Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Successive C1-C2 Bond Cleavage: Mechanism of Vanadium(V)-Catalyzed Aerobic Oxidation of D-Glucose to Formic Acid in Aqueous Solution

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Table S1. Signal assignment of ^{13}C-labeled compounds in ^{13}C NMR appeared in text.

Compound name	Chemical shift /ppm	Compound name	Chemical shift /ppm
D-glucose-1-^{13}C	95.92, 92.11	D-arabinose-5-^{13}C	66.36, 62.44
D-glucose-2-^{13}C	74.13, 71.47	D-arabinonicacid-1-^{13}C	176.18
D-glucose-3-^{13}C	76.02, 72.55	D-arabinonicacid-2-^{13}C	73.75
D-glucose-6-^{13}C	60.79, 60.63	D-tetrose-1-^{13}C	101.02, 95.87
D-mannose-1-^{13}C	94.01, 93.64	D-tetrose-4-^{13}C	71.47, 71.11
D-mannose-2-^{13}C	70.65, 70.20	D-glyceraldehyde-3-^{13}C	62.31
D-arabinose-1-^{13}C	96.94, 92.75	D-glycolaldehyde-2-^{13}C	64.47
D-arabinose-2-^{13}C	72.16, 68.70	glycolic acid-2-^{13}C	59.25

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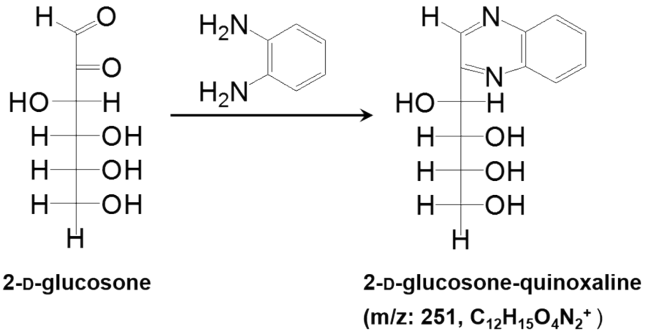
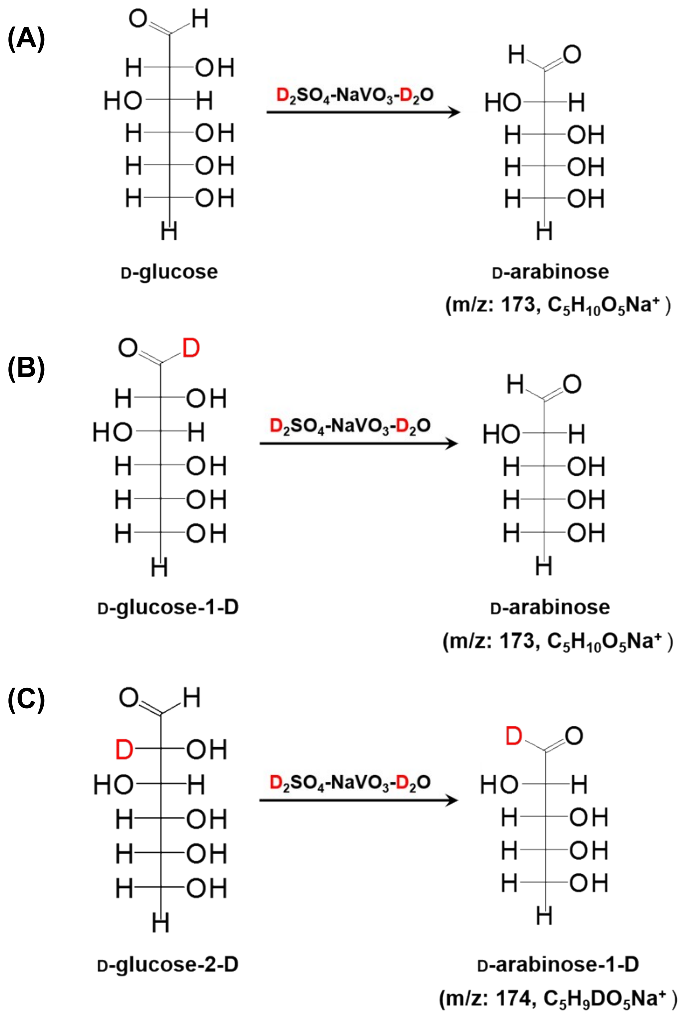


Scheme S1. Reaction of 2-D-glucosone and *o*-phenylenediamine for detection of α-dicarbonyl structure.



Scheme S2. Reactions of (A) D-glucose, (B) D-glucose-1-D and (C) D-glucose-2-D oxidation catalyzed by $NaVO_3$-D_2SO_4 in D_2O.

