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Note

Formation of lactic acid from glycolaldehyde by alkaline hydrothermal reaction

Hisanori Kishida,[a] Fangming Jin,[b,*] Xiuyi Yan,[b] Takehiko Moriya[c] and Heiji Enomoto[b]

[a]*Environmental Systems Headquarters, Environmental Research and Development Center, Hitachi Zosen Corporation, Kyoto 625-8501, Japan*

[b]*Department of Environmental Science and Technology, Graduate School of Environmental Studies, Tohoku University, Sendai 980-8579, Japan*

[c]*Research and Development Center, Tohoku Electric Power Co., Inc., Sendai 981-0952, Japan*

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Abstract—Alkali hydrothermal experiments with glycolaldehyde were carried out at 300 °C. Glycolaldehyde was converted into lactic acid in a yield of 28% based on the starting carbon mass of glycolaldehyde. A conversion pathway for glycolaldehyde into lactic acid is proposed and our results suggest that the pathway via glycolaldehyde is also important in the conversion of glucose into lactic acid.

Keywords: Hydrothermal reaction; Carbohydrates; Biomass; Lactic acid; Alkaline catalyst

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The hydrothermal process is one of the most promising processes for the conversion of biomass into chemicals, because at high-temperatures and high-pressures water behaves as a reaction medium having unusual properties. There has been, therefore, extensive research on the conversion of biomass into chemicals by hydrothermal treatment. Our past studies on the conversion of carbohydrate biomass into useful substances showed that lactic acid can be formed by this process without the addition of any catalyst, probably due to a base catalytic effect of high-temperature water.[1–3] We have also shown that lactic acid can be selectively formed by adding a basic catalyst.[4] Lactic acid has recently been receiving attention as a material for the preparation of biodegradable polymers with limited environmental impact. To increase lactic acid production, an understanding of its formation from carbohydrates by hydrothermal processes is needed.

It is generally known in carbohydrate chemistry that lactic acid is generated via base-catalyzed decomposition of the three-carbon atom aldose, glyceraldehyde, which is formed by the reverse aldol condensation of hexoses. Our previous study on the conversion mechanism of glucose to lactic acid in hydrothermal reactions also showed that the transformation appeared to follow the pathway that was elucidated for the conversion of sugar to lactic acid in an alkaline solution.[3] However, few studies report on whether glycoaldehyde, an aldose containing two carbon atoms, can produce lactic acid, although glycoaldehyde is also generated by the reverse aldol condensation of hexoses. The purpose of this study was to examine the formation of lactic acid from glycoaldehyde in an alkaline hydrothermal reaction.

To examine if lactic acid can be formed from glycolaldehyde, an experiment was done with this aldose at 300 °C for 10 min in 0.75 M NaOH. HPLC analyses of the solution after the reaction (Fig. 1) showed a large lactic acid peak, indicating that glycolaldehyde also produces lactic acid, in addition to formic acid, acetic acid, and acrylic acid. Acrylic acid is most likely the dehydration product of lactic acid while acetic acid is the decarbonylation product. A confirmatory experiment was carried out under the same conditions. Mok

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[*] Corresponding author. Tel./fax: +81 22 795 7385; e-mail: jin@mail.kankyo.hotoku.ac.jp

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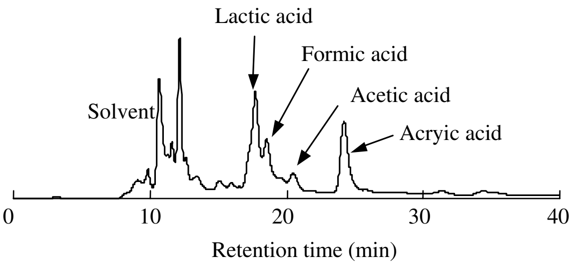

Figure 1. HPLC chromatogram of the sample after alkali hydrothermal treatment of glycolaldehyde (temperature: 300 °C; reaction time: 10 min, 0.75 M NaOH).

