Title	Retro-aldol-type fragmentation of reducing sugars preferentially occurring in polyether at high temperature: Role of the ether oxygen as a base catalyst
Author(s)	Matsuoka, Seiji; Kawamoto, Haruo; Saka, Shiro
Citation	Journal of Analytical and Applied Pyrolysis (2012), 93: 24-32
Issue Date	2012-01
URL	http://hdl.handle.net/2433/152376
Right	© 2011 Elsevier B.V.
Type	Journal Article
Textversion	author

Retro-aldol-type Fragmentation of Reducing Sugars Preferentially Occurring in Polyether at High Temperature: Role of the Ether Oxygen as a Base Catalyst

Seiji Matsuoka, Haruo Kawamoto*, Shiro Saka

* Corresponding author: Haruo Kawamoto

Graduate School of Energy Science, Kyoto University

Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Tel/Fax: +81-75-753-4737

E-mail address: kawamoto@energy.kyoto-u.ac.jp

Abstract:

The pyrolysis behavior of reducing monosaccharides was compared in the presence and absence of tetraethyleneglycol dimethylether (TEGDE), a polyether (N_2/150-250 °C). The pyrolytic pathways changed drastically in TEGDE. Glucose started to decompose at >160 °C under the neat conditions, and polysaccharides, anhydrosugars (levoglucosan and 1,6-anhydroglucofuranose), a colored substance and char were the major products. However, glucose was completely stabilized against decomposition in TEGDE and instead converted into fragmentation products including formaldehyde, glycolaldehyde, glyceraldehyde, 1,3-dihydroxyacetone, erythrose and erythrulose at higher temperatures. The total yield of the fragmentation products reached a 74.9 wt % at 250 °C. An aldose-ketose isomerization and retro-aldol fragmentation including a six-membered cyclic transition state were suggested as the principle mechanisms. Several other polyethers gave similar results. This unique property of polyether can be explained by the basicity of the ether oxygen which acts as a proton acceptor for the hydroxyl groups in the sugar. This H-bonding between the polyether and glucose may prevent inter- and intramolecular H-bonding (H-donation to the oxygen atoms) of glucose, which results in stabilization against transglycosylation and dehydration reactions. Such inter- and intramolecular H-bonding (H-donation) may also be involved in the thermal decomposition of the melt sugar as an activation (acid catalysis) mechanism.

Keywords:

Reducing sugar; Controlled pyrolysis; Polyether; Retro-aldol fragmentation; Hydrogen bond.

1. Introduction

Pyrolysis is an effective method for obtaining fuels and chemicals from organic resources. Methanol used to be produced from wood pyrolyzates [1]. Catalytic cracking is currently available for production of gaseous and liquid fuels and commodity chemicals from petroleum [2,3]. Biomass has great potential as a future renewable resource for fuels and chemicals production [1,4]. Thermochemical methods such as fast pyrolysis [5,6] and gasification [5,7] are promising ways for converting biomass into fuels and chemicals. However, low product selectivity arising from the complex reactions of biomass pyrolysis makes the application of these pyrolysis-based processes difficult. Understanding the molecular mechanisms of biomass pyrolysis and their control would be useful for improving the product selectivity.

Carbohydrates are a major component of biomass resources, and hence, pyrolysis of reducing [8,9] and non-reducing sugars [10-12] and polysaccharides [13-15] has been studied extensively. Reducing monosaccharides are known to be degraded at a much lower temperature range (> 160 °C) than the non-reducing sugars, and their thermal decomposition has been discussed in connection with a caramelization process [8]. Thermal glycosylation into polysaccharides and formation of furanic compounds, char and colored substances through dehydration are reported to be pyrolytic reactions occurring during caramelization [8]. At temperatures higher than > 250 °C, formation of low molecular weight (MW) products including anhydrosugars (levoglucosan (1,6-anhydro-β-D-glucopyranose), 1,6-anhydro-β-D-glucofuranose), furanic compounds (furfural, 5-hydroxymethylfurfural), fragmentation products (hydroxyacetone, glycolaldehyde) and organic acids (acetic acid, formic acid, etc.) becomes more important [8,16,17].

Recently, Hosoya et al. [18] have reported that levoglucosan, an important intermediate in cellulose pyrolysis, was selectively converted into gaseous products (CO and CO_2) in the gas phase at 400 °C, while it was converted into polysaccharides, char

and low MW products as described above in the liquid phase. Thus, the pyrolytic pathway varies depending on the phase of pyrolysis, that is, gas or liquid phase. As a related phenomenon, Hosoya et al. [19] also reported that levoglucosan was stabilized up to 350°C in aromatic substances, and they related this unexpected feature to the dispersion of levoglucosan molecules in the aromatic substance through C-H/π interactions.

Because of the drastic differences in the reactivity reported for some pyrolysis conditions, we hypothesize that inter- and intramolecular hydrogen bonding initiates the pyrolysis reactions such as glycosylation and dehydration of sugars. Hydrogen-donation to the oxygen atoms of the sugar may act as an acid catalysis at high temperature. To confirm this hypothesis, polyether, which is expected to act only as a hydrogen acceptor, was tested. Most of the experiments were conducted with tetraethyleneglycol dimethylether (TEGDE) as the model polyether because this has a high boiling point (280 °C) and can solubilize glucose up to 2 wt % (150 °C). Pyrolysis of aldo (glucose and glyceraldehyde) and keto (fructose and 1,3-dihydroxyacetone) sugars was conducted in TEGDE. The roles of intra and intermolecular hydrogen bonding in sugar pyrolysis are discussed.

2. Experimental

2.1. Materials

Glucose, fructose, and glyceraldehyde were from Nacalai Tesque Inc., Japan. Glycolaldehyde, 1,3-dihydroxyacetone, erythrose, and erythrulose were from Sigma-Aldrich Co., USA. Tetraethyleneglycol dimethylether, 18-crown-6, isosorbide dimethylether, diethyleneglycol dibutylether, and levoglucosan were from Tokyo Chemical Industry Co. Ltd., Japan. Cellotriose and cellohexaose were purchased from Seikagaku Biobusiness Corporation, Japan. 1,6-Anhydro-β-D-glucofuranose was

prepared by heat treatment of glucose in sulfolane (tetramethylene sulfone) at 250 °C.

2.2. Method of sugar pyrolysis

Sugar (20 mg), polyether (2 g) including 3,5-dibuthyl hydroxyl toluene (BHT, 0.5 wt % as a stabilizer), and a glass-coated stir bar were placed at the bottom of a 30 ml flask. A condenser, a three-way tap, and a nitrogen balloon were connected to the flask. After the air inside the reactor was replaced with N_2 by using an aspirator connected through the three-way tap, the flask was heated in an oil bath which was preheated at 150-250 °C, and the mixture was stirred with a magnetic stirrer for 10-60 min. After heating, the flask was removed from the oil bath and cooled with flowing air (30 s) and then in cold water (30 s). BHT was used as a stabilizer for polyether. However, influences of the addition of BHT on the products composition were only small under the present pyrolysis conditions. Neat sugar pyrolysis was also conducted without addition of polyether, BHT, and the stir bar.

2.3. Recovery of the products and unreacted sugar

To remove polyether and BHT, *n*-hexane (20 mL) was added to the reaction mixture. The mixture was left for 1 h at room temperature to give a colorless crystalline substance or a syrup as the precipitate, which was recovered by centrifugation at 8000 rpm for 10 min. After washing with another 20 mL of *n*-hexane and subsequent drying in air, the precipitate was dissolved in 2 mL of water, and 0.1 mL of the resulting solution was dried in a vacuum desiccator and subsequently trimethylsilylated with a 0.1 mL of silylation reagent (BSTFA: TMCS: Pyridine = 2:1:7) at 60 °C for 10 min. Recovery of the unreacted sugar was measured by GC-FID analysis. The GC analysis was performed on a Shimadzu GC-14B with the following chromatographic conditions, column: CBP5-M25-O25 (25 m, 0.22 mm in diameter), injector temperature: 250 °C, detector temperature: 250 °C, column temperature: 160→250 °C (0→9 min), 250 °C

(9→15 min), carrier gas: He, flow rate: 1.5 mL/min, detector: FID.