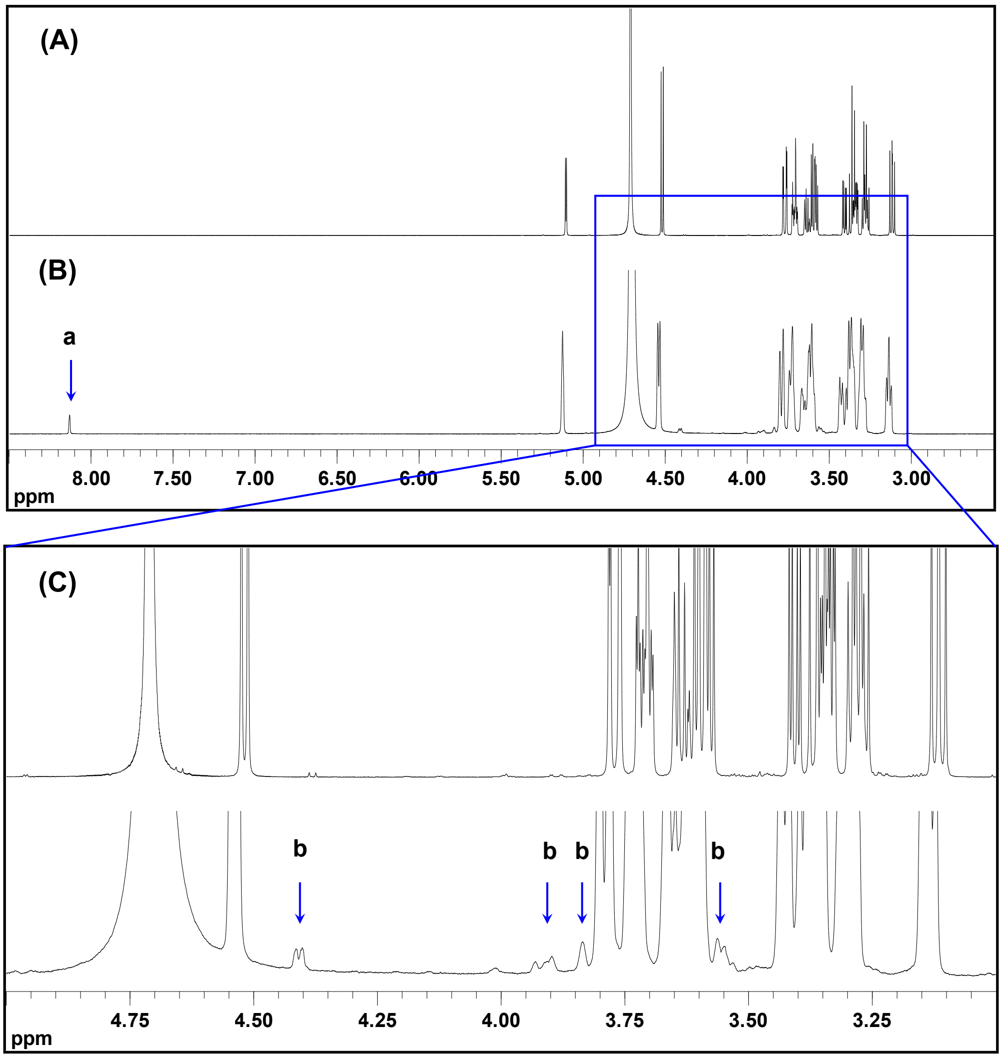


Figure S1. The ^1H NMR spectra of the reaction mixture with D-glucose as the substrate (A) before and (B) after reaction. (B) full spectrum, showing the signal of FA (**a**). (C) the region of 3 ~ 5 ppm of (A) and (B), showing signals of D-arabinose (**b**). Reaction conditions of (B): D-glucose, 0.01 g; $NaVO_3$, 0.35 wt%; D_2SO_4, 1 wt%; D_2O, 0.5 cm^3; initial O_2: 3 MPa; temperature, 100 ^oC; reaction time, 10 min.

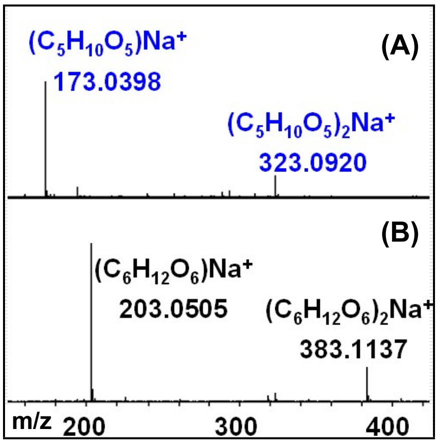


Figure S2. The MS spectra of the D-arabinose (A) and the substrate D-glucose (B). Reaction conditions: D-glucose, 0.1 g; $NaVO_3$, 0.35 wt%; H_2SO_4, 1 wt%; H_2O, 6 cm^3; initial O_2: 3 MPa; temperature, 100 ^oC; reaction time, 2 h.

