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Borate-stabilized transformation of C6 aldose to C4 aldose

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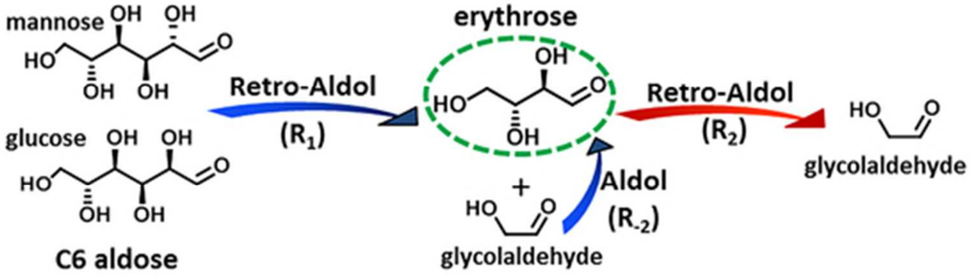

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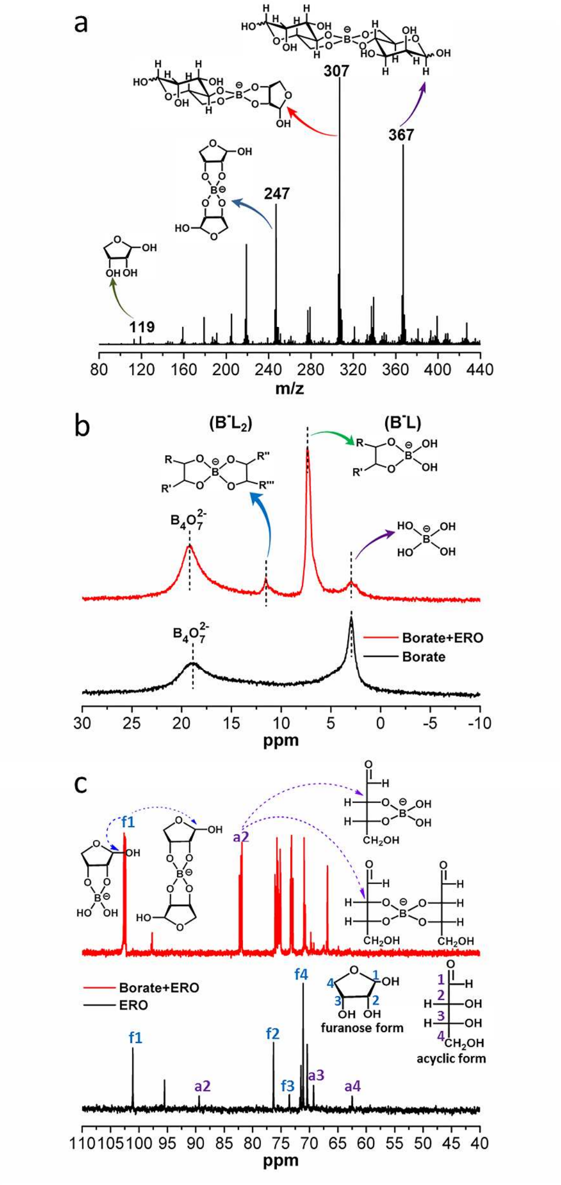

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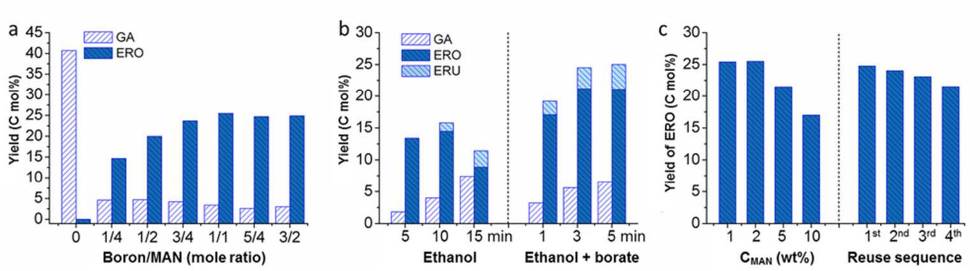