2.4. Isolation and identification of the products

The mixtures obtained as the precipitates were purified further using silica gel column chromatography; eluent: chloroform and then 20% MeOH/chloroform. Formaldehyde was recovered according to the method as described below. Glycolaldehyde, glyceraldehyde, 1,3-dihydroxyacetone and erythrose were identified by comparing the ^{1}H-NMR spectra of these oxime derivatives (with hydroxylamine) with those of the authentic compounds. Chemical shift and coupling constant were shown as δ and Hz, respectively. The ^{1}H-NMR spectra were measured in D_2O on a Varian AVANCE 400 spectrometer (400MHz): Glycolaldehyde oxime (*Z*, *E*-isomer): δ 7.49 (t, *J* = 4.8, 1 H, H-C=N, *E*), 6.90 (t, *J* = 4.0, 1 H, H-C=N, *Z*), 4.35 (t, *J* = 4.0, 2 H, -CH_2-OD, *Z*), 4.13 (d, *J* = 4.8, 2 H, -CH_2-OD, *E*); 1,3-dihydroxyacetone oxime: δ 4,44 (s, 2 H), 4.25 (s, 2 H); glyceraldehyde oxime (*E*-isomer): δ 7.42 (d, *J* = 6.0, 1 H, C_1-H), 4.27 (ddd, *J* = 4.8, 6.0, 6.0, 1 H, C_2-H), 3.65 (dd, *J* = 4.8, 12.0, 1 H, C_3-H), 3.61 (dd, *J* = 6.0, 11.6, 1 H, C_3-H); erythrose oxime (*E*-isomer): δ 7.47 (d, *J* = 6.4, 1 H, C_1-H), 4.18 (t, *J* = 6.4, 1 H, C_2-H), 3.75-3.79 (m, 1 H, C_3-H), 3.67 (dd, *J* = 4.0, 12.0, 1 H, C_4-H), 3.55 (dd, *J* = 6.4, 12.0, 1 H, C_4-H). erythrulose was identified by comparing the ^{1}H-NMR spectrum (without oximation) with the authentic compound: δ 4.55 (d, *J* = 19.2, 1 H, C_1-H), 4.48 (d, *J* = 19.2, 1 H, C_1-H), 4.41 (t, *J* = 4.0, 1 H, C_3-H), 3.82 (d, *J* = 4.0, 1 H, C_4-H) , 3.81 (d, *J* = 4.0, 1 H, C_4-H).

2.5. Quantification

Quantification of the products was carried out by GC-FID after oxime-TMS derivatization according to the method reported by Hosoya et al. [20] The reaction mixture in the flask and on the condenser wall was carefully extracted with 5 mL of pyridine which included anthracene (10 mg, as an internal standard) and hydroxylamine

hydrochloride (50 mg, as an oximation reagent). 0.05 mL of the solution was trimethylsilylated with a 0.1 mL of silylation reagent (BSTFA: TMCS: pyridine = 2:1:7) at 60 °C for 10 min. The GC analysis was performed on a Shimadzu GC-14B with the following chromatographic conditions: column: CBP5-M25-O25 (25 m, 0.22 mm in diameter), injector temperature: 250 °C, detector temperature: 250 °C, column temperature: 120°C (0→1 min), 120→170°C (1→13.5 min), 170→250 °C (13.5→23.5 min), 250 °C (23.5→28 min), and carrier gas: He, flow rate: 1.5 mL/min, detector: FID.

Quantification of formaldehyde was difficult due to the recovery problem of the gaseous formaldehyde. With a liquid N_2 trap, formation of formaldehyde from glyceraldehyde and 1,3-dihydroxyacetone was confirmed. For quantitative analysis by GC-FID, benzylhydroxylamine hydrochloride (200 mg) was used as an oximation reagent instead of hydroxylamine hydrochloride, and biphenyl (10 mg) was used as an internal standard instead of anthracene. The GC analysis was conducted with a slightly changed column temperature profile: 120 °C (0→3 min), 120→180 °C (3→9 min), 180 °C (9→13 min), 180→250 °C (13→16.5 min), 250 °C (16.5→18 min). Since a small amount of formaldehyde was also observed in a blank test (without any sugars) due to thermal decomposition of TEGDE, the formaldehyde yields in this paper are presented after correction for this formaldehyde arising from the TEGDE decomposition.

2.6. GPC analysis

The GPC analysis of the water soluble products was performed on a Shimadzu LC-10 with the following chromatographic conditions: column: Asahipak GS-220, column temperature: 60 °C, eluent: water, flow rate: 0.5 mL/min, detector: RI and UV $_{254nm}$.

2.7. FTIR analysis

IR Spectra were recorded with a Shimadzu IR-8300 spectrometer using a liquid cell. The mixtures of 1,3-dihydroxyacetone and various amounts of TEGDE were preheated at 150 °C before analysis to solubilize 1,3-dihydroxyacetone completely in TEGDE.

3. Results and discussion

3.1. Pyrolysis behavior of glucose in the presence or absence of TEGDE

Fig. 1 shows the photographs of the pyrolyzates (neat conditions: solubilized in 1 mL of water after pyrolysis) (a) and temperature dependency (b) of the recovery of glucose in the presence or absence of TEGDE (N_2/ 30 min). Under neat conditions, color formation was observed at > 160 °C, and the color darkened with increasing temperature. At 240 °C the formation of char, which was not soluble in water, was additionally observed. The decrease in glucose recovery was correlated with the coloration and char formation.

Glucose was comparatively stabilized in TEGDE as shown by the higher glucose recovery at each temperature (Fig. 1(b)). Interestingly, even at 250 °C where glucose disappeared completely, the solution after pyrolysis in TEGDE remained almost colorless without formation of any insoluble products (char) (Fig. 1 (a)). Accordingly, formation of char and colored substances was completely inhibited in TEGDE, even though glucose decomposed into other substances.

Using GPC, the MW distribution of the pyrolyzates can be determined as illustrated in Fig. 2. Under the neat conditions, the intensity of the glucose signal (18.5 min) decreased with increasing temperature, and broad signals in the higher MW region became significant (Fig. 2 (a)). These results indicate that the oligosaccharides formation through thermal glycosylation reaction proceeded under the neat conditions.

Similar glycosylation is reported for glucose [21] and the reducing end of cellulose [22]. Although no significant signals were observed at 150-200 °C with an UV_{254nm} detector, higher MW products obtained at 220 °C showed obvious UV absorptivity which suggests the conjugated double bond formed through dehydration.

The pyrolyzates obtained in TEGDE gave very different chromatograms (Fig. 2 (b)). No signals were observed in the higher MW region other than the glucose signal. The decreasing rate of the intensity of the glucose signal with increasing temperature was lower than that of neat glucose pyrolysis. This is consistent with the recovery data (Fig. 1(b)). Instead of the formation of high MW products under the neat condition, the product signals were observed in the lower MW region.

Fig. 3 shows the results of GC-FID analysis of the pyrolyzates obtained at 220 °C/30 min (as TMS derivatives). Chromatograms (b) and (d) show the results of the oximation products in an effort to identify the low MW hydroxyl aldehydes and hydroxyl ketones. Under the neat conditions (Fig. 3 (a) and (b)), levoglucosan (0.98 wt%) and its furanose isomer (0.71 wt%) were identified at 8.2 and 8.6 min, respectively. These are the products of the intramolecular glycosylation of glucose after pyranose-furanose isomerization. These signals were not observed in the pyrolyzates obtained in TEGDE (Fig. 3 (c) and (d)). The lack of formation of these anhydrosugars suggests that the inhibition of the oligosaccharides formation in TEGDE is not explainable merely by the dilution effect. Formation of a reactive intermediate itself would be inhibited in TEGDE, although the glycosylation mechanism is not well-understood. On the contrary, glycolaldehyde, glyceraldehyde, 1,3-dihydroxyacetone, erythrose and erythrulose were identified as their oxime-TMS derivatives (*Z* and *E* isomers). Formation of these products was also confirmed by ^{1}H-NMR analysis of the isolated compounds.