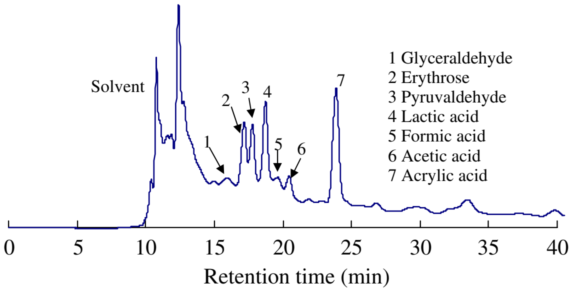

Figure 3. HPLC chromatogram of the sample after alkali hydrothermal treatment of glycolaldehyde (temperature: 300 °C; reaction time: 1 min; 0.75 M NaOH).

et al.[5] and Lira et al.[6] also reported that in sub- and supercritical water, lactic acid underwent dehydration to give acrylic acid, and that decarbonylation to acetic acid also occurred. Therefore, formic acid would also be a by-product in the formation of lactic acid from glycolaldehyde. Furthermore, as shown in Figure 2, γ-butyrolactone, which contains four-carbon atoms, was also detected by GC–MS analyses. For compounds **1** and **2** (Fig. 2), a spectral library provided no good matches. The mass spectra of the two compounds have a strong peak at $m/z = 56$, which is a characteristic peak for lactones, suggesting that these compounds most likely had this structural motif. These observations suggest that a condensation reaction occurs in the alkali hydrothermal reaction of glycolaldehyde. In addition, an experiment with glycolaldehyde was performed at a short reaction time (1 min), which led to the identification of more intermediate products. As shown in Figure 3, erythrose, pyruvaldehyde, and glyceraldehyde were also produced.

On the basis of these experimental findings and basic theories in alkaline degradation of monosaccharides, we propose a pathway for the formation of lactic acid from glycolaldehyde under these conditions (Fig. 4). Because erythrose, **2**, was identified, glycolaldehyde **1**, may undergo aldol condensation to give erythrose. Lactic acid may be produced from **2** by one of the three pathways. First (pathway **i**), considering that the dehydration easily occurs under hydrothermal conditions, erythrose may lose water to form a carbon–carbon double bond between the α- and β-carbon atoms, yielding 2,4-dihydroxybutanal (**3**). At the same time, **3** may undergo the keto-enol tautomerization to **4**, which may subsequently decompose to formaldehyde and pyruvaldehyde (**5**) by a reverse aldol condensation. Finally, **5** may undergo benzilic acid rearrangement to lactic acid (**7**). A possible second pathway (**ii**) is based not only on the traditional theory of the conversion of carbohydrates to lactic acid in alkaline solution but also on recent studies on hydrothermal reaction pathways of monosaccharide model compounds.[7] In pathway **ii**, erythrose may rearrange into **8** by a Lobry de Bruyn–Albeda van Ekenstein transformation (LBAE). Subsequent cleavage via a reverse aldol condensation results in formic acid and glyceraldehyde (**9**), which then undergoes isomerization to dihydroxyacetone (**10**). Both glyceraldehyde and dihydroxyacetone can undergo dehydration to give pyruvaldehyde (**6**), which subsequently undergoes the benzilic acid rearrangement to lactic acid. The identification of glyceraldehyde may provide support for the presence of pathway **ii**. A possible co-product with **8**, if the LBAE transformation occurs, would be 1,2-enediol, **11**. Glyceraldehyde could also be formed by cleavage of **11** (pathway **iii**), because the formation of the double bond between carbon 1 and carbon 2 in erythrose would be expected to weaken the single bond between carbon 3 and carbon 4.

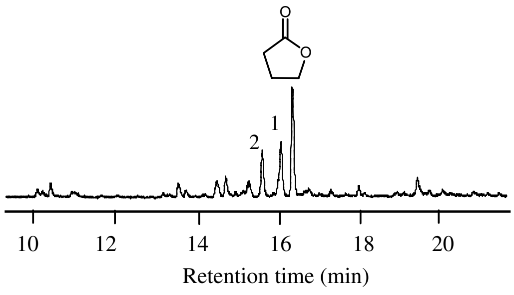

Figure 2. GC–MS chromatogram of the sample after alkali hydrothermal treatment of glycolaldehyde (temperature: 30 °C, reaction time: 10 min; 0.75 M NaOH).

In all three pathways, formaldehyde would be formed and, given the basic reaction medium, this by-product may be converted into formic acid and methanol by the Cannizzaro reaction, a process in which aldehydes containing no α-hydrogens undergo self-oxidation and reduction to yield a mixture of a carboxylic acid salt and an alcohol.[8] To test this, an experiment with formaldehyde (a 40% aqueous solution of formaldehyde with methanol as a stabilizer) was performed at 300 °C in 0.75 M NaOH. Under these conditions, a considerable yield (15.7%) of formic acid was obtained. Furthermore, ^{1}H NMR analyses of the reaction mixtures for both glycolaldehyde and formaldehyde showed a strong signal for the methyl protons of methanol at 3.5 ppm,

