Biomimetic Conversion of Glucose to Organic Acid Facilitated by Metalloporphyrin under Mild Conditions

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Biomimetic catalytic conversion of carbohydrates to low-molecular weight (LWM) organic acids was investigated in the presence of sulfonated metalloporphyrins (MTSPP, M = Fe, Mn, Co, Cu), with dioxygen as the oxidant. The results showed that the selectivity of lactic acid reached 70%, starting from glucose with an iron complex of *meso*-tetra(4-sulfonato-phenyl)porphyrin (TSPPFeCl) as the catalyst at 433 K, and 0.6 MPa of O_2 in 0.05 M NaOH aqueous solution. The effects of various metalloporphyrins on the selectivity of oxidative products were also considered. Experimental results show that TSPPFeCl exhibited the highest catalytic performance compared with TSPPMnCl, TSPPCo, and TSPPCu.

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INTRODUCTION

Carbohydrates are favorable renewable feedstocks for the synthesis of various organic compounds in industry (Lichtenthaler and Peters 2004). Carboxylic acids represent an important class of renewable chemicals that are derived from carbohydrates (Song *et al*. 2013). Currently, the production of high-value organic acids from carbohydrates is mostly based on fermentative processes (Wang *et al*. 2015a). A significant example is the fermentation of glucose to lactic acid (LA), which is one of the top value-added chemicals derived from carbohydrates with promising applications in the food, pharmaceutical, and polymer industries (Martinez *et al*. 2013). However, there are some limitations with this biotechnological method. For instance, there is a need to deal with the large amounts of $CaSO_4$ byproduct (Dusselier *et al*. 2013). In view of this, homogeneous catalysis, heterogeneous catalysis, and hydrothermal processes for the chemo-catalytic transformation to produce LA have been recently and rapidly developed (Jin and Enomoto 2009; Dusselier *et al*. 2013; Song *et al.* 2013). For example, Esposito and Antonietti (2013) reported the hydrothermal conversion of glucose to lactic acid in 0.1 M $Ba(OH)_2$ solution, giving a 57% yield of lactic acid after 180 min at 250 °C. Wang *et al.* (2015b) improved the yield of lactic acid up to 68% using a hydrothermal treatment of cellulose, with erbium ion-exchanged montmorillonite K10 as an efficient solid acid catalyst at 240 °C under 2 MPa of N_2 for 30 min. These hydrothermal processes require high temperature and pressure to pose stress on the reactor. Sn-based zeolites, as solid catalysts, can catalyze the conversion of sucrose to methyl lactate, a precursor of LA, approaching 64% selectivity (Holm *et al*. 2010). However, the selectivity of methyl lactate decreased to 43% with glucose as a substrate. Alumina-supported potassium hydroxide (KOH) was found to remarkably enhance the yield of LA to 75%, in a microwave-assisted process at 180 °C (Epane *et al*. 2010). However, a strong alkaline condition of 1.5 equivalents of KOH is

required for this catalytic process. Homogeneous attempts using metal salts as Lewis acid catalysts show excellent catalytic performance in the conversion of carbohydrates to LA. Wang *et al.* (2013a) found a highly efficient method for lactic acid production from cellulose, using Pb(II) salt as the catalyst at 190 °C for 4 h under 3 MPa of N_2; it produced a 68% yield of LA, including a lot of wastewater containing lead ions. Recently, the highest yield of LA from cellulose, approximately 90%, was achieved using $Er(OTf)_3$ as the catalyst (Wang *et al*. 2013b). However, these homogeneous catalysts suffer from difficult separation and recovery from the reaction mixtures. Therefore, the development of an economically and environmentally friendly approach for the selective conversion of carbohydrates to LA under mild conditions is still highly desired.