Based on these characterization results, it is concluded that glucose is selectively converted into several fragmentation products without undergoing

glycosylation and dehydration reactions which give anhydrosugars, oligosaccharides, char and colored substances.

3.2. Fragmentation pathway in TEGDE

To obtain more information on the fragmentation pathway, glyceraldehyde and 1,3-dihydroxyacetone were pyrolyzed in TEGDE as the simplest aldo and keto sugars, respectively. Fig. 4 shows the time course of the product formation from these sugars. Gaseous formaldehyde was difficult to analyze. The formaldehyde yields presented here are the tentative values obtained by collection using a liquid N_2 trap. In the early stage of reaction, a significant amount of 1,3-dihydroxyacetone was formed from glyceraldehyde. Thus, the aldose-ketose isomerization (Lobry-de Bruyn-van Ekenstein transformation) is an important initial reaction (Fig. 5). The 1,3-dihydroxyacetone/glyceraldehyde ratios were usually much higher than 1 during pyrolysis of these sugars, even glyceraldehyde. This suggests that 1,3-dihydroxyacetone is more favorable in this aldose-ketose isomerization probably due to its greater stability arising from its more substituted carbonyl structure.

Glycolaldehyde and formaldehyde were formed from these C3 sugars. This is explained with the retro-aldol-type fragmentation mechanism (Fig. 5). A six-membered cyclic transition state may be involved in this reaction according to the literature reporting the thermal decomposition of β-hydroxy ketones [23] and esters [24]. 1,3-Dihydroxyacetone, which cannot form such a cyclic transition state, is more stable against fragmentation than glyceraldehyde. Glycolaldehyde and formaldehyde observed during the pyrolysis of 1,3-dihydroxyacetone would be formed via glyceraldehyde after isomerization.

Product formation behaviors from C6 sugars, glucose (an aldose) and fructose (a ketose), are shown in Fig. 6. Gaseous formaldehyde was not collected in these experiments. The suggested fragmentation mechanisms starting from their open-chain

241 forms are also illustrated in Fig. 7. Their product compositions were more complicated
242 than those of the C3 sugars, since some C4 sugars, that is, erythrose (an aldose) and
243 erythrulose (a ketose), were additionally observed. These C4 sugars are expected to
244 form by splitting off of the C2 glycolaldehyde from the reducing (reaction c) and
245 non-reducing (reaction i) sides of the sugars.

246 Glucose gave fructose in the early stage of pyrolysis at 220 °C, and the yield
247 reached 7.2 wt% of the amount of the reacted glucose at 10 min. Accordingly,
248 glucose-fructose isomerization also occurs in glucose pyrolysis and the decomposition
249 pathway via fructose is competitive with the direct fragmentation of glucose.
250 Fragmentation of glucose (reaction c) gives erythrose and glycolaldehyde. Erythrose
251 was the major C4 sugar from glucose in early stage of pyrolysis at 220 °C, and then, the
252 C4 sugar composition gradually shifted towards an erythrulose-rich one with an
253 increase in the heating time. This is explainable by the isomerization from erythrose into
254 erythrulose. Since the erythrulose/erythrose ratios at 220 °C/60 min and 250 °C/10 and
255 20 min were greater than 1, erythrulose is suggested to be more stable. This greater
256 stability of erythrulose can be also explained by its more substituted carbonyl structure
257 which is similar to 1,3-dihydroxyacetone as mentioned above.

258 Contrary to this, erythrulose was only observed as a C4 sugar from fructose
259 (Fig. 6), and the yield was as high as 30.8 wt% at 220 °C/30 min. This would be
260 explained by formation of a 3-hexulose via isomerization of fructose (reaction b),
261 although isolation of this C5 sugar failed probably due to its high decomposition
262 reactivity. A retro-aldol fragmentation of the 3-hexulose (reaction i) gave a C4 enol,
263 which was isomerized into more stable erythrulose preferably instead of erythrose.
264 Some of the erythrulose formed from glucose (220 and 250 °C) probably originated
265 from this reaction. Fragmentation into a C5 sugar (reaction m) is also possible for the
266 3-hexulose, although this sugar was not identified.

267 As for the formation of C3 sugars, many pathways (reactions e, g, j and o) are

possible as shown in Fig. 7. Interestingly, glyceraldehyde tends to form more selectively than 1,3-dihydroxyacetone in the early stage of pyrolysis at 220 °C. In Fig. 7, only the fructose fragmentation (reaction g) gives glyceraldehyde directly, while the initial product of other reactions is a C3 enol, which can be isomerized into both glyceraldehyde and 1,3-dihydroxyacetone. Accordingly, the isomerization into glyceraldehyde is probably favored kinetically. The 1,3-dihydroxyl structure in the C3 enol would be preferable in association with the ether oxygen of TEGDE. As the heating time increased, glyceraldehyde was gradually converted into the more thermodynamically favorable 1,3-dihydroxyacetone. The greater isomerization rate observed for the pyrolysis of glyceraldehyde (Fig. 4) may be explained by its higher solubility in TEGDE which promoted the isomerization before heating and during the heating up process. Although glucose and fructose were soluble in TEGDE only at high temperature, glyceraldehyde and 1,3-dihydroxyacetone were soluble even at room temperature.

Along with the glyceraldehyde fragmentation (Fig. 7), fragmentation of some C4-C6 sugars (reactions c, d, l and o) also gives glycolaldehyde. This yield from glucose was dramatically increased by increasing the pyrolysis temperature from 220 to 250 °C. Total yield of the identified fragmentation products reached a 74.9 wt% at 10 min. Direct fragmentation of glucose and subsequent fragmentation of erythrose (reactions c and d, respectively) are expected to be the major sources of this enhanced formation of glycolaldehyde. Such fragmentation reactions from aldoses may become kinetically more favorable at higher temperature than the isomerization into fructose and erythrulose which is thermochemically favorable.

Based on these lines of evidence, fragmentation via a cyclic six-membered transition state involving a -OH···O=C< type of hydrogen bonding is suggested as a selective fragmentation mechanism. Isomerization into the more stable ketose with a more substituted >C=O structure changes the fragmentation pathway. These reactions

295 are controlled both kinetically and thermodynamically.

296

297 3.3. Role of polyether

298 Fig. 8 shows the influence of the TEGDE loading level on the yields of the
299 fragmentation and isomerization products (N_2/250 °C/30 min). With an increase in the
300 TEGDE/glucose ratio (T/G, w/w), the yield of glycolaldehyde increased drastically,
301 while the C4 sugars and glucose were observed only at the lower T/G ratios < 200. The
302 yield of 1,3-dihydroxyacetone was almost constant in the T/G range 50-500.
303 Accordingly, the fragmentation reactivity tended to increase with an increase in the
304 loading level of TEGDE.

305 Fig. 9 illustrates the change in the IR spectrum (OH stretching region) of
306 1,3-dihydroxyacetone as the loading level of TEGDE (T/D, w/w) increased from 20 to
307 1000. 1,3-Dihydroxyacetone is known to exist as dimers in the solid phase [25], which
308 is formed through intermolecular hemiketalization. The broad IR spectrum at T/D 20
309 was similar to that reported for the solid sample [25]. The signals observed in the range
310 of 3100-3400 cm^{-1} were reduced by increasing the T/D ratio, and the spectrum (T/D
311 1000) became rather close to that [26] of the gaseous 1,3-dihydroxyacetone (monomer).
312 These results indicate that TEGDE assists the liberation of 1,3-dihydroxyacetone from
313 the dimer through cleavage of the hemiketal kinkage. Hydrogen bonding between the
314 ether oxygens of TEGDE and the hemiketal/hemiacetal hydroxyl groups may act as a
315 base catalysis for conversion of hemiketal/hemiacetal into ketone/aldehyde and alcohol.
316 Similar conversion would be possible also for other C2-C4 compounds.

