Electronic Supplemental Information

Intramolecular Dehydration of Mannitol in High-Temperature Liquid Water without Acid Catalysts

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Experimental section

D-sorbitol and D-mannitol were purchased from Wako Pure Chemical Industries, Ltd. and used without any further purification.

The dehydration of sugar alcohols was carried out in a batch reactor (inner volume: 6 cm^3) made of a SUS316 1/2 OD tube.[9d,10] Sugar alcohol aqueous solution (3 cm^3) was loaded in the reactor, and then it was purged with argon gas to remove air. The reactor was submerged into a molten-salt bath at a desired reaction temperature for a given reaction time and then submerged into a water bath for cooling to ambient temperature quickly after the reaction. A mixture of the reactant and liquid products was taken out from the reactor with distilled water and separated from solid products by filtration.

The quantitative analysis of the unreacted reactant and liquid products was conducted by a high-performance liquid chromatography (Shimadzu, HPLC) with a refractive index detector (Shimadzu, RID-10A) and a UV-Vis detector (Shimadzu, SPD-20AV) equipped with SUGAR SC1211 column (Shodex). The products were identified by comparing with the retention times of the standard materials: 1,4-anhydro-D-sorbitol (1,4-AHSO, Tronto Research Chemicals Inc.), 1,5-anhydro-D-sorbitol (1,5-AHSO, Carbosynth Ltd.), 2,5-anhydro-D-sorbitol (2,5-AHSO, Tronto Research

Chemicals Inc.), 1,4-3,6-dianhydro-D-sorbitol (isosorbide, Alfa Aesar), 1,4-anhydro-D-mannitol (1,4-AHMA, Carbosynth Ltd.), 1,5-anhydro-D-mannitol (1,5-AHMA, Carbosynth Ltd.), 2,5-anhydro-D-mannitol (2,5-AHMA, Carbosynth Ltd.), and 1,4-3,6-dianhydro-D-mannitol (isomannide, Tokyo Chemical Industries Co., Ltd.). The other possible trace product 3,6-anhydro-D-sorbitol (3,6-AHSO) and 2,6-anhydro-D-sorbitol (2,6-AHMA) could not be identified in this manuscript.

Rate equations of mannitol dehydration with the kinetic parameters in Scheme 1

$$\frac{d[\text{Mannitol}]}{dt} = -k_{1\text{M}}[\text{Mannitol}] - k_{2\text{M}}[\text{Mannitol}] - k_{3\text{M}}[\text{Mannitol}] - k_{6\text{M}}[\text{Mannitol}] \quad (1)$$

$$\frac{d[\text{1,4 - AHMA}]}{dt} = k_{1\text{M}}[\text{Mannitol}] - k_{4\text{M}}[\text{1,4 - AHMA}] \quad (2)$$

$$\frac{d[\text{2,5 - AHMA}]}{dt} = k_{2\text{M}}[\text{Mannitol}] \quad (3)$$

$$\frac{d[\text{1,5 - AHMA}]}{dt} = k_{3\text{M}}[\text{Mannitol}] \quad (4)$$

$$\frac{d[\text{Isomannide}]}{dt} = k_{4\text{M}}[\text{1,4 - AHMA}] - k_{5\text{M}}[\text{Isomannide}] \quad (5)$$

$$[\text{Mannitol}] = [\text{Mannitol}]_{\text{i}} \exp\{(-k_{1\text{M}} - k_{2\text{M}} - k_{3\text{M}} - k_{6\text{M}})t\} \quad (6)$$

$$[\text{1,4 - AHMA}] = \frac{k_{1\text{M}}}{k_{4\text{M}} - k_{1\text{M}} - k_{2\text{M}} - k_{3\text{M}} - k_{6\text{M}}}[\text{Mannitol}]_{\text{i}} \left[\exp\{(-k_{1\text{M}} - k_{2\text{M}} - k_{3\text{M}} - k_{6\text{M}})t\} - \exp(-k_{4\text{M}}t)\right] \quad (7)$$

$$[\text{2,5 - AHMA}] = \frac{k_{2\text{M}}}{k_{1\text{M}} + k_{2\text{M}} + k_{3\text{M}} + k_{6\text{M}}}[\text{Mannitol}]_{\text{i}} \left[1 - \exp\{(-k_{1\text{M}} - k_{2\text{M}} - k_{3\text{M}} - k_{6\text{M}})t\}\right] \quad (8)$$