Metalloporphyrins are a class of highly efficient and selective Lewis acid catalyst and oxidative catalysts used for catalytic hydration (Tachinami *et al.* 2013), C-C bond formation (Zhou *et al.* 2012; Jiang *et al.* 2013; Sheng *et al.* 2013), and oxidation (Liu and Guo 2012). For instance, cobalt porphyrin has been used as a biomimetic catalyst for the industrial-scale oxidation of hydrocarbon with air under mild conditions (Liu and Guo 2012). It is worth noting that this biomimetic catalyst does not need to be recycled because of its very low concentration. On the other hand, metalloporphyrins also exhibit a high catalytic performance for the oxidative cleavage C-C bond of vicinal diols, or α-ketols, to carbonyl compounds with molecular oxygen (Ortiz de Montellano 2004). Carbohydrates typically have the structure of a carbonyl group or an acetal equivalent, with many vicinal diol or α-ketol moieties. Although a few studies have been performed on the subject of the catalytic oxidative cleavage of C-C bonds of carbohydrates by metalloporphyrins and their analogues (Sorokin 2013), the application of homogeneous metalloporphyrin-based catalysts for conversion of glucose to organic acid is not known. Moreover, all of these works were conducted for the functionalization of carbohydrates with H_2O_2 as the oxidant.

This study reports a highly selective conversion of carbohydrates to LA with oxygen by using ppm concentration of water-soluble metalloporphyrins under mild conditions. Glucose was chosen as the carbohydrate model compound to explore the catalytic activities of several metalloporphyrin catalysts. The biomimetic process for the conversion of glucose is depicted in Scheme 1.
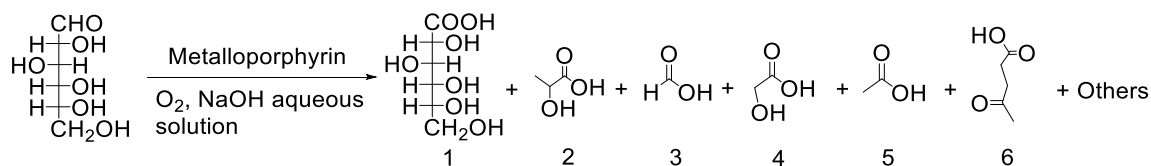
Scheme 1. Oxidation of glucose with molecular oxygen that has been catalyzed by metalloporphyrin in NaOH aqueous solution

EXPERIMENTAL

Materials

All reagents were obtained commercially and used without further purification. Glucose, gluconic acid, lactic acid, and glycolic acid were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Formic acid, levulinic acid, and acetic acid were purchased from J&K Scientific Ltd (Beijing, China). Sulfonated metalloporphyrins

TSPPMCl (M = Fe, Mn, Co, Cu) were synthesized from *meso*-tetraphenylporphyrin (TPPH$_2$) according to the literature (Adler *et al*. 1970; Fleischer *et al*. 1971).

Methods

General reaction conditions for the carbohydrate oxidation were as follows: In a 15-mL autoclave, 1×10^{-5} mmol of metalloporhyrin was added to a reaction mixture containing 2.8 mmol of substrate and 5 mL of NaOH (0.05 M) aqueous solution. After the reaction mixture was stirred at 433 K under 2.0 MPa of O$_2$ for 2 h, the reaction mixture was added to 10 mL of water and directly analyzed using a Shimadzu LC-20A liquid chromatograph (Shimadzu Corporation, Japan). The organic acid products and H$_2$O$_2$ were analyzed with a VP-ODS C18 column and DAD detector, using phenols as the internal standard, while the carbohydrates were analyzed with SUGAR SH1101 columns and RI detector, using xylose as the internal standard. The definitions of carbohydrate conversion and product selectivity are elucidated in the Appendix.