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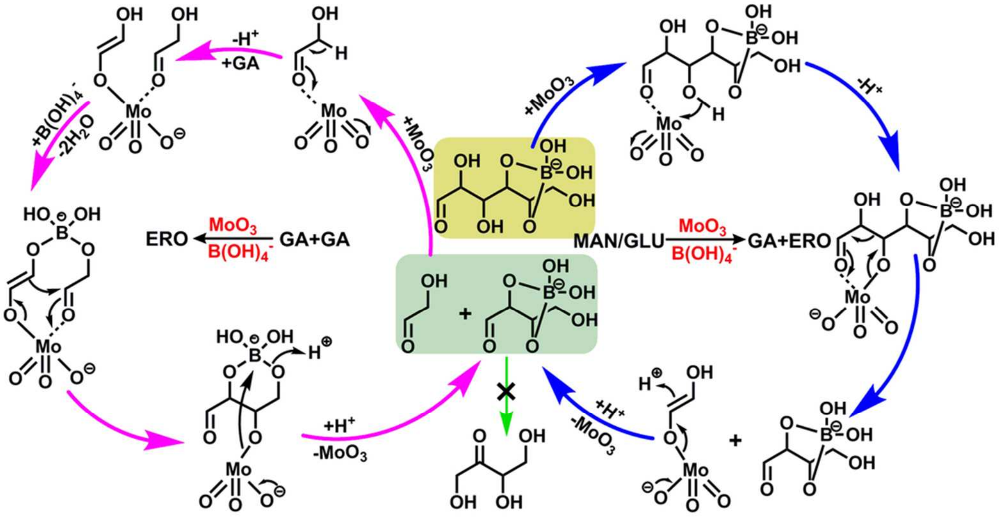

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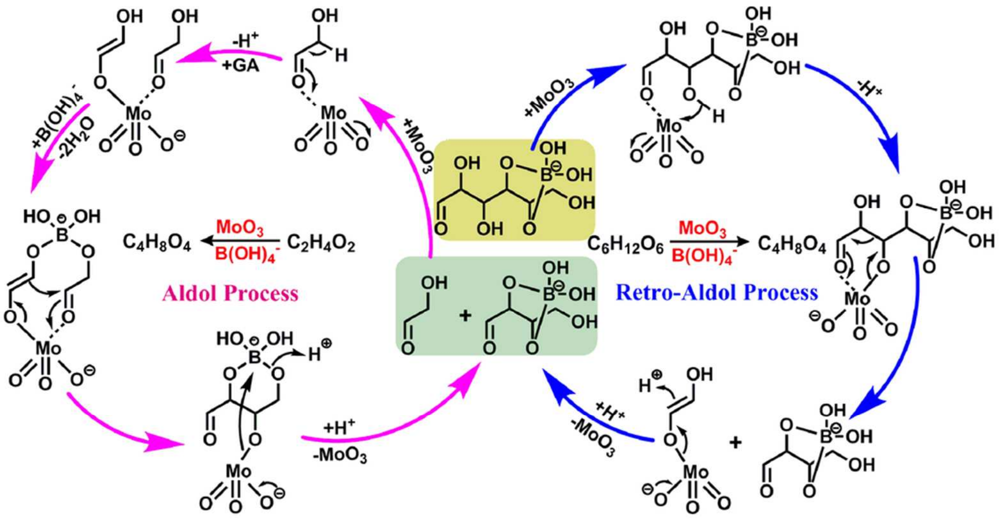

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Borate-stabilized transformation of C6 aldose to C4 aldose

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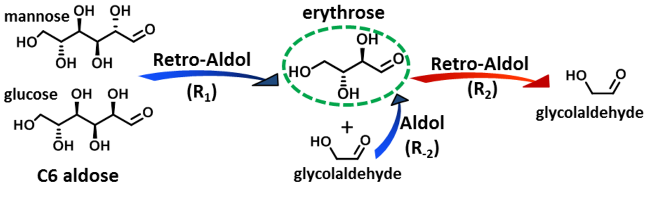
ABSTRACT: High-efficient transformations of biomass-derived sugars into various valuable chemicals are of topical interest. Tetrose with a four-carbon bone is the root of most of biomass-derived C4 products, but its extreme instability obstructs the blossoming of C4 products presently. Herein, we describe a borate-stabilized catalytic strategy to high-selectively accumulate erythrose from C6 aldose via retro-aldol and aldol processes in alcohol solvent. In our proposed mechanism, borate can stabilize erythrose and avoid its further retro-aldol splitting or isomerization, and induce the production of erythrose again via the aldol condensation of above generated glycolaldehyde.

