system on the basis of the initial amount of VG. The data were obtained in three different runs

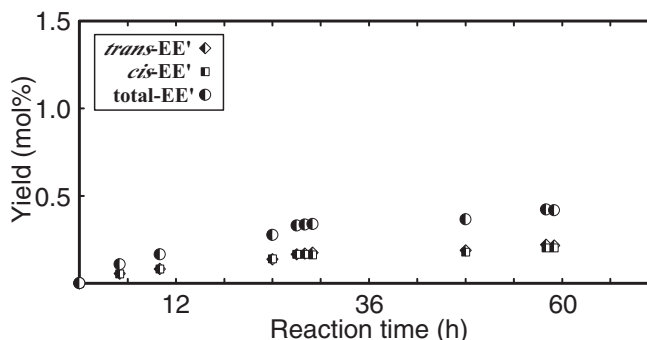


Fig. 6. Change in the yields of EE' in the H₂SO₄ system on the basis of the initial amount of VG

on the basis of the initial amount of VG. The lines in Fig. 5 are drawn as the best-fit curves, although the data points of VG, G, and HK' varied widely, especially for the latter two. The yield change of a minor reaction product, EE', is shown in Fig. 6. The wide variations of the data points make it difficult to discuss the disappearance and formation of chemical species in detail. However, it is possible to discuss their trends.

The disappearance of VG was significantly slower in the H₂SO₄ system than that in the HCl system. It is known that the disappearance of VG is fast in a system with high proton activity. It is considered that almost no HSO₄⁻ dissociates to SO₄²⁻ in the reaction solution because the pK_a value of HSO₄⁻ is 1.99 and the pH of the solution must be markedly lower than this value. The level of production of G seems to be slightly lower than the quantitative yield on the basis of the disappearance of VG, although the wide variations of the data do not support a clear judgment. The amount of HK' may be slightly smaller than that of G, and only a small amount of HK was produced. Small amounts of EE' were

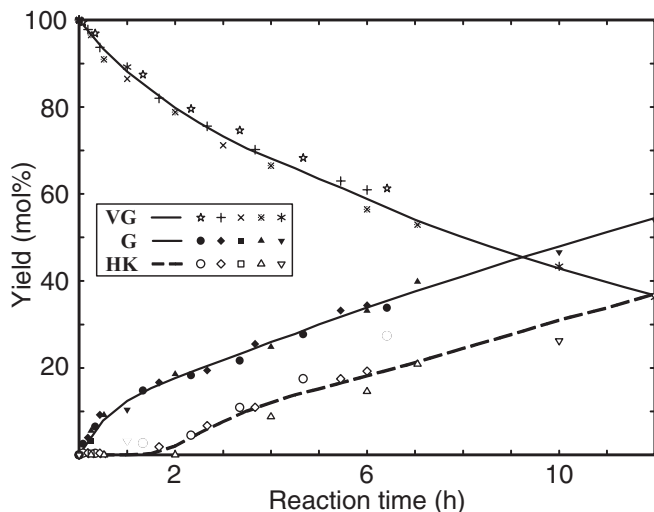


Fig. 7. Change in the yields of VG, G, and HK in the HBr system on the basis of the initial amount of VG. The data were obtained in five different runs

detected. Almost no condensation products were observed. These results indicate that the predominant reaction mode is route II in the H_2SO_4 system, whereas routes I and III are minor modes, which is in good accordance with the suggestion of the earlier articles.^{12,13} It has been suggested that the difference in size between HSO_4^- and Cl^- results in the dependence of the reaction route of VG (BC) on the type of acid applied,¹² although nothing could be suggested on why this dependence occurred in this study. The amounts of the *trans* and *cis* forms of EE' detected were similar in the H_2SO_4 system, which is different from the results for the HCl system.

On acidolysis using HBr

The changes in the yields of VG, G, and HK when VG was acidolyzed in the HBr system are illustrated in Fig. 7 on the basis of the initial amount of VG. The lines in Fig. 7 are drawn as the best-fit curves. The yields of minor reaction products EE' and HK' are shown in Fig. 8.

The disappearance of VG was much more rapid in the HBr system than in the HCl system, which is in accordance with the results obtained in a previous study.¹³ Because the proton activities are not very different between the two systems, the rapid disappearance of VG in the HBr system cannot be explained by the difference in the proton activities. This fact suggests that Br^- decisively participates in the disappearance reaction of VG. The most significant result observed in the HBr system is that G is quantitatively formed accompanying the disappearance of VG, whereas HK and the minor reaction products EE' and HK' were not observed in the first 2 h of the reaction. Route II is a minor mode in the whole reaction period of the HBr system. These results strongly suggest that an unknown reaction mode or modes other than routes I–V exists, affording the quantitative yield of G without the formation of HK in the first 2 h