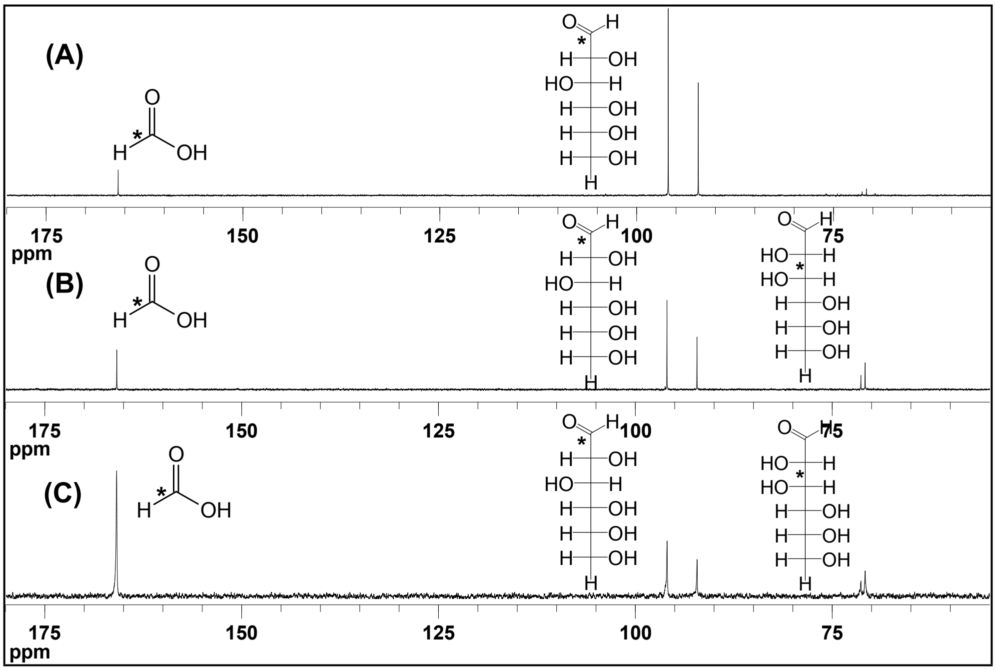


Figure S3. The ^{13}C NMR spectra of the reaction mixture with D-glucose-1-^{13}C as the substrate at different reaction times. (A) 0.5 h, (B) 2 h, (C) 6 h. Reaction conditions: D-glucose-1-^{13}C, 0.005 g; $NaVO_3$, 0.2 wt%; D_2SO_4, 1 wt%; D_2O, 6 cm^3; initial O_2: 3 MPa; temperature, 100 °C.

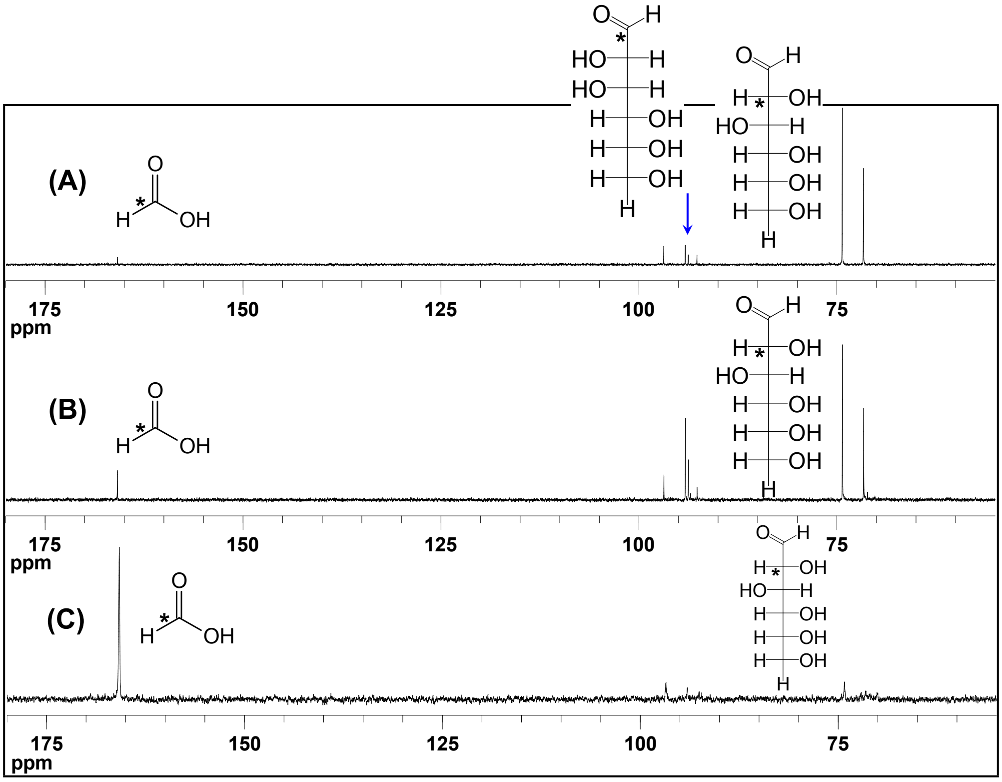
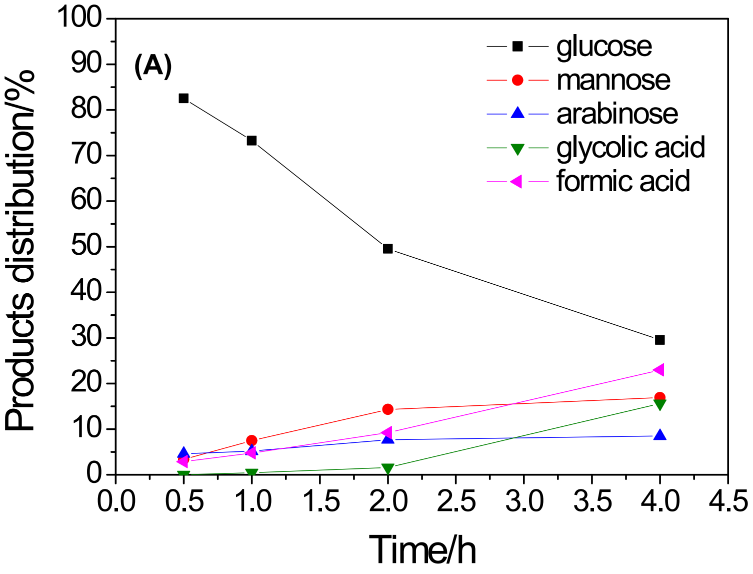


Figure S4. The ^{13}C NMR spectra of the reaction mixture with D-glucose-2-^{13}C as the substrate at different reaction times. (A) 0.5 h, (B) 2 h, (C) 6 h. Reaction conditions: D-glucose-2-^{13}C, 0.005 g; $NaVO_3$, 0.2 wt%; D_2SO_4, 1 wt%; D_2O, 0.5 cm^3; initial O_2: 3 MPa; temperature, 100 °C.