RESULTS AND DISCUSSION

We started our investigation with an initial testing of product screening as a function of reaction time in the conversion of glucose. In addition to gluconic acid (1) that was formed as an oxidative product of the aldehydic C-H bond, lactic acid (2), formic acid (3), glycolic acid (4), acetic acid (5), and levulinic acid (6) were obtained as C-C bond cleavage products. There are also some unidentified products, noted as others, which included other water-soluble organic compounds, gas, and humins. The product distribution as a function of reaction time is illustrated in Fig. 1.
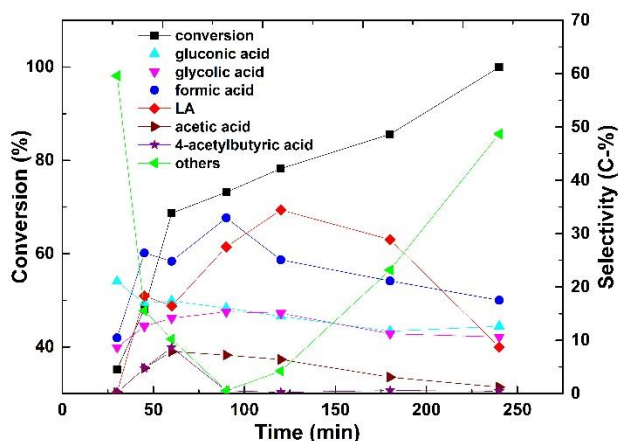

Fig. 1. Influence of reaction time on glucose conversion and product selectivity; reaction conditions: glucose= 2.8 mmol, FeTSPPCl=1×10^{-5} mmol, 0.05 M NaOH= 5 mL, P(O$_2$)= 2.0 MPa, and *T*= 433 K

The selectivity of the C-C bond cleavage products initially increased and then decreased. On the contrary, the selectivity of the unidentified products decreased markedly before 1.5 h, and then increased remarkably with prolonged time. After 1.5 h, the decomposition of the C-C bond cleavage products to gas products or humins could easily take place (Möller *et al*. 2011; Yin and Tan 2012). As shown in Fig. 1, the selectivity of

gluconic acid decreased slightly with prolongation of the reaction time, which suggests that gluconic acid might also be an intermediate for the formation of C-C bond cleavage products.

Table 1 shows the product selectivity for the conversion of glucose by various sulfonated metalloporphyrin catalysts, and without catalyst, in 0.05 M NaOH aqueous solution at 433 K for 2 h. As shown in Table 1, TSPPFeCl gave much better results than that of $FeCl_3$ as the catalyst or without catalyst. In addition, TSPPFeCl displayed the highest catalytic performance among the metalloporphyrins tested, especially in strong alkaline conditions (Table 1, entry 5), followed by TSPPCu and TSPPCo; TSPPMnCl showed the lowest catalytic activity. This order of catalytic activity of metalloporphyrins is consistent with what was observed in metallophthalocyanine-catalyzed starch oxidation with H_2O_2 (Sorokin 2013).

Table 1. Effects of the Type of Metalloporphyrin on Glucose Conversion and Product Selectivity [a]

Entry	Catalyst	Conv.(%)	Selectivity (C-%)						
			1	2	3	4	5	6	others
1	Blank	32.6	56.2	—	9.7	16.8	13.2	—	4.1
2	$FeCl_3$	56.6	10.3	—	6.1	14.7	11.4	—	57.5
3	TSPPFeCl	78.3	14.6	34.5	25.2	15.1	6.5	—	4.1
4	TSPPFeCl [b]	41.5	30.8	16.0	17.0	11.0	20.3	2.0	2.9
5	TSPPFeCl [c]	100	10.0	—	14.8	6.5	30.1	1.3	37.3
6	TSPPFeCl [d]	53.1	14.0	70.3	4.1	14.8	2.7	—	—
7	TSPPFeCl [e]	67.7	12.4	52.5	4.6	13.3	3.0	—	14.2
8	TSPPFeCl [f]	68.6	15.4	33.7	3.2	11.2	8.9	—	27.6
9	TPPSMnCl	37.8	10.8	—	6.1	14.5	5.9	—	62.7
10	TPPSCo	40.7	9.4	—	4.9	10.3	12.8	—	18.5
11	TPPSCu	49.5	13.2	—	10.3	18.5	4.4	—	53.6

[a] Glucose 2.8 mmol, catalyst 1×10^{-5} mmol (based on moles of metal atom), 0.05 M NaOH = 5 mL, $P(O_2)$ = 2.0 MPa, T= 433 K, and t= 2 h;
[b] in 0.5 M H_3PO_4 aqueous solution; [c] in 0.5 M NaOH aqueous solution;
[d] $P(O_2)$ = 0.6 MPa; [e] $P(O_2)$ = 1.0 MPa;
[f] P(air) = 2 MPa