$$[\text{1,5 - AHMA}] = \frac{k_{3\text{M}}}{k_{1\text{M}} + k_{2\text{M}} + k_{3\text{M}} + k_{6\text{M}}}[\text{Mannitol}]_{\text{i}} \left[1 - \exp\{(-k_{1\text{M}} - k_{2\text{M}} - k_{3\text{M}} - k_{6\text{M}})t\}\right] \quad (9)$$

$$[\text{Isomannide}] = \frac{k_{1\text{M}}k_{4\text{M}}}{k_{4\text{M}} - k_{1\text{M}} - k_{2\text{M}} - k_{3\text{M}} - k_{6\text{M}}}[\text{Mannitol}]_{\text{i}} \left[\frac{\exp\{(-k_{1\text{M}} - k_{2\text{M}} - k_{3\text{M}} - k_{6\text{M}})t\} - \exp(-k_{5\text{M}}t)}{k_{5\text{M}} - k_{1\text{M}} - k_{2\text{M}} - k_{3\text{M}} - k_{6\text{M}}} - \frac{\exp(-k_{4\text{M}}t) - \exp(-k_{5\text{M}}t)}{k_{5\text{M}} - k_{4\text{M}}}\right] \quad (10)$$

Rate equations of sorbitol dehydration with the kinetic parameters in Scheme 2

$$\frac{d[\text{Sorbitol}]}{dt} = -k_{1\text{S}}[\text{Sorbitol}] - k_{2\text{S}}[\text{Sorbitol}] - k_{3\text{S}}[\text{Sorbitol}] - k_{6\text{S}}[\text{Sorbitol}] \quad (11)$$

$$\frac{d[\text{1,4-AHSO}]}{dt} = k_{1\text{S}}[\text{Sorbitol}] - k_{4\text{S}}[\text{1,4-AHSO}] \quad (12)$$

$$\frac{d[\text{2,5-AHSO}]}{dt} = k_{2\text{S}}[\text{Sorbitol}] \quad (13)$$

$$\frac{d[\text{1,5-AHSO}]}{dt} = k_{3\text{S}}[\text{Sorbitol}] \quad (14)$$

$$\frac{d[\text{Isosorbide}]}{dt} = k_{4\text{S}}[\text{1,4-AHSO}] - k_{5\text{S}}[\text{Isosorbide}] \quad (15)$$

$$[\text{Sorbitol}] = [\text{Sorbitol}]_{\text{i}} \exp\{(-k_{1\text{S}} - k_{2\text{S}} - k_{3\text{S}} - k_{6\text{S}})t\} \quad (16)$$

$$[\text{1,4-AHSO}] = \frac{k_{1\text{S}}}{k_{4\text{S}} - k_{1\text{S}} - k_{2\text{S}} - k_{3\text{S}} - k_{6\text{S}}}[\text{Sorbitol}]_{\text{i}} \left[\exp\{(-k_{1\text{S}} - k_{2\text{S}} - k_{3\text{S}} - k_{6\text{S}})t\} - \exp(-k_{4\text{S}}t)\right] \quad (17)$$

$$[\text{2,5-AHSO}] = \frac{k_{2\text{S}}}{k_{1\text{S}} + k_{2\text{S}} + k_{3\text{S}} + k_{6\text{S}}}[\text{Sorbitol}]_{\text{i}} \left[1 - \exp\{(-k_{1\text{S}} - k_{2\text{S}} - k_{3\text{S}} - k_{6\text{S}})t\}\right] \quad (18)$$

$$[\text{1,5-AHSO}] = \frac{k_{3\text{S}}}{k_{1\text{S}} + k_{2\text{S}} + k_{3\text{S}} + k_{6\text{S}}}[\text{Sorbitol}]_{\text{i}} \left[1 - \exp\{(-k_{1\text{S}} - k_{2\text{S}} - k_{3\text{S}} - k_{6\text{S}})t\}\right] \quad (19)$$

$$[\text{Isosorbide}] = \frac{k_{1\text{S}}k_{4\text{S}}}{k_{4\text{S}} - k_{1\text{S}} - k_{2\text{S}} - k_{3\text{S}} - k_{6\text{S}}}[\text{Sorbitol}]_{\text{i}} \left[\frac{\exp\{(-k_{1\text{S}} - k_{2\text{S}} - k_{3\text{S}} - k_{6\text{S}})t\} - \exp(-k_{5\text{S}}t)}{k_{5\text{S}} - k_{1\text{S}} - k_{2\text{S}} - k_{3\text{S}} - k_{6\text{S}}} - \frac{\exp(-k_{4\text{S}}t) - \exp(-k_{5\text{S}}t)}{k_{5\text{S}} - k_{4\text{S}}}\right] \quad (20)$$