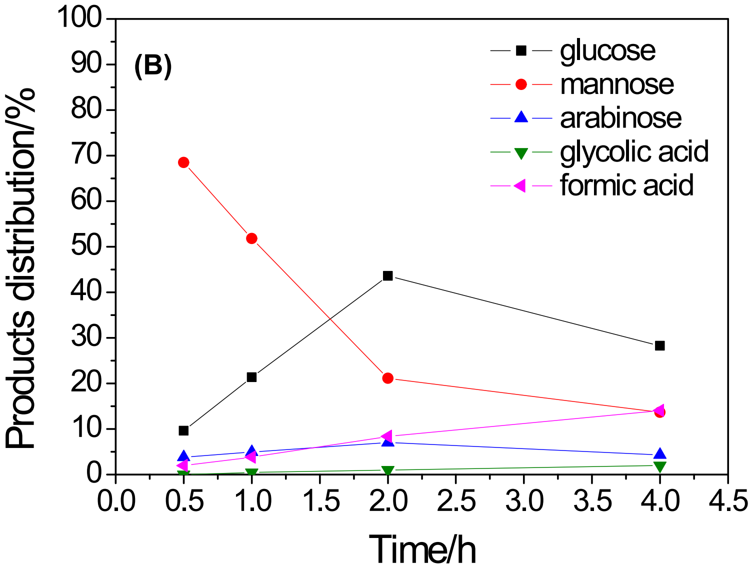


Figure S5. Dependence of products distribution on reaction time with (A) D-glucose and (B) D-mannose as the substrate. Reaction conditions: D-glucose or D-mannose, 0.045 g; $NaVO_3$, 0.2 wt%; H_2SO_4, 1 wt%; H_2O, 6 cm^3; initial O_2: 3 MPa; temperature, 100 ^oC.

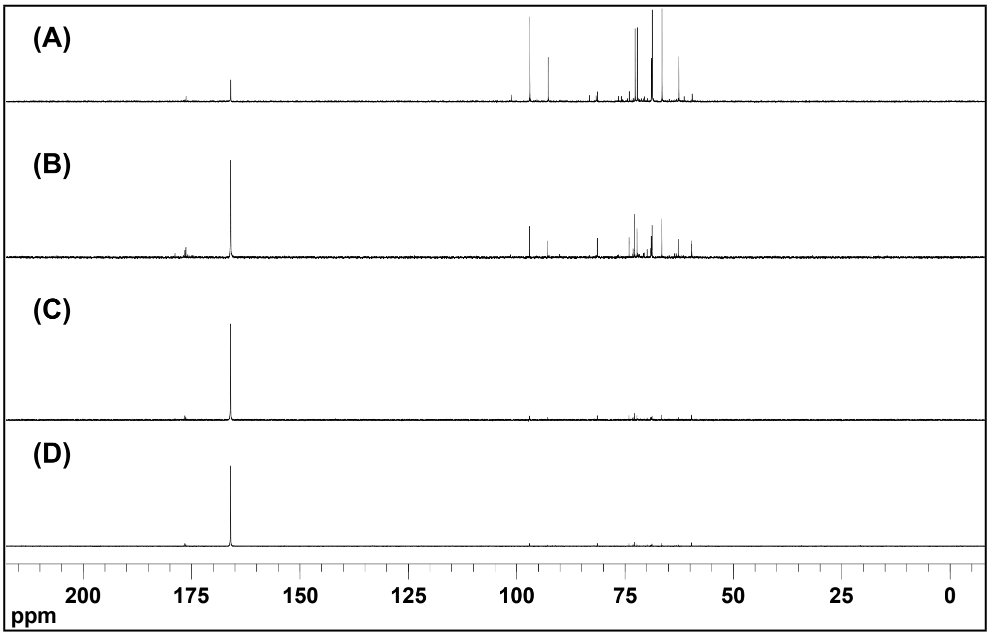


Figure S6. The ^{13}C NMR spectra of the reaction mixture with D-arabinose as the substrate at different reaction times. (A) 0.5 h, (B) 1 h, (C) 1.5 h, (D) 2 h. Reaction conditions: D-glucose, 1 g; $NaVO_3$, 0.35 wt%; H_2SO_4, 1 wt%; H_2O, 6 cm^3; initial O_2: 3 MPa; temperature, 100 °C.