Product analysis revealed that gluconic acid was the major oxidative product in the absence of a catalyst and that selectivity was up to 56%, as seen in Table 1, entry 1. Instead of gluconolactone, a primary product of TSPPFeCl-catalyzed oxidation of a glucose C-H bond with an *in situ* reduced coenzyme (Maid *et al*. 2011), LWM acids were the main products in the present catalytic approach without a reductant. Furthermore, the product selectivity also depends noticeably on the temperature, O_2 pressure, and the pH value of the reaction solution (Tables S1, S2, and S3 in the Appendix). Relatively high selectivity for lactic acid, of approximately 70%, was attained at a 53% conversion of glucose with TSPPFeCl as the catalyst under the optimized conditions, as can be seen in Table 1, entry 6.

When the temperature was increased from 413 K to 453 K, the conversion of glucose increased significantly and kept full conversion after heating to 453 K, whereas, for the selectivity of LA, it was initially increased then decreased remarkably (Table S1 in the Appendix). This result indicated that complete conversion of glucose required a relatively high reaction temperature; decomposition of formed LA occurred due to raising

the temperature; and keeping appropriate temperature was crucial to achieve high selectivity of LA.

With increasing oxygen pressure, the selectivity of LA decreased, which can be seen in Table 1, entries 6, 7, and 3. This can be ascribed to the easy oxidative decomposition of LA to acetic acid and formic acid in high concentrations of oxygen (Esposito and Antonietti 2013). However, using air as the oxidant did not improve the selectivity of LA, as shown in Table 1, entry 8. Under acidic conditions, TSPPFeCl provided 30% gluconic acid (Table 1, entry 4), while 30% acetic acid was obtained under concentrated base conditions (Table 1, entry 5). It may be that the high concentration of NaOH could increase the concentration of the acetic acid (Yan *et al*. 2007).

To understand the role of metalloporphyrins and the pathway of LA formation in biomimetic carbohydrate oxidation, high-performance liquid chromatography (HPLC) analysis was employed to detect the H_2O_2 that was generated in the biomimetic oxidation of glucose. The results given in Table 2 indicated that a simple mixture of glucose and NaOH aqueous solution in an oxygen atmosphere resulted in H_2O_2 formation, which is shown by entry 4, in Table 2. This performance is very similar to that observed in the process of the oxidation of glucose to gluconic acid over a gold catalyst (Comotti *et al*. 2006). Moreover, the H_2O_2 concentration decreased with increasing TSPPFeCl concentration.

When a tenfold excess of catalyst was added, the H_2O_2 concentration was decreased by 40%, which can be seen from entries 1 through 3 in Table 2. Under alkaline conditions, the iron(III)-peroxo species, acknowledged as nucleophilic oxidant intermediates, are subjected to production by the reaction of H_2O_2 with iron porphyrins and non-heme iron complexes (Cho *et al*. 2011; Franke *et al*. 2012). Thus, it is reasonable to assume that the metalloporphyrins in glucose oxidation might be responsible for the formation of the metalo-peroxo species, (TSPPMO$_2^-$), by the addition of H_2O_2 generated *in situ*. The TSPPMO$_2^-$ then cleaves the C-C bond of glucose, to form LA *via* catalytic pathways similar to those seen in the process of the oxidative modification of starch using metallophthalocyanine complexes and H_2O_2 (Sorokin 2013). Because the iron porphyrins have long been considered the best metalloporphyrin catalysts to decompose H_2O_2 to a hydroxyl radical (Bruice 1991), the radical pathway could not be excluded (Arts *et al*. 1997).