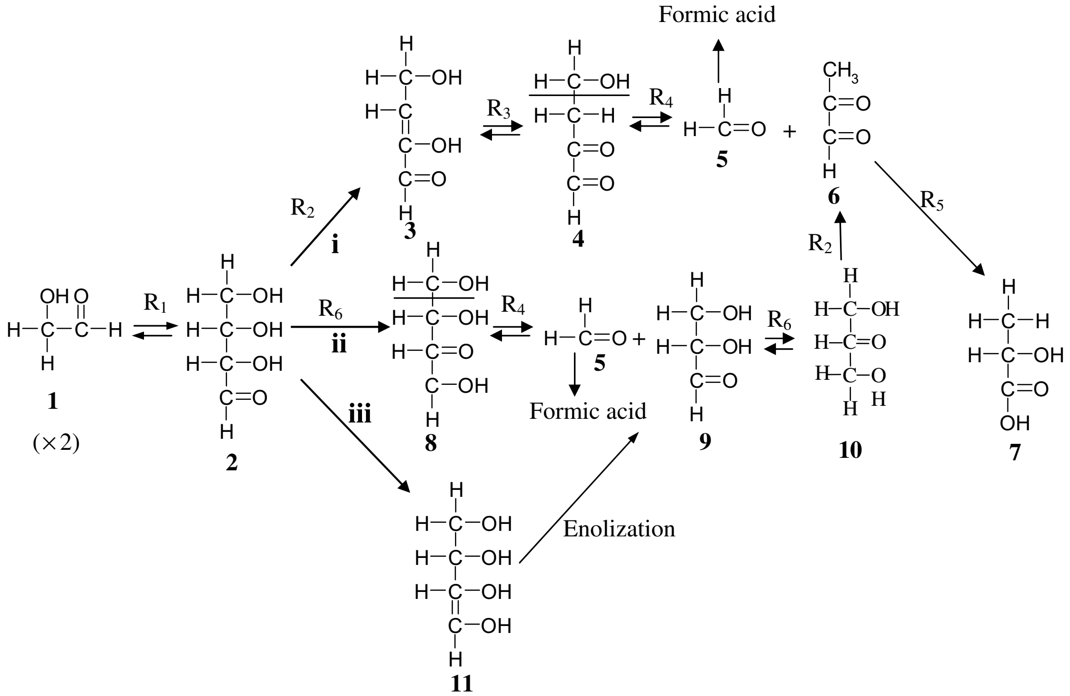

Figure 4. Proposed pathways for the conversion of glycolaldehyde into lactic acid. R_1: Aldol condensation; R_2: elimination of H_2O; R_3: keto-enol tautomerization; R_4: reverse aldol condensation; R_5: benzilic acid rearrangement; R_6: Lobry de Bruyn–Albeda van Ekenstein transformation (LBAE).

indicating that a considerable amount of methanol was also formed. Moreover, because five-membered ring lactones were also found, **2** and/or **3**, **8**, **10** may also cyclize into lactones via an aldol condensation.

Although aldol and reverse aldol condensations as well as keto-enol tautomerization occur in both basic and acidic solutions, the reactions in basic solution are generally much faster, because of the greater catalytic effect of hydroxide ions.[9] In addition, the benzilic acid rearrangement occurs only in a basic solution. Thus, the formation of lactic acid from glycolaldehyde is critically dependent upon the concentration of the base. Experiments were performed by changing the concentration of NaOH at 300 and 200 °C. As expected (Table 1), at both temperatures, the yield of lactic acid decreased with the decreasing concentration of NaOH. These observations further support the conversion mechanisms shown in Figure 4. Furthermore, from the data in Table 1, it can be seen that an increase in temperature leads to an increase in the yield of lactic acid. For glycolaldehyde, the acidity of its α-hydrogen is lower than that of aldehydes without the OH group at the α-carbon, due to the inductive effect of the oxygen. Thus, the aldol condensation for glycolaldehyde may be more difficult than for other aldehydes. This may be a reason why glycolaldehyde produces little lactic acid at a lower temperature.