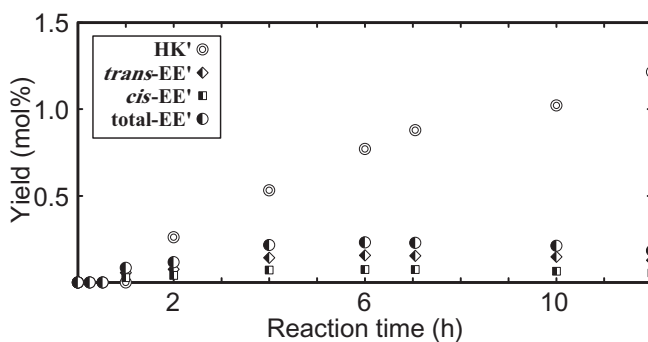


Fig. 8. Change in the yields of HK' and EE' in the HBr system on the basis of the initial amount of VG

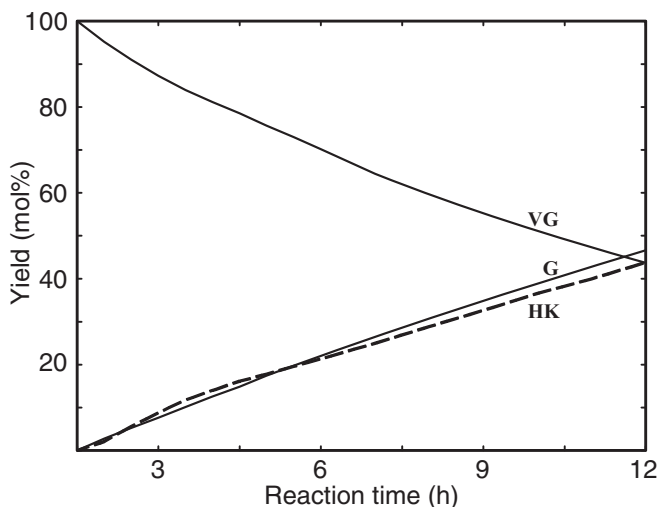


Fig. 9. Change in the yields of VG, G, and HK in the HBr system on the basis of the amount of VG at a reaction time of 1.5 h

of reaction in the HBr system. A possible candidate for this mode is that G and an unknown compound are primarily formed and HK is produced from the unknown compound. However, this is not in accordance with the experimental observation because the formation rates of G and HK seem to be similar after the production of HK is initiated. The disappearance of VG and the formation of G and HK are shown in Fig. 9 using the amount of VG at a reaction time of 1.5 h as 100%. The formation of G and HK are certainly similar. The formation rate of HK would still be slower than that of G after the initiation of HK formation if HK is produced from an unknown compound in the whole period of the reaction. It is reasonable to consider that routes I and III are the major reaction modes after the initiation of HK formation. The only hypothesis that can currently be proposed is that an unknown reaction mode or modes is operative only in the first 2 h of reaction in which G is quantitatively afforded without the formation of HK.

Several HPLC peaks of reaction products other than G, HK, EE, EE', and HK' did appear when the reaction solution of HBr acidolysis of VG was analyzed. One of these peaks was identified as a Hibbert's ketone-type compound,

HK-2 (Fig. 1), which may be converted from another Hibbert's ketone-type compound, 3-hydroxy-1-(3,4-dimethoxyphenyl)propan-1-one (HK-3 in Fig. 1). The formation of HK is initiated at a reaction time of around 1.5–2 h and the rate seems to be similar to that of G. Corresponding to these phenomena, the size of the HPLC peak of HK-2 increased with reaction time until about 1.5–2 h and did not change after this time. These results seem to support the hypothesis described above that an unknown reaction mode or modes is operative only in the first 2 h of reaction.

Because it is surprising that an unknown reaction mode or modes is operative only in the early stage of the reaction, a special character of Br^- is expected to produce this phenomenon. It is well known that Br^- unexpectedly participates in reactions of Br^- owing to the lability of Br^- to oxidation. For instance, the orientation of the addition reaction of HBr to an alkene often follows the anti-Markovnikov's rule, which is explained by the participation of Br^\bullet in the reaction instead of Br^- . The orientation follows Markovnikov's rule when extremely pure reagents are used with the blocking of light. To suppress the possible radical reaction, VG was acidolyzed in the HBr system with the blocking of light. The results were identical to those obtained without the blocking of light. The possible participation of Br^\bullet is also refuted by the fact that the experimental reproducibility is fairly high in the HBr system. It can safely be stated that the character of Br^- that induces the radical reaction is not related to the results obtained in the HBr system. As another trial, VG was acidolyzed in the HBr system with twice the initial concentration of VG (10 mmol/l). The results were identical to those obtained when the common initial concentration (5.0 mmol/l) was applied. It can be suggested that the disappearance reaction of VG is first order with respect to VG. No clear reaction could be proposed for an unknown reaction mode or modes in this study.

The amount of the *trans* form of EE' detected was greater than that of its *cis* counterpart, although the total amount of EE' detected was small. This tendency is similar to the result obtained in the HCl system. The formation of EE' also seems to be suppressed during the early stage.