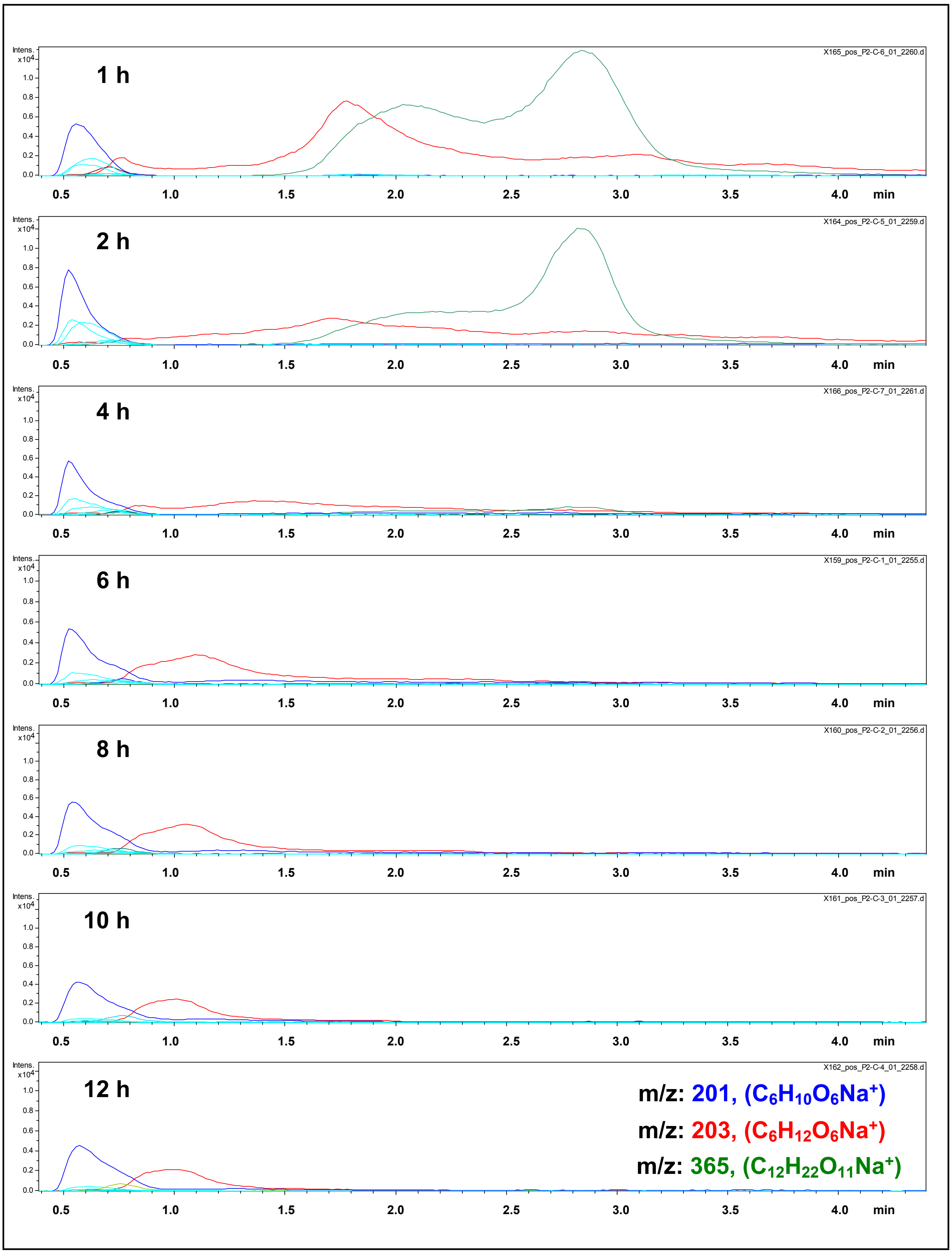


Figure S7. The ion extracted chromatograms of LCMS of the reaction mixture with D-glucose as the substrate at different reaction times. The chromatograms of $C_{12}H_{22}O_{11}Na^+$, $C_6H_{12}O_6Na^+$ and $C_6H_{10}O_6Na^+$ are shown in green, red and blue, respectively. Other ion chromatograms are in relatively low intense and are shown in light blue (shown in Figure S8). Reaction conditions: D-glucose, 0.1 g; $NaVO_3$, 0.35 wt%; H_2SO_4, 1 wt%; H_2O, 6 cm^3; initial O_2: 3 MPa; temperature, 100 ^oC.