317 These IR results also suggest that a similar base-catalyzed reaction accelerates
318 the formation of the open-chain form of glucose from its pyranose and furanose isomers,
319 although a similar IR measurement was not possible for glucose due to the limited
320 solubility in TEGDE at ambient temperature. Recovery of glucose only at a low
321 TEGDE/glucose ratio of 20 (Fig. 8) is understandable with this proposal.

Table 1 summarizes the yields of fragmentation and isomerization products from glucose in TEGDE and three other polyethers, 18-crown-6, isosorbide dimethylether (IDE) and diethyleneglycol dibutylether (DEGDBE) (N_2/250 °C/30 min). TEGDE, 18-crown-6, and IDE exhibited similar product compositions, and the yield of glycolaldehyde increased in the order: 18-crown-6 < TEGDE < IDE. This order may be related to the ability of the ether oxygens to interact with the hydroxyl groups of glucose as discussed above. The results of DEGDBE support this proposal, since DEGDBE with only three oxygen atoms was not effective for these fragmentation reactions. Thus, the selective fragmentation reaction occurs only when enough ether oxygen is provided by the polyether.

Sulfolane, which is also an aprotic solvent, has been used for conversion of cellulose into levoglucosan and other low MW products [27]. Unlike polyether, however, formation of the dehydration products and colored substances is reported in sulfolane. Sulfolane may accelerate the dehydration reaction with some specific mechanism. Amarasekara et al. proposed the dehydration mechanism of fructose to 5-hydroxymethylfurfural in dimethyl sulfoxide [28].

3.4. Role of inter- and intramolecular hydrogen bonding in sugar pyrolysis: an activation mechanism

Thermal glycosylation (oligosaccharide and anhydrosugar formation) and dehydration reactions were effectively inhibited during pyrolysis of reducing sugars in polyether. This can be explained by the formation of hydrogen bonds between the ether oxygens and protons of the hydroxyl groups in the sugar. As illustrated in Fig. 10 (for glucose), all of the protons of the hydroxyl groups in glucose are expected to associate with the ether oxygens when enough of the ether oxygen is provided. Under these conditions, all of the hydroxyl oxygen atoms of glucose increase their electron densities, and hence, the C_1-OH bond is expected to be stabilized for cleavage even in the

presence of the electron-donation from the lone pair of the ring oxygen. Consequently, formation of the reactive intermediate (an oxonium ion) is inhibited.

Such discussion implies the role of intra and intermolecular hydrogen bonding in the pyrolysis of reducing sugar melt where these hydrogen bonds are possible. Unlike the polyether conditions, proton donation by hydroxyl groups of another glucose molecule is also possible as illustrated in Fig. 10 (neat pyrolysis). Such proton donation on the C_1-oxygen may act as an acid catalysis which promotes the elimination of OH from the C_1 atom. In this process, the hydroxyl group which associates with the C_1-oxygen is converted into the hydroxide anion. These transformations make the glycosylation reaction quite easy.

Proposed dehydration mechanisms are illustrated in Fig. 11. The basicity of the carbonyl oxygen is stronger than those of the ether oxygens. Consequently, the -OH···O=C< type hydrogen bonding is possible even in polyether. This would be the reason for the retro-aldol-type fragmentation selectively occurring in polyether. Enolation is also expected because the aldose-ketose isomerization was observed in polyether. Dehydration via an enol may be an important dehydration pathway of a reducing sugar since simple polyalcohols such as glucitol were stable under the conditions where dehydration of the reducing sugar was observed. This dehydration reaction may be inhibited by the formation of hydrogen bonds between the ether oxygens and the protons of the hydroxyl groups in the sugar. The hydroxyl group hydrogen-bonded with the ether oxygen is stabilized for cleavage of the C-OH bond. Contrary to this, the combination of the hydrogen bonds as illustrated in Fig. 11 (neat pyrolysis) substantially enhances the dehydration reaction. This type of dehydration mechanism may be involved in the pyrolysis of reducing sugar melt.

4. Conclusions

Reducing sugar was stabilized in polyether against glycosylation and other dehydration reactions at 150-250°C. Reducing sugars were selectively converted into the fragmentation products formaldehyde, glycolaldehyde, glyceraldehyde, 1,3-dihydroxyacetone, erythrose, and erythrulose. Formation of these products was explained with a retro-aldol-type fragmentation mechanism including a cyclic six-membered transition state. A conversion mechanism in polyether was proposed in which the ether oxygen acts as a base to attract protons from the hydroxyl groups of the sugar. The increasing electron densities of the oxygen atoms of the hydroxyl groups may reduce the elimination reactivity of OH from sugar. Contrary to this, formation of the cyclic six-membered -OH···O=C< type hydrogen bonding is possible even in polyether since the carbonyl oxygen is more basic than the ether oxygen, which promotes the retro-aldol-type fragmentation. As an alternative, an activation (acid-catalysis) mechanism by proton-donation through intra and intermolecular hydrogen bonding was proposed for glycosylation and dehydration mechanisms of the neat pyrolysis of the melt sugar.

Acknowledgments

This work was supported by the Kyoto University Global COE program of “Energy Science in the Age of Global Warming” and a Grant-in-Aid for Scientific Research (B) (2) (No.20380103 2008.4-2011.3).

References

[1] R. C. Brown, Biorenewable Resources: Engineering New Products from Agriculture, Wiley-Blackwell, Hoboken, 2003; pp. 3.

[2] M. S. Rana, V. Sámano, J. Ancheyta, J. Diaz, Fuel 86 (2007) 1216.

[3] S. Ahmed, A. Aitani, F. Rahman, A. Al-Dawood, F. Al-Muhaish, Appl. Catal. A: Gen. 359 (2009) 1.

[4] P. A. M. Claassen, J. B. van Lier, A. M. Lopez Contreras, E. W. J. van Niel, L. Sijtsma, A. J. M. Stams, S. S. de Vries, R. A. Weusthuis, Appl. Microbiol. Biotechnol. 52 (1999) 741.

[5] A. V. Bridgwater, J. Anal. Appl. Pyrol. 51 (1999) 3.

[6] D.Mohan, C. U. Pittman, P. H. Steele, Energy & Fuels 20 (2006) 848.

[7] S. Rapagnà, N. Jand, P. U. Foscolo, Int. J. Hydrogen Energy 23 (1998) 551.

[8] P. Tomasik, P. Mieczysław, W. Stainsław, in: Advances in Carbohydrate Chemistry and Biochemistry; R. S. Tipson, D. Horton (Eds.), Academic Press, New York, 1989, pp. 203-278.

[9] E. B. Sanders, A. I. Goldsmith, J. I. Seeman, J. Anal. Appl. Pyrol. 66 (2003) 29.

[10] T. L. Lowary, G. N. Richards, Carbohydr. Res. 198 (1990) 79.

[11] F. Shafizadeh, J. Polym. Sci.: Polym. Symp. 36 (1971) 21.

[12] Y. Houminer, S. Patai, Israel J. Chem. 7 (1969) 535.

[13] F.Shafizadeh, J. Anal. Appl. Pyrol. 3 (1982) 283.

[14] M. J. Antal, Adv. Solar Energy 1 (1983) 61.

[15] P. Tomasik, P. Mieczysław, W. Stainsław, in: Advances in Carbohydrate Chemistry and Biochemistry; R. S. Tipson, D. Horton (Eds.), Academic Press, New York, 1989, pp. 279-335.

[16] K. Kato, Agr. Biol. Chem. 31 (1967) 657.

[17] Y. Houminer, S. Patai, Israel J. Chem. 7 (1969) 513.

[18] T. Hosoya, H. Kawamoto, S. Saka, J. Anal. Appl. Pyrol. 83 (2008) 64.