KEYWORDS: C4 aldose, retro-aldol/aldol condensation, stabilizing effect, biomass, heterogeneous catalysis

Renewable biomass resources containing rich carbohydrates or lignin are the only alternative carbon source for the construction of chemicals and materials for human survival in the future. Various strategies for their efficient use as chemical feedstocks are being established in the interest of supplementing and ultimately replacing of fossil fuels.[1-2] Nowadays, biomass-derived carbohydrates have been converted into a variety of platform chemicals containing C2 to C6 skeletons. Most of them can be obtained by catalytic conversion of biomass-derived C5~C6 sugars.[3-24] However, the synthesis of C4 skeleton compounds from much more abundant C6 sugars is still in its infancy. Representative C4 chemicals contain erythritol, methyl vinyl glycolate (MVG), methyl-4-methoxy-2-hydroxybutanoate (MMHB), α-hydroxy-γ-butyrolactone (HBL), which have great potential as novel biomass-derived platform molecules or as building blocks for green solvents and biodegradable polyester plastics.[12, 25-27]

Recently, the C4 products (MVG, MMHB and their acids) can be produced in good yields when glycolaldehyde or tetroses (erythrose, threose, and erythrulose) are used as substrates.[25-27] However, they are not directly obtained or isolated from biomass. To enable the formation of these C4 compounds from abundant C6 sugars, retro-aldol process is required to fragment the carbon backbone of hexose (R_1 in Scheme 1). Unfortunately, so far, tetrose can hardly be obtained in such process, and it is sequentially transformed into C2 because the aparent activation energy of C4 to C2 (R_2) is greatly lower than that of C6 to C4+C2 process (R_1).[28] As a result, developing the proper strategy to accumulate tetrose is one of prerequisite for achieving the wider variety of C4 skeleton chemicals to flourish.



Scheme 1. The retro-aldol/aldol reaction route started from C6 aldose.

Herein, we report a new strategy to successfully accumulate erythrose (ERO) from C6 aldoses via a borate-assistant retro-aldol (R_1)/aldol (R_{-2}) process in alcohol solvent (Scheme 1). Thanks to the stabilizing effect of borate on ERO, this process achieves carbon atom yield of ERO up to 26% from C6 aldoses. Also, a cascade transformation of ERO into ERU is achieved due to the easy disassembly of borate-sugar complex at the further conversion step.

To achieve the smooth proceeding of retro-aldol splitting, herein, commercial MoO_3 solid is used as heterogeneous catalyst to carry out the retro-aldol process of C6 aldose because of its good capacity to catalyze 1,2-intramolecular carbon shift (1,2-CS) reaction of aldoses at moderate temperature.[29] More importantly, we assume that ERO might be accumulated in the presence of borate by forming the stable borate-sugar complex with two hydroxyl groups.[30, 31] To test this hypothesis, we studied the catalytic performance of MoO_3 for the conversion of C6 aldose (mannose and glucose) in absence or presence of sodium borate in methanol (Table 1). In agreement with our speculation, the data in Table 1 show that the addition of borate greatly changes the product distribution of mannose (MAN) and glucose (GLU) conversion, and readily achieves the accumulation of ERO in high yield at all the temperature range. To be specific, when no borate is added, glycolaldehyde (GA) is dominantly produced, and only small amount of ERO can be detected. The highest carbon yield of GA reaches 44.7% after reacting at 170 °C for 60 s when using MAN as substrate, while ERO becomes immeasurable after reacting for 30 s. These mean that the retro-aldol splitting of MAN towards GA and ERO (R_1 in Scheme 1) as well as ERO towards GA (R_2 in Scheme 1) has serially occurred, and ERO cannot be reserved in such condition. On the contrary, when sodium borate is involved in the above reaction system, the production of GA is efficiently suppressed and the selectivity towards ERO increases prominently. The selectivity of ERO can reach up to 88.4% at 150 °C for 5 s, and the highest carbon yield of ERO reaches 25.8% after reacting at 150 °C for 15 s in methanol, indicating the effective accumulation of ERO in such borate-containing catalytic system. Similarly, when GLU is used as substrate, only trace ERO can be observed in the absence of borate, whereas the yield of ERO reaches 13.5% in borate-containing system at 150 °C for 15 s. Furthermore, in both absence and presence of sodium borate systems (Table 1), higher reaction temperature leads to faster reaction rate, higher yield of retro-aldol products (ERO or GA) and carbon balance. This is owing to the fact that low temperature is in favor of the inter-conversion among MAN, GLU and fructose (FRU) rather than the retro-aldol condensation process.

Table 1. Conversion of MAN and GLU in methanol with or without borate using MoO_3 as catalyst.