Moreover, it should be noted that according to the proposed mechanism shown in Figure 4, an increase in NaOH should lead to an increase in the formation of formic acid. However, the yield of formic acid obtained using 0.75 M NaOH was lower than that with 0.25 M NaOH (see Table 1). This does not necessarily indicate that these results are inconsistent with the mechanism proposed in Figure 4. In general, the Cannizzaro reaction occurs in the presence of concentrated alkali at a low temperature. The decrease in formic acid with an increase in NaOH may be due to the high temperature and pressure, which may lead to other reactions. The results of the experiments with formaldehyde showed that the yield of formic acid using 0.75 M NaOH was also lower than that using 0.25 M NaOH (Table 1). Furthermore, from Figure 4, it can be seen that the formation of lactic acid from glycolaldehyde proceeds via erythrose. This means that a four-carbon aldose can also form lactic acid, probably with a yield similar to or less than that from glycolaldehyde. However, experiments to confirm this cannot be completed because pure erythrose is not available. From the discussion above, glycolaldehyde and erythrose can produce lactic acid by the alkali hydrothermal treatment. That is, the pathway via glycolaldehyde is also an important pathway for the conversion of glucose into lactic acid.

Finally, to examine the contribution of these aldoses to lactic acid production from glucose, the experiments with glyceraldehyde and glucose were carried out at 300 °C with 0.75 M NaOH. As shown in Table 1, the yields of lactic acid from glyceraldehyde and glucose were 39.9% and 23.6%, respectively. The higher

Table 1. Yields of products from $C_n(H_2O)_n$ ($n = 1,2,3,6$) by alkali hydrothermal treatment

Hydrothermal conditions			Yield[a] (%)			
Initial material	Temp (°C)	NaOH (M)	Lactic acid	Formic acid	Acetic acid	Acrylic acid
Glycolaldehyde $C_2(H_2O)_2$	200	0.25	11.0	10.1	1.9	1.0
		0.75	17.9	5.4	1.6	1.3
	300	0.25	17.8	13.7	8.8	5.0
		0.75	28.1	8.9	3.9	3.8
Glyceraldehyde $C_3(H_2O)_3$	200	0.25	20.6	5.8	4.3	
		0.75	30.8	4.3	1.3	
	300	0.25	27.8	5.2	4.9	
		0.75	39.9	4.8	3.1	
Acetaldehyde $C(H_2O)$	200	0.25	2.9	35.2	8.3	
		0.75	5.8	26.9	3.6	
	300	0.25	3.7	29.9	9.8	
		0.75	0.0	15.7	0	
Glucose $C_6(H_2O)_6$	300	0.75	23.6	4.3	3.1	

Reaction time: 10 min.

[a] The percentage of products compared to the initial material based on carbon mass.

yield from glyceraldehyde suggests that the major pathway for the conversion of glucose into lactic acid proceeds via this aldose. The lower yield of lactic acid from glucose suggests that degradation of glucose in alkali hydrothermal reaction is very complex and many significant side-reactions occur.

1. Experimental

1.1. Materials

Glycolaldehyde (Aldrich, #10503TB) was used; NaOH (99%) was used as the alkaline catalyst. Other chemicals, such as acetaldehyde (36–38% solution), DL-glyceraldehyde (99%), and glucose (99.9%) were obtained from Wako Pure Chemicals Industries Ltd.

1.2. General procedures

All experiments were conducted in a batch reactor system described elsewhere.[10,11] A brief description of the experimental procedure is given below. Water (4 mL, 40% water fill) containing the desired amount of NaOH and the test material was added to the reactor, which was immersed in a salt bath preheated to the desired temperature. After the reaction, the reactor was quickly cooled in cold water. All experiments were performed with degassed water and by purging the reactor with nitrogen. A liquid sample was filtered through a 0.45 μm filter, and then the pH of the solution was adjusted to 6–7 with sulfuric acid.

1.3. Products analyses

After the reaction, the liquid sample was analyzed by HPLC and GC–MS. ^{1}H NMR analyses were also carried out. For GC–MS analyses, a Hewlett–Packard model 5890 Series II Gas Chromatograph equipped with a model 5890B Mass Selective Detector was used. The samples were separated on a HP-INNOWAX capillary column (Cross-Linked Polyethylene Glycol) using helium as the carrier. HPLC analysis was performed with a Waters HPLC system equipped with a tunable absorbance detector (UV–vis detector) and a differential refractometer (RI detector). Samples were separated through a series of two identical columns of RSpak KC-811 to obtain a better separation. ^{1}H NMR spectra were recorded on a JEOL JNM-LA300 spectrometer operating at 300 MHz. Details on the conditions for GC–MS, HPLC, and ^{1}H NMR analyses are available elsewhere.[2,11] Quantitative analyses for major products were carried out by HPLC. In general, quantitative data were obtained by comparing the area of the peak. When a compound peak was not well separated, quantitative data were obtained by the height of the peak.

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