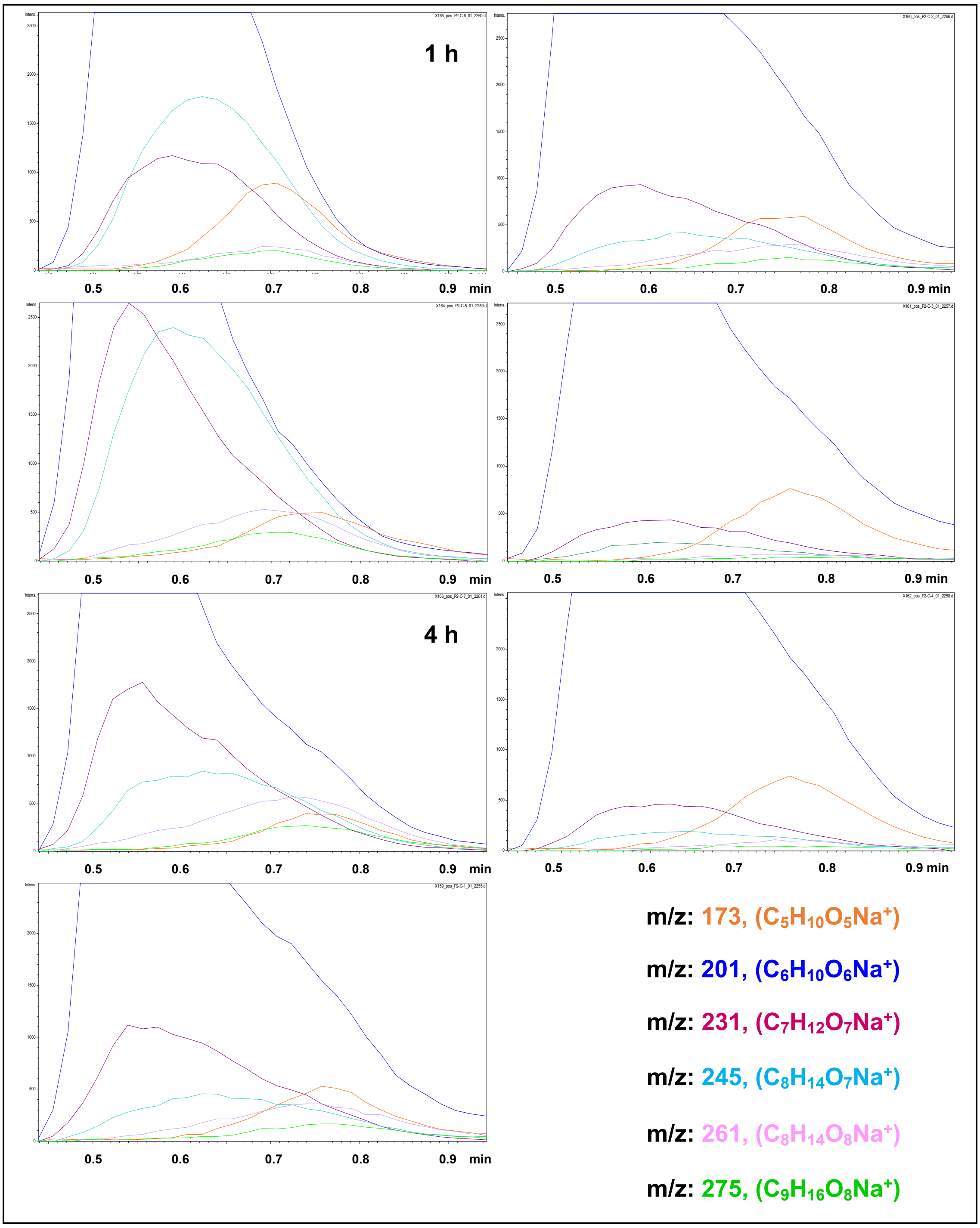


Figure S8. The ion extracted chromatograms of LCMS of the reaction mixture with D-glucose as the substrate at different reaction times (partially shown from Figure S7). Ion chromatograms are shown in different colors. $C_5H_{10}O_5Na^+$ represents D-arabinose. Reaction conditions: D-glucose, 0.1 g; $NaVO_3$, 0.35 wt%; H_2SO_4, 1 wt%; H_2O, 6 cm^3; initial O_2: 3 MPa; temperature, 100 ^oC.