Substrate	Temp. [°C]	Time	Conv.$_{\text{retro-aldol}}$ [mol%]^c	Selec. and Y. [C mol%]^d GA		ERO		Carbon balance [mol%]^e
				Selec.	Y.	Selec.	Y.	
MAN^a	170	15 s	13.9	37.4	5.2	56.1	7.8	99.1
		30 s	54.4	53.5	29.1	0.0	0.0	74.7
		60 s	73.4	60.9	44.7	0.0	0.0	71.3
	150	5 min	31.3	50.8	15.9	10.5	3.3	87.9
		10 min	62.3	57.8	36.0	0.0	0.0	73.7
		20 min	73.1	55.7	40.7	0.0	0.0	67.6
	130	5 min	11.4	36.0	4.1	28.9	3.3	96.0
		10 min	45.7	67.8	31.0	0.0	0.0	85.3
		30 min	61.2	57.4	35.1	0.0	0.0	73.9
	110	60 min	13.3	72.2	9.6	0.0	0.0	96.3
		120 min	31.1	74.3	23.1	0.0	0.0	92.0
		240 min	47.5	68.0	32.3	0.0	0.0	84.8
MAN^b (borate)	150	5 s	23.2	10.3	2.4	88.4	20.5	99.7
		15 s	44.0	9.3	4.1	58.6	25.8	85.9
		30 s	57.5	9.2	5.3	40.9	23.5	71.3
	140	30 s	19.9	9.0	1.8	88.4	17.6	99.5
		1 min	35.1	8.5	3.0	66.7	23.4	91.3
		2 min	53.0	7.7	4.1	42.3	22.4	73.5
	130	3 min	33.9	7.1	2.4	61.7	20.9	89.4
		5 min	40.9	6.8	2.8	51.6	21.1	83.0
		10 min	58.1	7.2	4.2	32.5	18.9	65.0
	120	10 min	31.7	6.3	2.0	55.8	17.7	88.0
		20 min	50.5	6.1	3.1	34.7	17.5	70.1
		30 min	55.7	7.0	3.9	28.9	16.1	64.3
	110	40 min	26.8	5.6	1.5	57.8	15.5	90.2
		60 min	38.3	5.5	2.1	40.2	15.4	79.2
		80 min	46.0	5.4	2.5	30.7	14.1	70.6
	100	80 min	22.7	4.0	0.9	53.7	12.2	90.4
		120 min	31.8	4.4	1.4	40.9	13.0	82.6
		180 min	43.6	4.4	1.9	26.8	11.7	70.0
GLU^a	170	1 min	37.0	41.4	15.3	0.0	0.0	78.3
	150	20 min	41.0	34.4	14.1	4.6	1.9	75.0
	130	50 min	38.4	39.1	15.0	0.0	0.0	76.6
GLU^b (borate)	150	15 s	49.1	8.8	4.3	27.5	13.5	68.7
	140	2 min	60.6	6.8	4.1	20.8	12.6	56.1
	130	10 min	49.7	6.6	3.3	22.9	11.4	65.0

[a] Reaction condition: 100 mg of MAN/GLU and 12 mg of MoO_3 were added into 5 g of methanol and reactions were taken at 110~170 °C for different time. [b] Reaction condition: 100 mg of MAN/GLU, 53 mg of sodium borate (boron/hexose mole ratio = 1/1) and 12 mg of MoO_3 were added into 5 g of methanol and reactions were taken at 100~150 °C for different time. [c] Conv.$_{\text{retro-aldol}}$ means the consumed amount of hexose only for retro-aldol reaction, which is calculated by (Conv.$_{\text{MAN}}$ – Y.$_{\text{GLU}}$ – Y.$_{\text{FRU}}$) for MAN conversion or (Conv.$_{\text{GLU}}$ – Y.$_{\text{MAN}}$ – Y.$_{\text{FRU}}$) for GLU conversion. [d] Yields of GA and ERO are calculated by carbon atoms yield from the original hexoses, and their selectivities are calculated by (Y.$_{\text{GA/ERO}}$ / Conv.$_{\text{retro-aldol}}$). [e] Carbon balance is calculated by [Y.$_{\text{GA}}$ + Y.$_{\text{ERO}}$ + (1 – Conv.$_{\text{retro-aldol}}$)]. Y.: Yield, Conv.: Conversion, Selec.: Selectivity.