425 [19] T. Hosoya, H. Kawamoto, S. Saka, Carbohydr. Res. 341 (2006) 2293.
426 [20] T. Hosoya, H. Kawamoto, S. Saka, J. Anal. Appl. Pyrol. 77 (2006) 121.
427 [21] H. Sugisawa, H. Edo, J. Food Sci. 31 (1966) 561.
428 [22] S. Matsuoka, H. Kawamoto, S. Saka, Carbohydr. Res. 346 (2011) 272.
429 [23] G. G. Smith, B. L. Yates, J. Org. Chem. 30 (1965) 2067.
430 [24] B. L. Yates, J. Quijano, J. Org. Chem. 34 (1969) 2506.
431 [25] Y. Kobayashi, T. Igarashi, H. Takahashi, K. Higasi, J. Mol. Struct. 35 (1976) 85.
432 [26] R. Signorell, D. Luckhaus, J. Phys. Chem. A 106 (2002) 4855.
433 [27] H. Kawamoto, W. Hatanaka, S. Saka, J. Anal. Appl. Pyrol. 70 (2003) 303.
434 [28] A. S. Amarasekara, L. D. Williams, C. C. Ebede, Carbohydr. Res. 343 (2008) 3021.

Legends of Figures and Table

Fig. 1. Photographs of the pyrolyzates (a) and temperature dependence (b) of the recovery of glucose in the presence or absence of TEGDE (N_2/30 min). (●) neat glucose, (○) in TEGDE, TEGDE: tetraethyleneglycol dimethylether.

Fig. 2. GPC Chromatograms of glucose pyrolysis products in presence or absence of TEGDE (N_2/30 min), detector: RI (solid line) and UV_{254nm} (dotted line), Hex: cellohexaose, Tri: cellotriose, Glc: glucose, LG: levoglucosan, GA: glycolaldehyde, DHA: 1,3-dihydroxyacetone, TEGDE: tetraethyleneglycol dimethylether.

Fig. 3. Gas chromatograms of glucose pyrolysis products (N_2/220 °C/30 min). (a) neat glucose (TMS derivative), (b) neat glucose (oxime-TMS derivative), (c) in TEGDE (TMS derivative), (d) in TEGDE (oxime-TMS derivative), LG: levoglucosan, AF: 1,6-anhydro-β-D-glucofuranose, (●) glucose, (□) glycolaldehyde, (▲) glyceraldehydes, (△) 1,3-dihydroxyacetone, (♦) erythrose, (◊) erythrulose, TEGDE: tetraethyleneglycol dimethylether.

Fig. 4. Fragmentation and isomerization product formation from pyrolysis of 1,3-dihydroxyacetone and glyceraldehyde in TEGDE (20 mg/2 g) under N_2 at 250 °C. (▲) glyceraldehydes, (△) 1,3-dihydroxyacetone, (■) glycolaldehyde, (□) formaldehyde, TEGDE: tetraethyleneglycol dimethylether.

Fig. 5. Isomerization and retro-aldol fragmentation reaction of glyceraldehyde.

Fig. 6. Fragmentation and isomerization product formation from pyrolysis of glucose (a) and fructose (b) in TEGDE (20 mg/2 g) under N_2 at 220 and 250 °C. dotted line: total yield of fragmentation and isomerization product which were identified, (●) glucose, (○) fructose, (♦) erythrose, (◊) erythrulose, (▲) glyceraldehydes, (△) 1,3-dihydroxyacetone, (■) glycolaldehyde, TEGDE: tetraethyleneglycol dimethylether.

Fig. 7. Proposed isomerization and fragmentation pathways of glucose and fructose. FA: formaldehyde, GA: glycolaldehyde, GRA: glyceraldehydes, DHA: 1,3-dihydroxyacetone.

Fig. 8. Influence of TEGDE load on formation of fragmentation and isomerization products from glucose in TEGDE (N_2/250 °C/30 min). (●) glucose, (♦) erythrose, (◊) erythrulose, (▲) glyceraldehydes, (△) 1,3-dihydroxyacetone, (■) glycolaldehyde, TEGDE: tetraethyleneglycol dimethylether.

Fig. 9. Change in the IR spectra of 1,3-dihydroxyacetone dissolved in TEGDE; T/D: ratio of 1,3-dihydroxyacetone / TEGDE (w/w); TEGDE: tetraethyleneglycol dimethylether.

Fig. 10. A proposed mechanism explaining the stabilization of the reducing sugar against thermal glycosylation in

polyether.

Fig. 11. A proposed inhibition mechanism for dehydration occurring during pyrolysis of a reducing sugar in polyether.

Table 1 Yields of fragmentation and isomerization products obtained from pyrolysis of glucose in various polyether solvents (polyether/glucose = 20/1, w/w/ N_2/250 °C/30 min).

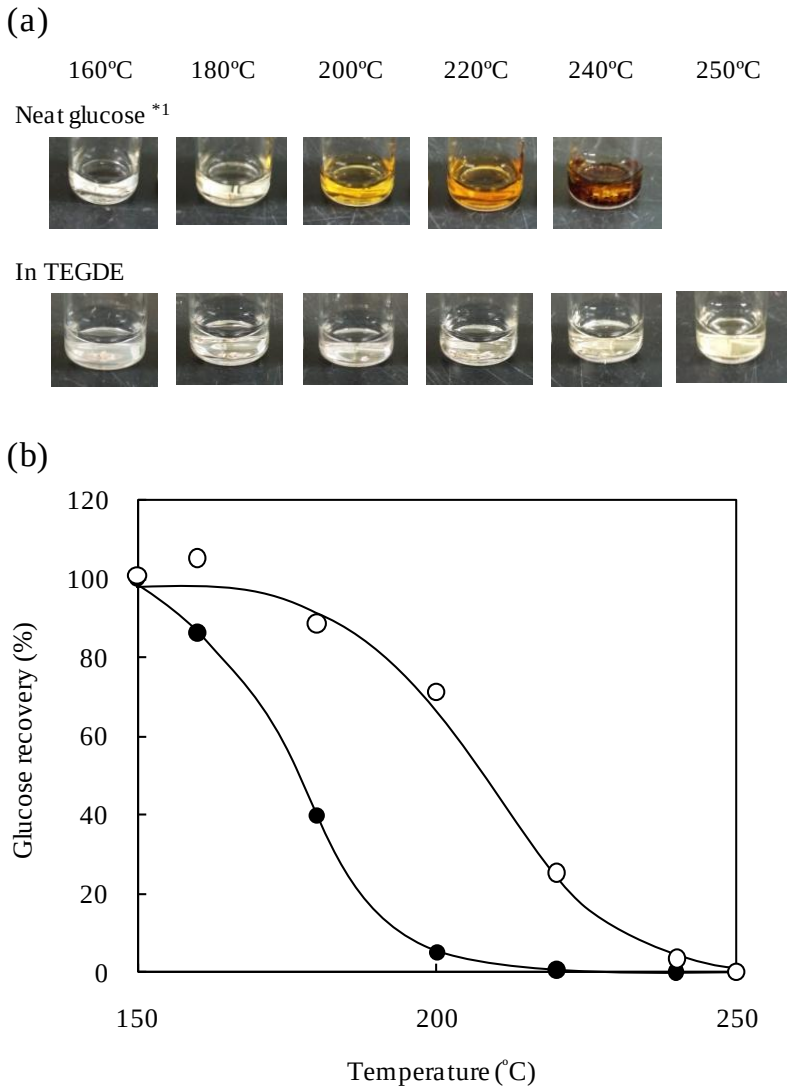
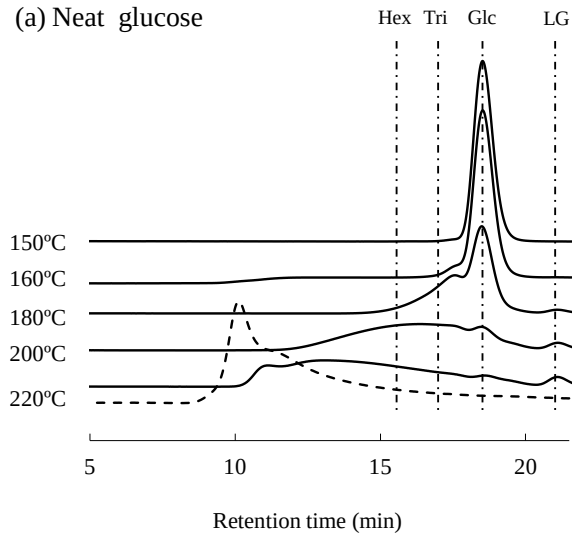


Fig. 1. Photographs of the pyrolyzates (a) and temperature dependence (b) of the recovery of glucose in the presence or absence of TEGDE (N_2/30 min). (●) neat glucose, (○) in TEGDE, TEGDE: tetraethyleneglycol dimethylether. *1: solubilized in water (1 mL) after pyrolysis.