Table S1 Kinetic parameters for dehydration reactions of mannitol and sorbitol

Reaction temperature (K)	523	548	560	573
$\frac{k_{2M}}{k_{1M}+k_{2M}+k_{3M}+k_{6M}}$	0.44	0.42	0.41	0.37
$\frac{k_{3M}}{k_{1M}+k_{2M}+k_{3M}+k_{6M}}$	0.068	0.054	0.050	0.040
$\frac{k_{2S}}{k_{1S}+k_{2S}+k_{3S}+k_{6S}}$	0.091	0.14	0.15	0.19
$\frac{k_{3S}}{k_{1S}+k_{2S}+k_{3S}+k_{6S}}$	0	0	0	0

Table S2 Kinetic parameters for dehydration reactions of sorbitol (initial sorbitol concentration: 1.0 mol dm^{-3})

T^a (K)	523	548	560	573	Activation energy (kJ mol^{-1})
k_{1S} (mol h^{-1})	0.13[b]	0.65[b]	1.2[b]	1.4[b]	127[b]
k_{2S} (mol h^{-1})	0.013[b]	0.11[b]	0.22[b]	0.32[b]	166[b]
k_{4S} (mol h^{-1})	0.016[b]	0.18[b]	0.36[b]	0.78[b]	195[b]
k_{5S} (mol h^{-1})	0.0083[b]	0.041[b]	0.098[b]	0.11[b]	136[b]

[a] Reaction temperature, [b] The values were reported in Ref 10.

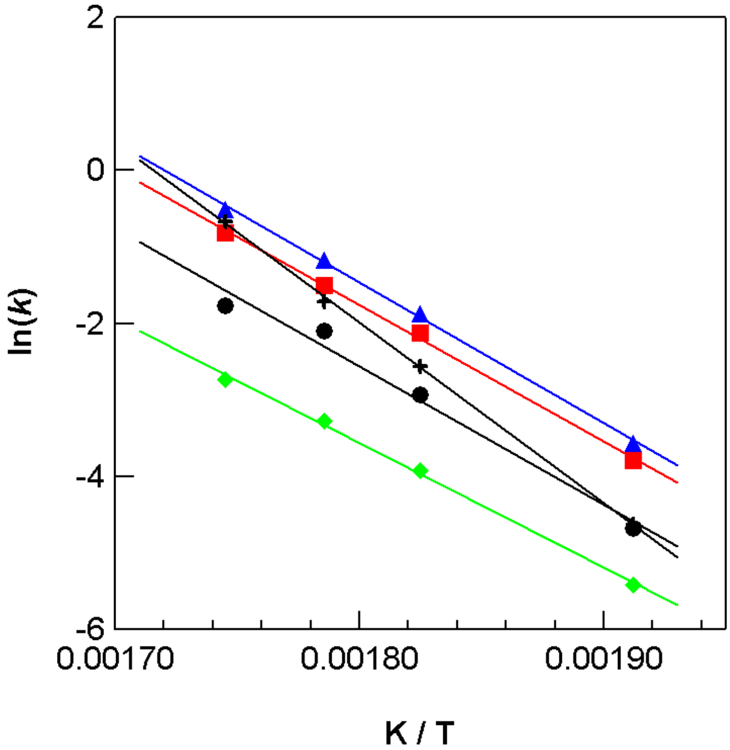
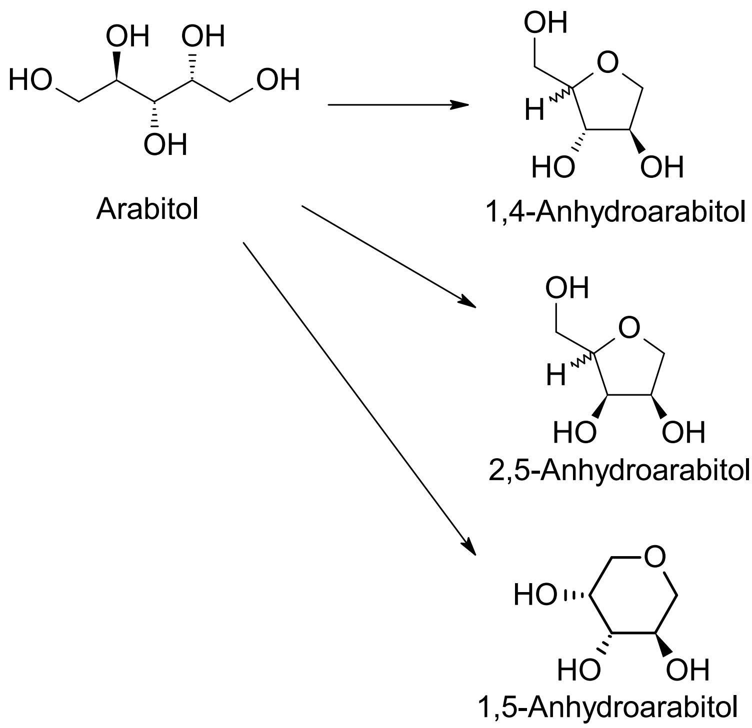