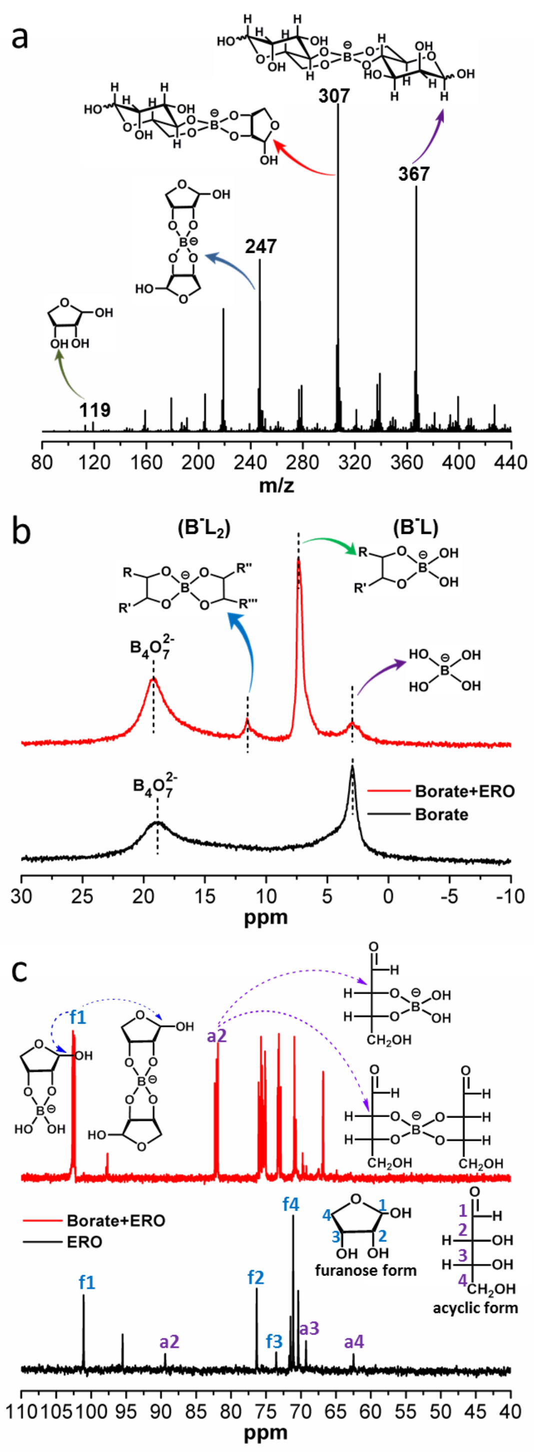


Figure 1. (a) MS analysis results of reaction solution after MAN conversion with borate in methanol using MoO_3 as catalyst. Reaction condition: 100 mg of MAN, 53 mg of sodium borate and 12 mg of MoO_3 were added into 5 g of methanol and reactions were taken at 150 °C for 15 s. (b) ^{11}B NMR spectra of sodium borate dissolved in methanol (black line), sodium borate and commercial ERO dissolved in methanol (red line). ^{11}B chemical shifts of borate esters were taken from Bekkum *et al.*[32] B^-L: $\delta = [7.0 \text{ to } 4.7]$. B^-L_2: $\delta = [11.9 \text{ to } 7.7]$. The values have been adjusted to the standard ^{11}B chemical reference. (c) ^{13}C NMR spectra of ERO (black line) and borate-containing ERO with a boron/ERO mole ratio of 1/1 (red line) in H_2O. Acyclic-aldehyde form of ERO: $\delta = [89.4, 69.3, 62.5]$. Furanose form of ERO: $\delta = [101.1, 76.3, 73.5, 71.5]$.