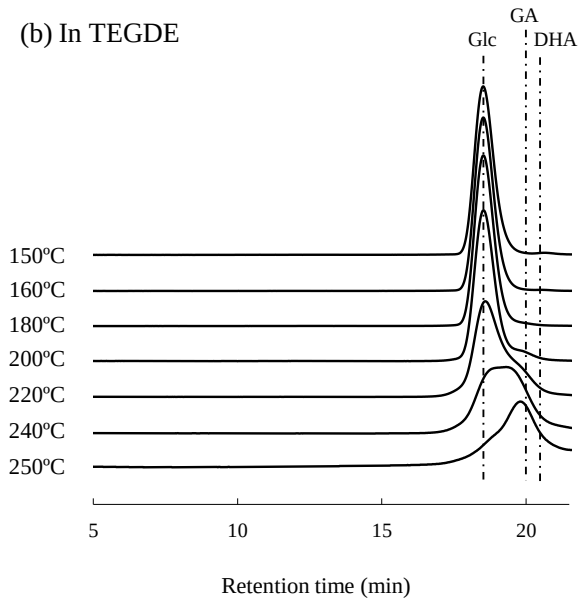


Fig. 2. GPC Chromatograms of glucose pyrolysis products in presence or absence of TEGDE (N_2/30 min), detector: RI (solid line) and UV_{254nm} (dotted line), Hex: cellohexaose, Tri: cellotriose, Glc: glucose, LG: levoglucosan, GA: glycolaldehyde, DHA: 1,3-dihydroxyacetone, TEGDE: tetraethyleneglycol dimethylether.

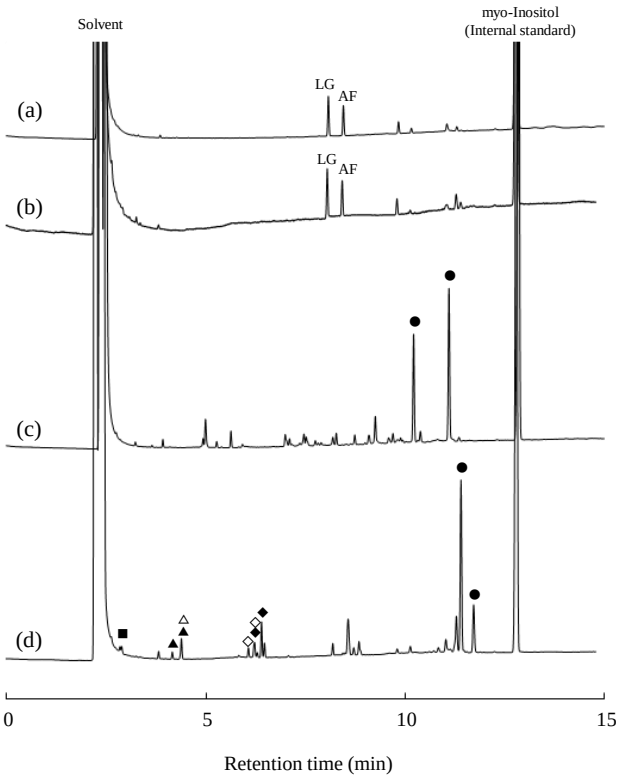


Fig. 3. Gas chromatograms of glucose pyrolysis products (N_2/220 °C/30 min). (a) neat glucose (TMS derivative), (b) neat glucose (oxime-TMS derivative), (c) in TEGDE (TMS derivative), (d) in TEGDE (oxime-TMS derivative), LG: levoglucosan, AF: 1,6-anhydro-β-D-glucofuranose, (●) glucose, (□) glycolaldehyde, (▲) glyceraldehydes, (△) 1,3-dihydroxyacetone, (♦) erythrose, (◊) erythrulose, TEGDE: tetraethyleneglycol dimethylether.

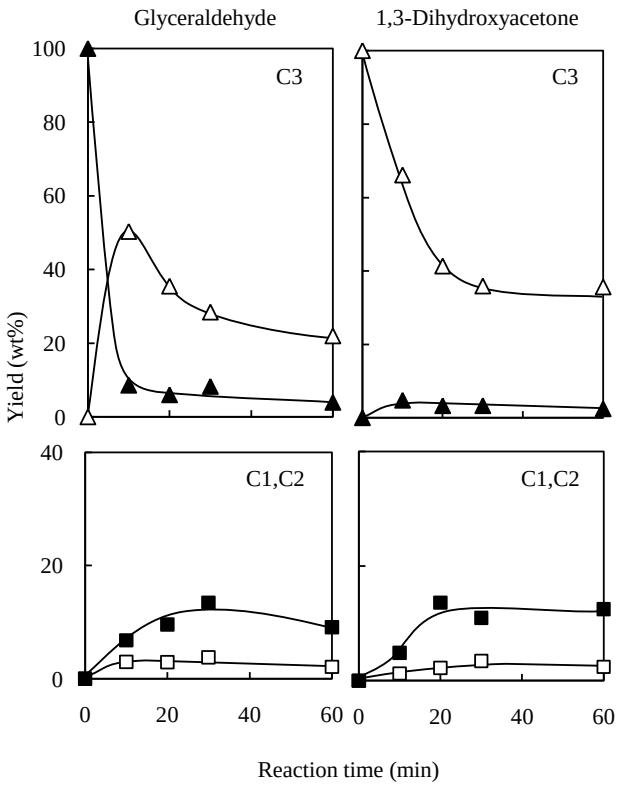


Fig. 4. Fragmentation and isomerization product formation from pyrolysis of 1,3-dihydroxyacetone and glyceraldehyde in TEGDE (20 mg/2 g) under N_2 at 250 °C. (▲) glyceraldehydes, (△) 1,3-dihydroxyacetone, (■) glycolaldehyde, (□) formaldehyde, TEGDE: tetraethyleneglycol dimethylether.

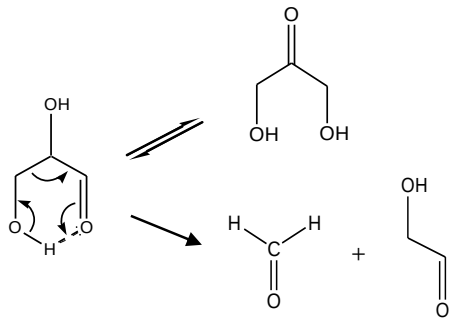


Fig. 5. Isomerization and retro-aldol fragmentation reaction of glyceraldehyde.