Fig. S1 Arrhenius plots of the rate constants (k_{1M} (■), k_{2M} (▲), k_{3M} (◆), k_{4M} (●), and k_{6M} (+) in Scheme 1) for the mannitol dehydration in high-temperature liquid water.



Scheme S1 The reaction pathway of arabitol dehydration

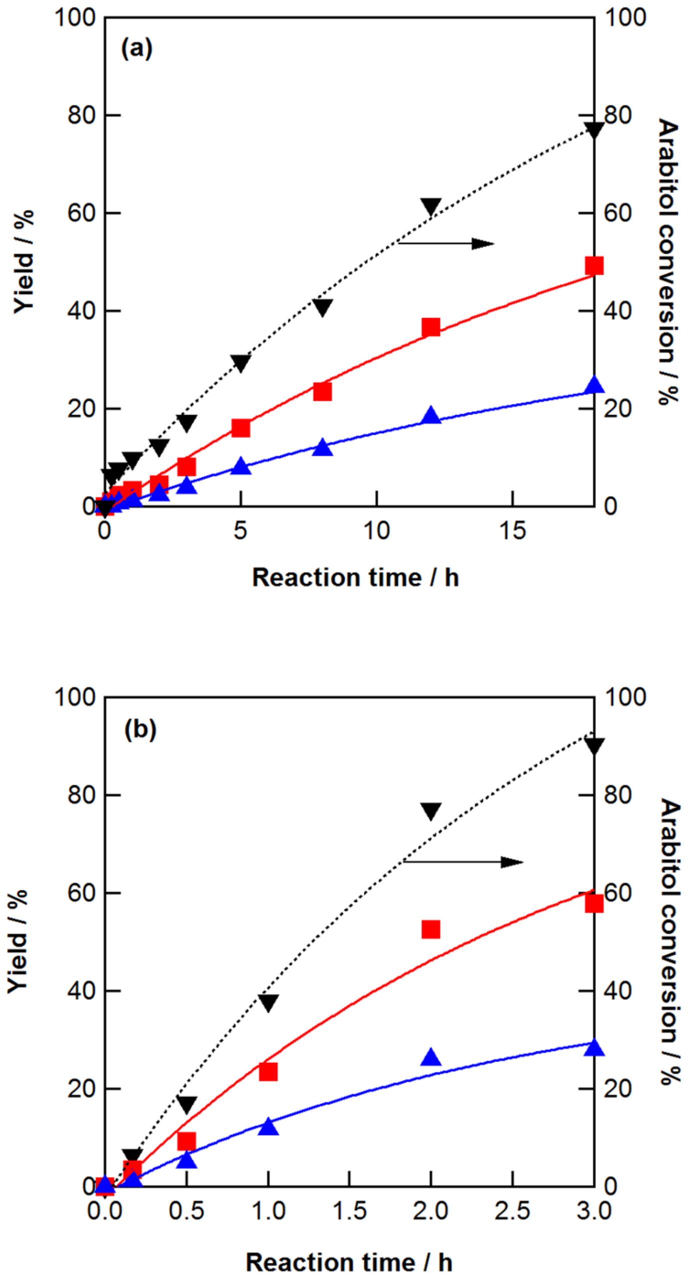


Fig. S2 Yields of 1,4-anhydroarabitol (■), 2,5-anhydroarabitol (▲) , and arabitol conversion (▼), as a function of elapsed time for arabitol dehydration reactions at (a) 548 and (b) 573 K in water (initial arabitol concentration: 0.5 mol dm^{-3})