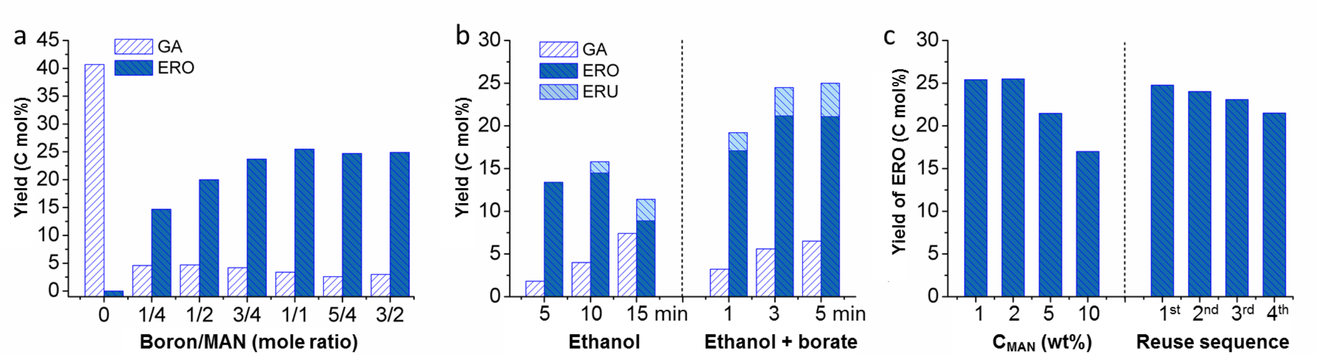


Figure 2. (a) Carbon yields of GA and ERO for MAN conversion in methanol containing different amounts of sodium borate using MoO_3 as catalyst at 150 °C. (b) Carbon yields of GA, ERO and ERU for MAN conversion in ethanol with or without borate using MoO_3 as catalyst at 150 °C for different time. (c) Carbon yields of ERO for MAN conversion with different MAN concentrations in borate-containing methanol (left), and reuse of MoO_3 catalyst for the conversion of MAN in borate-containing methanol (right). GA: glycolaldehyde, ERO: erythrose, ERU: erythrulose, MAN: mannose.

Besides, the addition of borate greatly accelerates the rate of retro-aldol reaction of C6 aldose (Table 1), which could be assigned to the interaction between borate and hexose/tetrose. The formation of borate-hexose complex is quite in favor of the C–C bond breaking of hexose. And after the retro-aldol reaction, GA drops out from the borate-hexose complex while the resultant borate-ERO complex accumulates. Furthermore, the aldose-ketose interconversion between ERO and erythrulose (ERU) catalyzed by Lewis acid is inhibited, which can be attributed to the stabilizing effect of borate on ERO by the formation of borate-ERO complex. Interestingly, in theory, the carbon yield ratio of GA/ERO should be 0.5 because 1 mole of MAN equally produces 1 mole of GA and 1 mole of ERO via retro-aldol process. However, their ratios in Table 1 are far lower than 0.5 in the presence of borate, probably due to the proceeding of aldol condensation of GA towards ERO with the aid of borate.

The resultant reaction solution was directly tested on mass spectrometer (MS), and a weak signal at m/z 119 can be observed, corresponding to the theoretical m/z of ERO under the negative mode (Figure 1a). More significantly, the MS analysis result of reaction mixture in Figure 1a displays three predominant signals at m/z 247, 307 and 367, respectively. These can be attributed to the formation of borate-sugar complexes in the solution. Previous reports have shown that borate readily interacts with molecules containing vicinal diols, forming stable monomeric and dimeric boroxy species.[30] Accordingly, these three m/z signals correspond to the complexes of ERO–$B(OH)_4^-$–ERO (247), ERO–$B(OH)_4^-$–MAN (307), and MAN–$B(OH)_4^-$–MAN (367), respectively. Furthermore, ^{11}B NMR spectra of borate solution and ERO dissolved borate solution are shown in Figure 1b. Two new resonances at $\delta = 7.3$ and 11.5 ppm dominantly appear in the ERO-containing borate solution, further confirming the presence of monomeric and dimeric sugar-borate complexes[32]. Moreover, ^{13}C nuclear magnetic resonance (NMR) analysis of ERO as well as borate-contanining ERO solution were tested to investigate the connection mode of borate on ERO. As shown in Figure 1c, the addition of borate into ERO solution leads to significant change of ^{13}C chemical shifts of ERO. For instance, the chemical shift (δ) of C-2 in acyclic-form ERO was shifted from 89.4 to 81.9 ppm, while C-1 in furanose-form ERO was migrated from 101.1 to 102.7 ppm. It can be speculated that the hydroxyls of borate connect with the 2,3-hydroxyls of ERO by forming stable five-member rings (Figure S1). Apart from ERO, ^{13}C NMR spectra for MAN/GLU solution with or without borate also confirm the presence of monomeric and dimeric borate-sugar complexes (Figure S1). In addition, the mutarotation of ERO from -9.4° to -16.7° in methanol with the addition of borate also implies the formation of borate-ERO complex (Table S1). These results demonstrate that borate can stabilize ERO via the formation of stable five-membered rings with its 2,3-hydroxyls, and avoid the further transformation of ERO towards other products (GA and ERU). Furthermore, the product separated from reaction solution displays a strong signal at m/z 119, and the signal of borate-ERO complex disappears (Figure S2). Its specific optical rotation (-16.9°) is quite close to the theoretical value of D-erythrose aqueous solution (-14.5°) (Table S1). These indicate that borate can be easily seperated with ERO, which is very important for the further conversion of ERO.