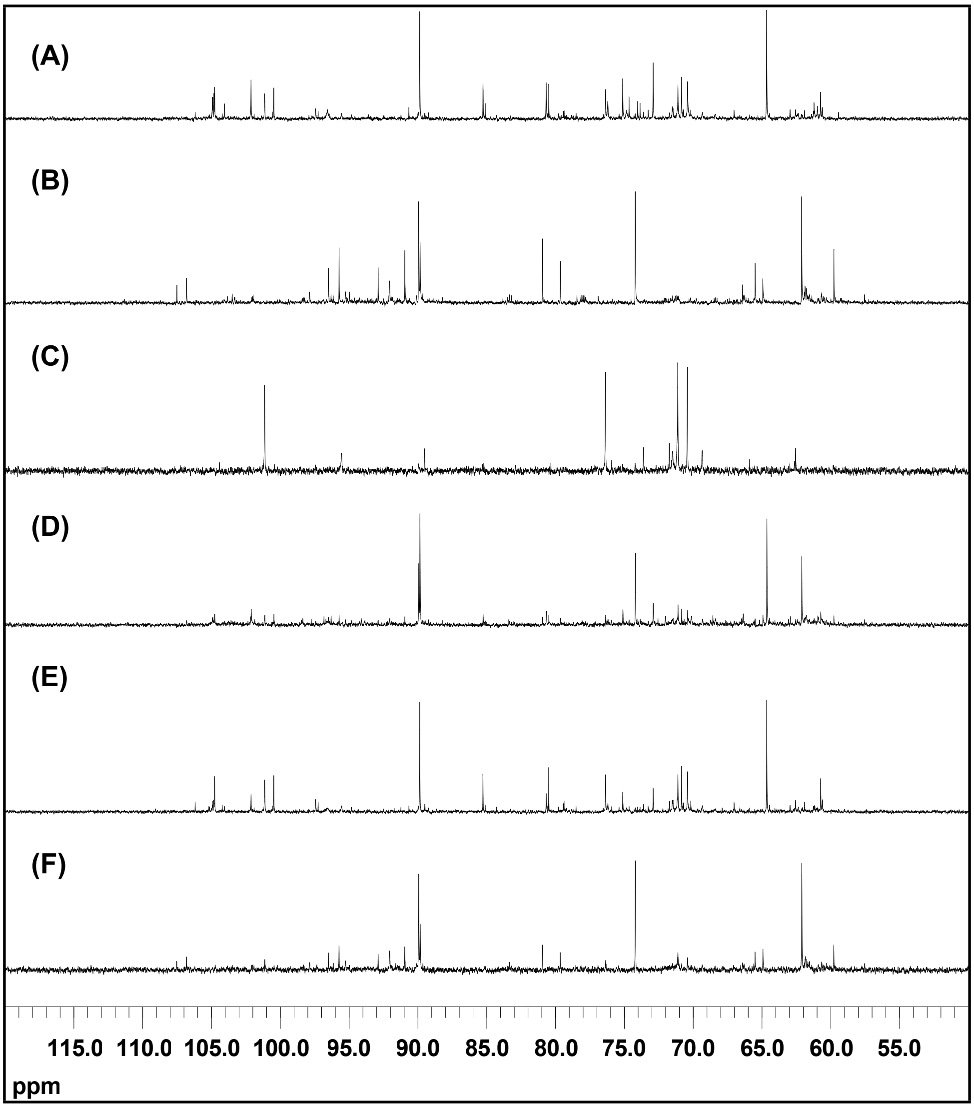


Figure S9. The ^{13}C NMR spectra of the reaction mixture with (A) glycolaldehyde (0.05 g), (B) D-glyceraldehyde (0.05 g), (C) D-erythrose (0.05 g), (D) glycolaldehyde (0.025 g) + D-glyceraldehyde (0.025 g), (E) glycolaldehyde (0.025 g) + D-erythrose (0.025 g), (F) D-glyceraldehyde (0.05 g) + D-erythrose (0.025 g) in H_2SO_4 aqueous solution with no $NaVO_3$ or O_2 (replaced by N_2 with the same initial pressure). (B), (D) and (F) contain signals in the regions of 15 ~ 25 ppm and in 209 ppm (not shown), which possibly refer to dehydration products of D-glyceraldehyde. Reaction conditions: H_2SO_4, 1 wt%; H_2O, 6 cm^3; initial N_2: 3 MPa; temperature, 100 ^{o}C, reaction time, 2 h.

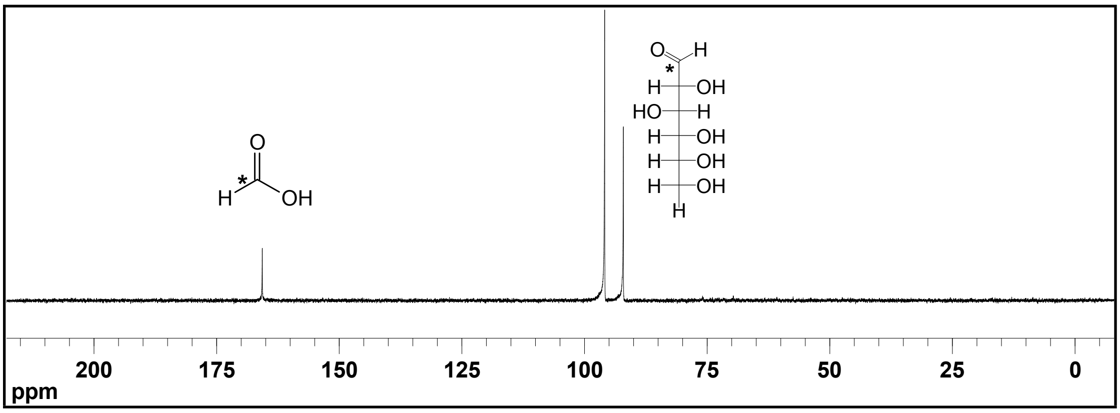


Figure S10. ^{13}C NMR spectra of the reaction mixture with D-glucose-1-^{13}C as the substrate with the absence of O_2. Reaction conditions: D-glucose-1-^{13}C, 0.005 g; $NaVO_3$, 0.2 wt%; D_2SO_4, 1 wt%; D_2O, 0.5 cm^3; initial N_2: 3 MPa; temperature, 100 ^{o}C; reaction time, 1 h.