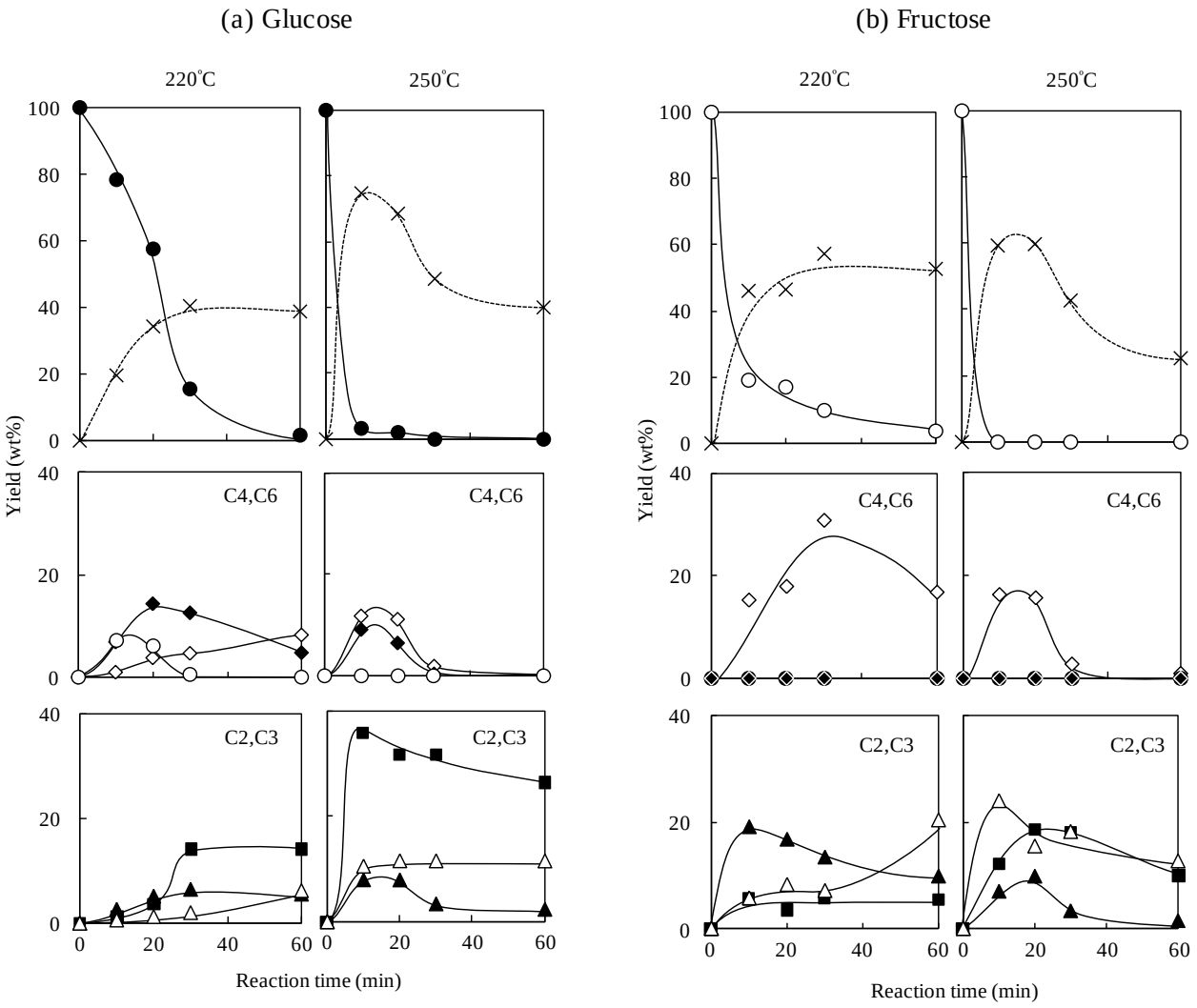


Fig. 6. Fragmentation and isomerization product formation from pyrolysis of glucose (a) and fructose (b) in TEGDE (20 mg/2 g) under N_2 at 220 and 250 °C. dotted line: total yield of fragmentation and isomerization product which were identified, (●) glucose, (○) fructose, (♦) erythrose, (◊) erythrulose, (▲) glyceraldehydes, (△) 1,3-dihydroxyacetone, (■) glycolaldehyde, TEGDE: tetraethyleneglycol dimethylether.

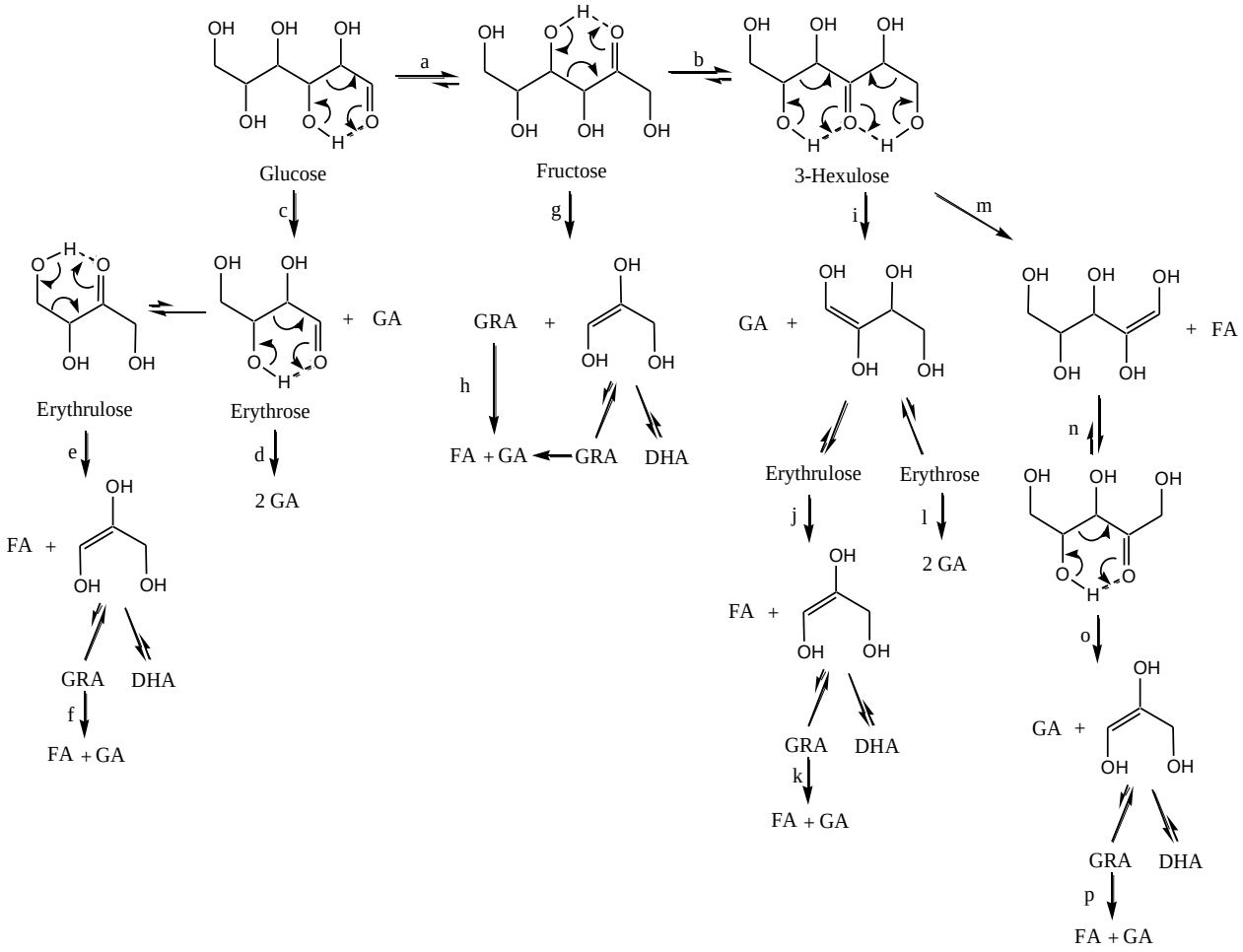


Fig. 7. Proposed isomerization and fragmentation pathways of glucose and fructose. FA: formaldehyde, GA: glycolaldehyde, GRA: glyceraldehydes, DHA: 1,3-dihydroxyacetone.

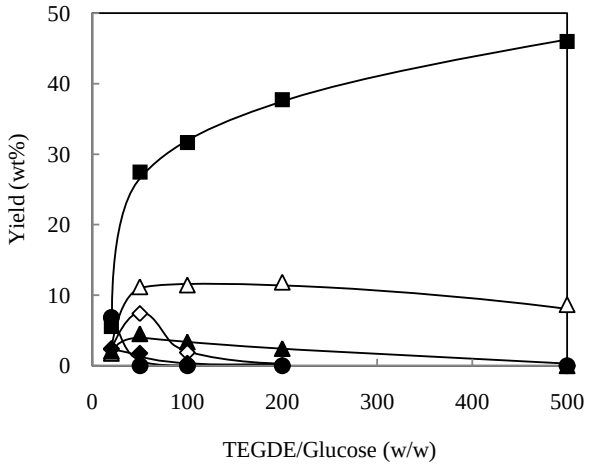


Fig. 8. Influence of TEGDE load on formation of fragmentation and isomerization products from glucose in TEGDE (N_2/250 °C/30 min). (●) glucose, (♦) erythrose, (◊) erythrulose, (▲) glyceraldehydes, (△) 1,3-dihydroxyacetone, (■) glycolaldehyde, TEGDE: tetraethyleneglycol dimethylether.