Next, the effects of addition amount of borate and solvent on the yield of ERO were further investigated. The product distribution is significantly different whether sodium borate is added or not, and even little amount of borate (boron/MAN = 1/4, mole ratio) can achieve noticeable accumulation of ERO (Figure 2a, Table S2). Increasing the addition amount of borate leads to the increasing ERO yield and the decreasing GA yield, and the highest yield of ERO is obtained at the boron/MAN mole ratio of 1/1 (Figure 2a, Table S2). Expanding organic solvent from methanol to ethanol leads to the decrease of reaction rate, which will be beneficial to the reservation of ERO (Figure 2b, Table S3). In detail, a certain amount of ERO (14.5%) and ERU (1.3%) can be observed after reaction at 170 °C for 10 min in ethanol with MoO_3 even when no borate is added (Figure 2b, left). In the borate-containing ethanol system (Figure 2b, right), the reaction rate is accelerated and the total carbon yield of tetrose increases to 25.0% within 5 min. The aldose-ketose interconversion between ERO and ERU occurs in ethanol, because too little of sodium borate can be dissolved in ethanol and the stabilizing effect of borate on ERO is weakened (Figure 2b, Table S3). Furthermore, the addition amount of MoO_3 catalyst was also optimized in the presence of sodium borate. A low conversion of MAN is observed when MoO_3 is absent (Table S4). This indicates that MoO_3 rather than borate is mainly reponsible for the retro-aldol condensation process of C6 aldose. The addition of MoO_3 pushes the reaction significantly, and the highest yield of ERO is obtained when weight ratio of MoO_3/MAN is 0.12 (Table S4). If the ratios of boron/MAN and MoO_3/MAN are fixed at the optimal condition, ERO yield can maintain 17.0% even if MAN of 10.0 wt% is used (Figure 2c left, Table S5). We also tested the prospect for reusing of MoO_3 solid. As shown in Figure 2c right, the carbon yield of ERO still reaches 21.5% after using four times.

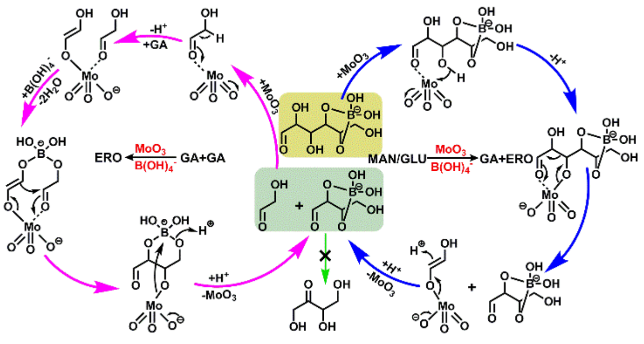
More importantly, ERO in high yield can also be obtained from GA in the presence of borate using MoO_3 as catalyst. As shown in Table 2, when no borate is added, ERO can hardly be obtained and the reaction rate of GA is rather slow at 150 °C. In the borate-containing system, ERO is dominantly produced by the aldol condensation of GA with the aid of borate at 100~150 °C, and the optimal mole ratio of boron/GA is 1/3. This not only implies the stabilization effect of borate on ERO but also explains the reason that the yield of GA is always lower than that of ERO in the presence of borate (Table 1). Theoretically, ERO and GA should be produced with 1/1 mole ratio during the retro-aldol splitting of hexose. However, part of GA obtained from hexose can re-convert into ERO via an aldol condensation process aided by borate. This is expected to greatly improve the utilization of carbon atoms during the transformation from C6 to C4 sugars.

Table 2. Conversion of GA in methanol with or without borate using MoO_3 as catalyst.

Boron/GA (mole ratio)[a]	Temp. [°C]	Time	Conv.$_{GA}$ [mol%]	Yield [C mol%]		Carbon balance [mol%][b]
				ERO	C6	
0	150	10 min	22.4	0.0	4.6	82.2
		30 min	24.4	0.0	5.9	81.5
		50 min	27.3	0.0	6.0	78.7
1/12	150	15 s	49.5	24.4	16.8	91.7
1/6	150	15 s	63.2	29.0	19.2	85.0
1/4	150	15 s	74.9	31.7	18.8	75.6
1/3	150	15 s	82.3	34.7	19.6	72.0
1/2	150	15 s	85.7	34.2	19.2	67.7
1/3	130	5 min	75.1	35.2	19.0	79.1
1/3	110	50 min	64.4	37.5	18.1	91.2
1/3	100	100 min	61.5	36.3	18.3	93.1

[a] Reaction condition: 100 mg of GA, 0~79 mg of sodium borate and 12 mg of MoO_3 were added into 5 g of methanol, and reactions were taken at 100~150 °C for different time. [b] Carbon balance is calculated by $[Y._{ERO} + Y._{C6} + (1 - Conv._{GA})]$, Y.: Yield, Conv.: Conversion. GA: glycolaldehyde, ERO: erythrose, C6: hexose.