Kinetic analysis of the disappearance of VG

Figure 10 shows logarithmic plots of the disappearance of VG in all the systems. The pseudo-first-order reaction rate constants were 3.61×10^{-2} , 8.08×10^{-3} , and $8.69 \times 10^{-2} \text{ h}^{-1}$ in the HCl, H_2SO_4 , and HBr systems and the R^2 values were 0.998, 0.946, and 0.987, respectively, when the whole disappearance process in each system was approximated to a pseudo-first-order reaction. The disappearance in the HCl system was approximated quite well. The disappearance was not approximated to a pseudo-first-order reaction in the H_2SO_4 system as indicated by the wide variation of the data points. The approximation was not as good in the HBr system as it was in the HCl system.

The disappearance of VG in the HCl and HBr systems seems to be faster in the initial stages than it is in the later

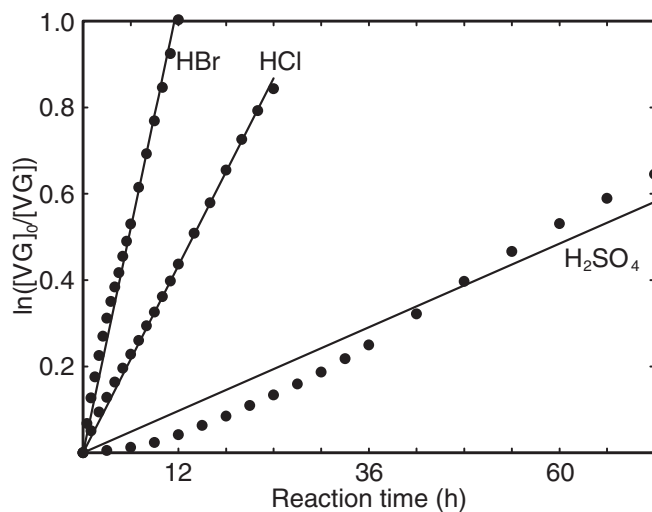


Fig. 10. Logarithmic plots of the disappearances of VG in the HCl, H_2SO_4 , and HBr systems. Slopes: $3.61 \times 10^{-2} \text{ h}^{-1}$ (HCl), $8.08 \times 10^{-3} \text{ h}^{-1}$ (H_2SO_4), and $8.69 \times 10^{-2} \text{ h}^{-1}$ (HBr)

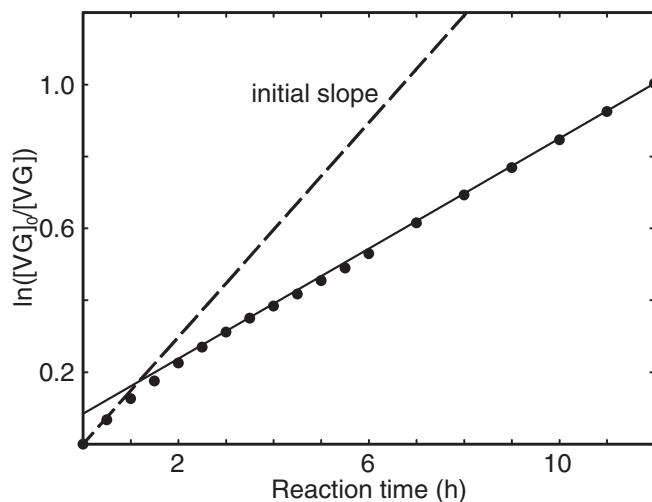


Fig. 11. Logarithmic plot of the disappearance of VG in the HBr system. Slopes: $1.38 \times 10^{-1} \text{ h}^{-1}$ (initial) and $7.65 \times 10^{-2} \text{ h}^{-1}$ (after a reaction time of 1.5–2 h)

stages of the reaction. This tendency is more pronounced in the HBr system. A logarithmic plot of the HBr system is shown in Fig. 11. The initial slope is $1.38 \times 10^{-1} \text{ h}^{-1}$, and the slope gradually decreases as the reaction progresses until about 1.5–2 h. Then, the slope reaches an almost constant value of $7.65 \times 10^{-2} \text{ h}^{-1}$. It was hypothesized in the previous section that an unknown reaction mode or modes participates in the disappearance of VG in the early stage of the HBr system. G is quantitatively formed, whereas HK is not produced in this reaction mode. This hypothesis seems to be supported by the results obtained in the kinetic analyses. It is also supported by the kinetic analyses that BC mostly follows routes I and III after a reaction time of about 1.5–2 h in the HBr system. A similar unknown reaction mode or modes might participate in the disappearance of VG in the

initial stage of the HCl system, although the degree of participation must be very small.

The rate constant is $7.65 \times 10^{-2} \text{ h}^{-1}$ after a reaction time of about 1.5–2 h in the HBr system, which is greater than the constant in the HCl system ($3.61 \times 10^{-2} \text{ h}^{-1}$) that is obtained by the approximation of the whole process. Because routes I and III are considered to be the major modes in both cases, some effects make the disappearance of VG more rapid in the HBr system than that in the HCl system. The possible effects proposed are as follows: the proton activity is higher in the HBr than in the HCl system, which causes the different disappearance rates of VG; Br⁻ may participate in reactions of modes I and III and the participation is more decisive than that of Cl⁻. This phenomenon is a topic of further research to examine these possibilities in detail.

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