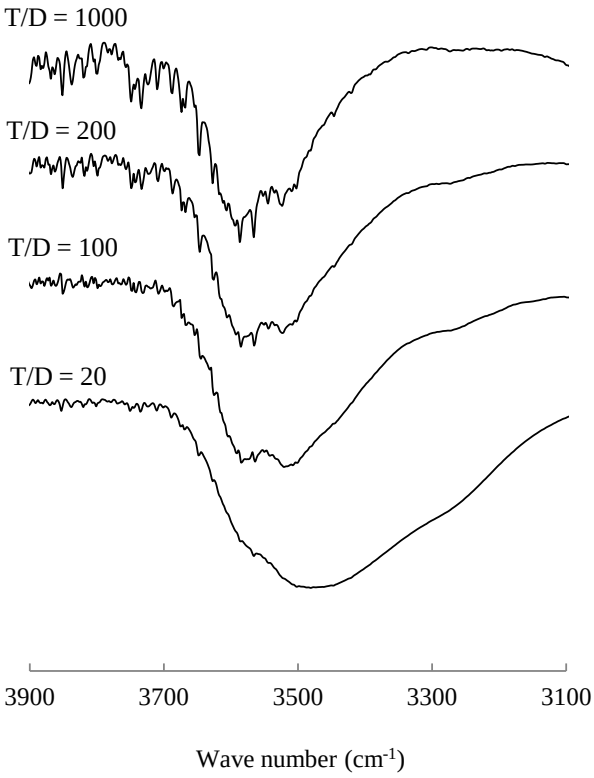


Fig. 9. Change in the IR spectra of 1,3-dihydroxyacetone dissolved in TEGDE; T/D: ratio of 1,3-dihydroxyacetone / TEGDE (w/w); TEGDE: tetraethyleneglycol dimethylether.

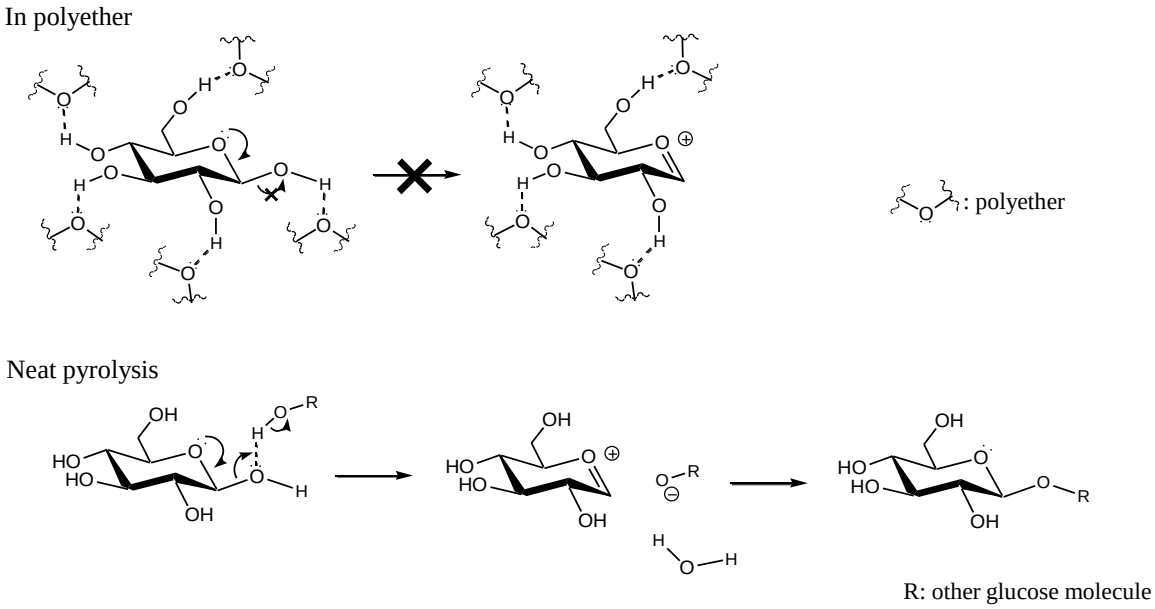


Fig. 10. A proposed mechanism explaining the stabilization of the reducing sugar against thermal glycosylation in polyether.

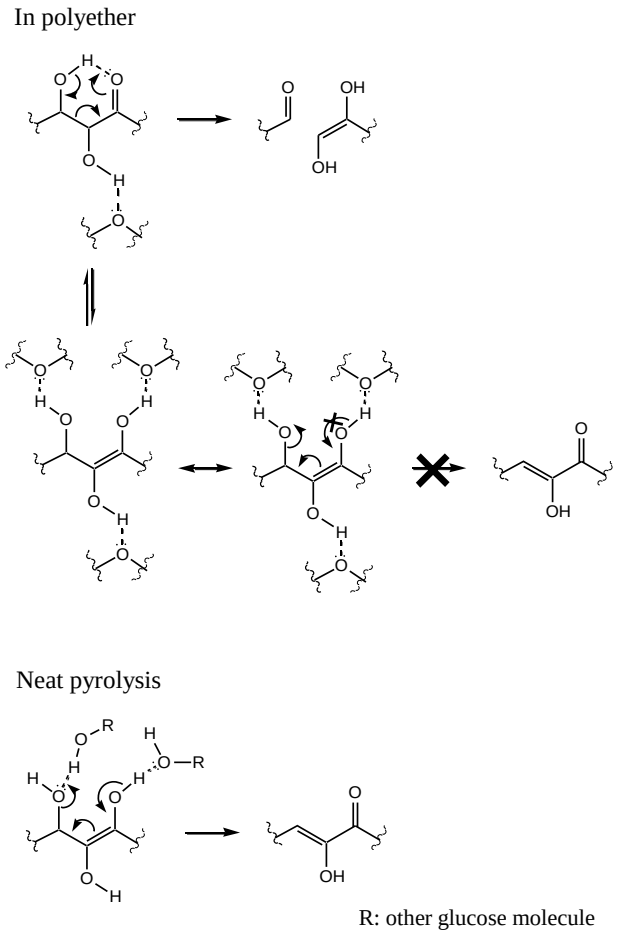
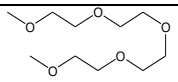
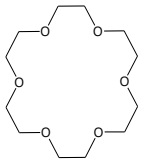
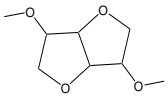
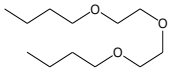


Fig. 11. A proposed inhibition mechanism for dehydration occurring during pyrolysis of a reducing sugar in polyether.

Table 1 Yields of fragmentation and isomerization products obtained from pyrolysis of glucose in various polyether solvents (polyether/glucose = 20/1, w/w/ N_2/250 °C/30 min).

Solvent	Yield (wt%)						Glucose recovery (%)
	GA	GRA	DHA	ETR	ETRL	Fru	
 TEGDE	40.6	7.4	12.4	0	2.8	0	0
 18-crown-6	35.1	5.9	17.2	0	5.4	0	0
 IDE	56.0	2.2	10.8	0	5.0	0	0
 *1 DEGDBE	4.1	1.3	1.1	2.4	1.6	1.27	16.5

*1 Glucose was not completely dissolved, GA: glycolaldehyde, GRA: glyceraldehydes, DHA: 1,3-dihydroxyacetone, ETR: erythrose, ETRL: erythrulose, Fru: fructose, TEGDE: tetraethyleneglycol dimethylether, IDE: isosorbide dimethylether, DEGDBE: diethyleneglycol dibutylether.