Table 2. H_2O_2 Formation in Various Reaction Conditions*

Entry	FeTSPPCl (mmol)	Glucose (mmol)	NaOH (M)	H_2O_2 (mM)
1	1×10^{-5}	2.8	0.05	2.5
2	1×10^{-4}	2.8	0.05	1.8
3	2×10^{-4}	2.8	0.05	1.4
4	0	2.8	0.05	3.9
5	1×10^{-5}	0	0.05	0
6	1×10^{-5}	2.8	0	0
*Note: T = 373 K, P(O$_2$) = 2.0 MPa, NaOH = 5.0 mL, and t = 2 h				

CONCLUSIONS

1. A novel metalloporphyrin-catalyzed selective oxidation of carbohydrates with molecular oxygen in the aqueous phase was developed. Under the standard conditions, the vicinal diol moiety of a carbohydrate was found to undergo oxidative cleavage easily to obtain a LWM organic acid (*e.g.*, LA).

2. The experimental results show that lactic acid is the main oxidation product starting from glucose (70%) using TSPPFeCl as the catalyst. The HPLC analyses indicate that H_2O_2 is generated in the biomimetic oxidation of glucose.

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APPENDIX

Carbohydrate Conversion and Product Selectivity Definitions

The conversion of glucose and product selectivities are defined as follows:

$$Conversion\ (\%) = 100 - \frac{Moles\ of\ unconverted\ glucose}{Moles\ of\ initial\ glucose} \times 100 \tag{A1}$$

$$Selectivity\ (C-\%) = \frac{Moles\ of\ carbon\ in\ product\ \times 100}{Moles\ of\ carbon\ in\ converted\ glucose} \tag{A2}$$

Others(C-%)=(100C-%)-{gluconic acid (C-%) + lactic acid (C-%) + formic acid (C-%) + glycolic acid (C-%) + acetic acid (C-%) + levulinic acid (C-%)}

$$\tag{A3}$$

Effects of Temperature, NaOH Concentration, and Oxygen Pressure on Glucose Conversion and Product Selectivity

Table S1. Effects of Temperature on Glucose Conversion and Product Selectivity[a]

Entry	Temp (K)	Conv. (%)	Selectivity (C-%)						
			1	2	3	4	5	6	others
1	413	40.1	14.0	11.0	5.2	12.7	1.8	—	55.3
2	423	47.7	15.2	14.3	9.0	19.1	1.8	—	40.6
3	433	78.3	14.6	34.5	25.2	15.1	6.5	—	4.1
4	453	100	5.4	9.7	4.6	7.8	15.1	—	57.4

[a] Glucose 2.8 mmol, TSPPFeCl 1×10^{-5} mmol, 0.05 M NaOH = 5 mL, $P(O_2)$ = 2.0, MPa, t = 2 h

Table S2. Effects of NaOH Concentration on Glucose Conversion and Product Selectivity[a]

Entry	NaOH (M)	Conv. (%)	Selectivity (C-%)						
			1	2	3	4	5	6	Others
1	0.005	63.9	21.0	16.3	29.9	8.9	1.5	—	22.4
2	0.05	78.3	14.6	34.5	25.2	15.1	6.5	—	4.1
3	0.1	85.8	12.3	33.5	20.0	11.1	2.9	4.1	16.1
4	0.5	100	9.9	30.1	14.8	6.5	1.3	—	37.4

[a] Glucose 2.8 mmol, TSPPFeCl 1×10^{-5} mmol, $P(O_2)$ = 2.0 MPa, T = 433 K, t = 2 h

Table S3. Effects of Oxygen Pressure on Glucose Conversion and Product Selectivity[a]

Entry	Oxygen (MPa)	Conv. (%)	Selectivity (C-%)						
			1	2	3	4	5	6	others
1	0.10	49.9	10.4	21.2	4.1	5.9	2.3	39.9	16.2
2	0.60	53.1	14.0	70.3	4.1	14.8	2.7	—	—
3	1.00	67.7	12.4	52.5	4.6	13.3	3.0	—	14.2
4	2.00	78.3	14.6	34.5	25.2	15.1	6.5	—	4.1
5	3.00	87.1	9.8	25.3	8.5	9.7	5.4	—	41.3
[a] Glucose 2.8 mmol, FeTSPPCl 1×10^{-5} mmol, 0.05 M NaOH = 5 mL, T = 433 K, t = 2 h									