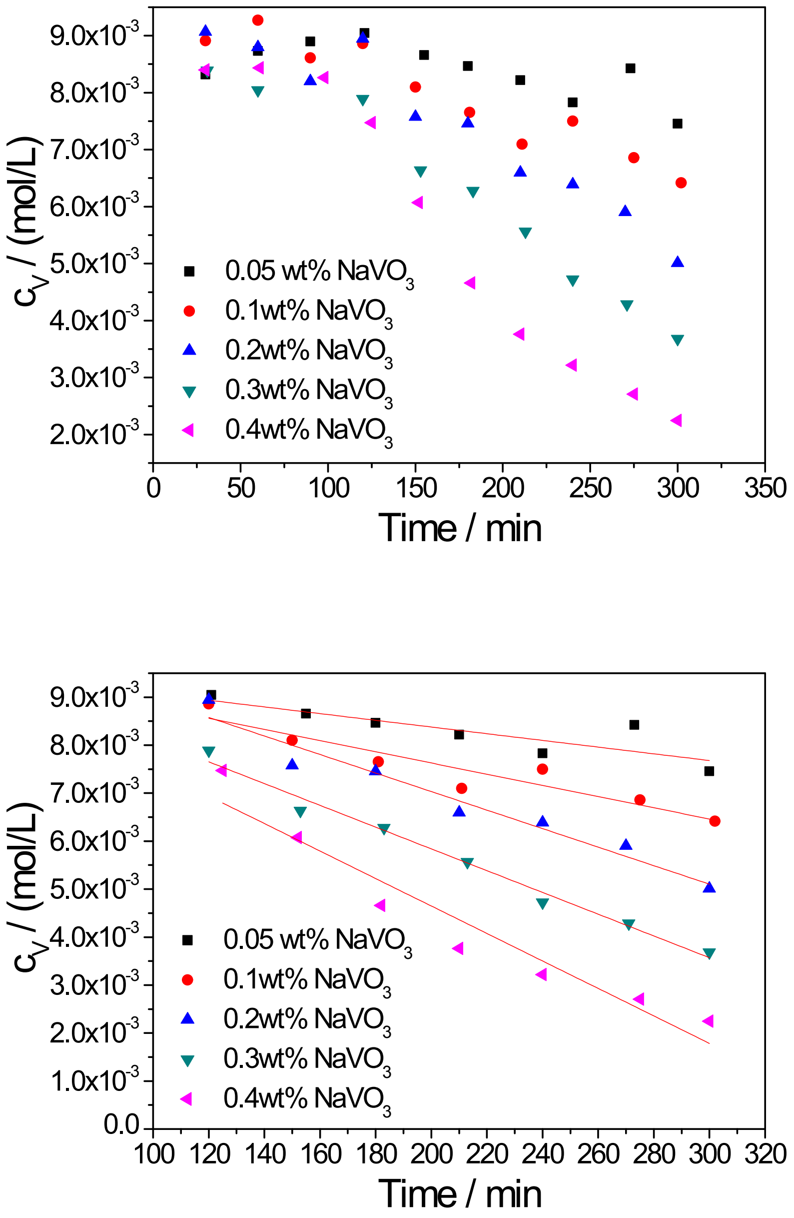
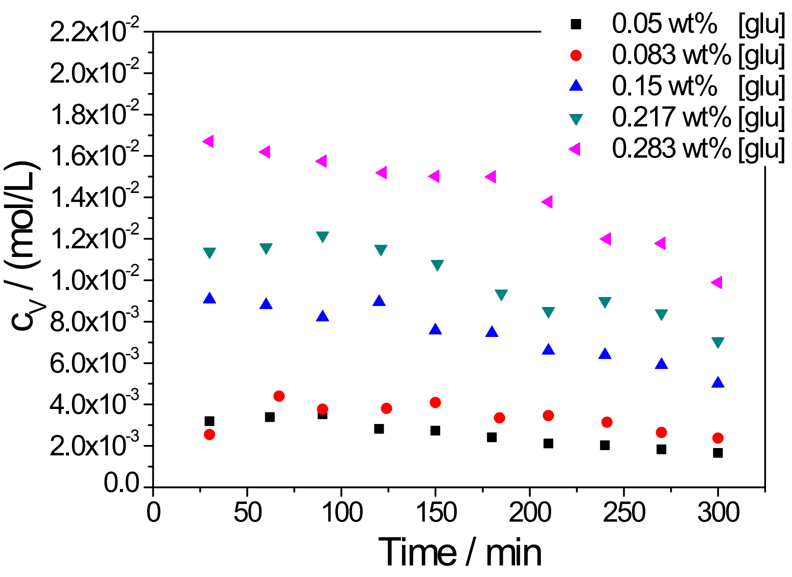


Figure S11. Time course data for D-glucose conversion in NaVO$_3$-H$_2$SO$_4$ aqueous solution with O$_2$ with varying NaVO$_3$ concentrations. Reaction conditions: D-glucose, 0.045 g; H$_2$SO$_4$, 1 wt%; H$_2$O, 30 cm^3; initial O$_2$: 3 MPa; temperature, 100 ^{o}C. The initial rate in Figure 11A was obtained from the slope of the linear fit to the timepoints (120 ~ 300 min).



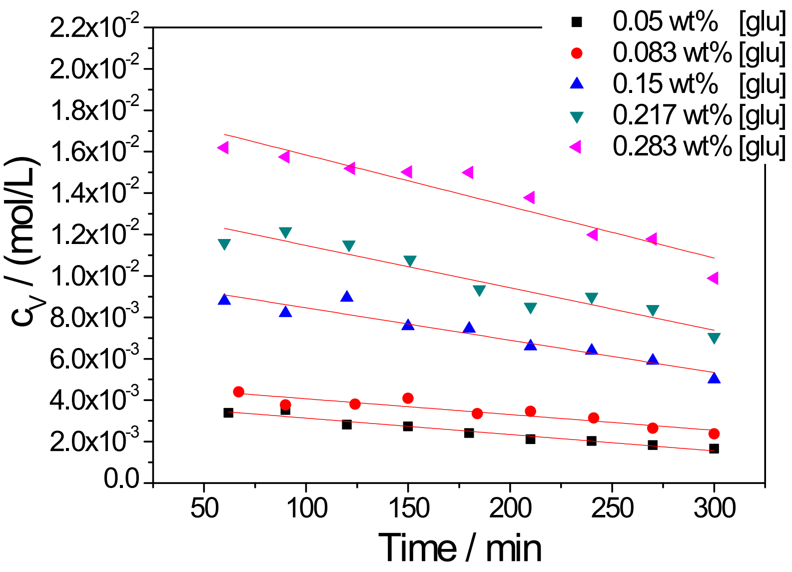


Figure S12. Time course data for D-glucose conversion in $NaVO_3$-H_2SO_4 aqueous solution with O_2 with varying D-glucose concentrations. Reaction conditions: $NaVO_3$, 0.2 wt%; H_2SO_4, 1 wt%; H_2O, 30 cm^3; initial O_2: 3 MPa; temperature, 100 ^oC. The initial rate in Figure 11B was obtained from the slope of the linear fit to the timepoints (60 ~ 300 min).