Up to now, we can confirm that, with MoO_3 catalyst, C6 aldose experiences a borate-assistant retro-aldol process to achieve GA and ERO, whereas generated GA goes through an aldol condensation to produce ERO again. The proposed reaction pathway for this borate-assistant C–C breaking and coupling process catalyzed by MoO_3 is depicted in Scheme 2. In our proposed mechanism, Mo atom with Lewis acidic activity not only polarizes the carbonyl group of MAN/GLU but also coordinates to its β-oxygen via a deprotonation process, which leads to a stable six-membered intermediate state. And then the C_α–C_β breaking occurs to generate Mo-enolate C2 intermediate and ERO. Because borate can form stable chelate complex with ERO by anchoring with α- and β-hydroxyl groups, the further retro-aldol process of ERO is inhibited owing to the absence of α- and β-hydroxyl sites. Simultaneously, the aldose-ketose isomerization between ERO and ERU through 1,2-HS is also inhibited. Notably, the generated two GA molecules can form one ERO molecule via an aldol condensation process with the aid of borate. That is, one GA forms one Mo-enolate C2 intermediate with MoO_3, and then aldehyde oxygen atom of the other GA further coordinates to the Mo center. The aldol addition of GA to the Mo-enolate C2 intermediate occurs, inducing the formation of ERO. Moreover, alkaline borate can facilitate the deprotonation process of β-hydroxyl and promote the formation of six-membered intermediate state, which greatly accelerates the whole reaction process (Table 1).



Scheme 2. The proposed borate-assistant mechanism pathway for retro-aldol condensation of MAN/GLU to ERO and GA, and aldol condensation of two GA into ERO catalyzed by MoO_3.

Additionally, we make an attempt to convert the as-prepared ERO into its isomer ERU, because ketose plays a key role as substrate in making a variety of value-added chemicals.[25,26] Herein, to enable the isomerization of as-prepared ERO, sodium borate was removed to release ERO from the borate-ERO complex by changing the solvent from methanol to isopropanol owing to the poor solubility of borate in isopropanol. And then Sn-β zeolite with Lewis acidity was added to catalyze the isomerization of ERO into ERU. After reacting in isopropanol at 100 °C for 1 h, ERU of 66.4% is yielded (Figure S3), which means the production of ERU with the total carbon yield of 17.1% from MAN.

To summarize, we propose an efficient strategy to accumulate ERO from biomass-derived C6 aldoses in the presence of borate. In such catalytic system, borate inhibits the further conversion of ERO into undesirable products by forming stable borate-sugar complexes and so accomplishes the accumulation of ERO. We also demonstrate that ERO can not only be obtained from a direct retro-aldol condensation of hexoses, but also be generated by a secondary aldol condensation of GA. This provides the possibility to achieve carbon atom utilization of 100% during the transformation of C6 sugars into C4 skeleton compounds. Finally, we achieve the cascade transformation of ERO into ERU due to the easy disassembly of borate-sugar complex at the further conversion step. The successful generation of tetrose from C6 aldose might be able to push the development and flourish of C4 skeleton chemicals. Future work will focus on further improvement of ERO/ERU accumulation in higher yield as well as carbon atom utilization through the use of more efficient structural stabilizers, catalysts or solvents.

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Author Contributions

All authors have given approval to the final version of the manuscript.

ASSOCIATED CONTENT

Supporting Information. Supporting Information is available free of charge via the Internet at http://pubs.acs.org. This material contains experimental materials, experimental methods, NMR, MS, specific optical rotation and catalytic reaction results (Figure S1~S3 and Table S1~S5).

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ABBREVIATIONS

ERO, erythrose; ERU, erythrulose; GA, glycolaldehyde; MAN, mannose; GLU, glucose; FRU, fructose; Conv., conversion; Selec., selectivity; Y., yield.

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Borate-stabilized transformation of C6 aldose to C4 aldose

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