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Reconsidering the activation entropy for anomerization of glucose and mannose in water studied by NMR spectroscopy

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HIGHLIGHTS

- We reexamine the thermodynamic parameters of the anomerization for glucose and mannose.
- NMR spectroscopy enable us to estimate the population of the both epimers in D_2O.
- The contribution of $\Delta S^{\ddagger}$ to $G^{\ddagger}$ for glucose in water is clearly different for glucose and mannose.
- It is suggested that the anomerization pathway is not the same for glucose and mannose.

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ABSTRACT

The anomerization of monosaccharides is a very important process to understand how their stereoisomers are stabilized in aqueous solutions. For glucose and mannose, it has been known that α- and β-anomers of hexopyranose exist as the major components. In order to examine the anomerization pathway for glucose and mannose in aqueous solutions, it is indispensable to determine the thermodynamic parameters such as the activation energy, the activation Gibbs free energy ($\Delta G^{\ddagger}$), enthalpy ($\Delta H^{\ddagger}$), and entropy ($\Delta S^{\ddagger}$). Although several research groups reported these quantities in aqueous solution, they have still been controversial especially for $\Delta S^{\ddagger}$. In this paper, we employ ^{1}H NMR spectroscopy for monitoring the population of both α- and β-anomers of glucose and mannose. The contribution of $\Delta S^{\ddagger}$ to $\Delta G^{\ddagger}$ for glucose in water is estimated to be ca. 30%, while that for mannose is 8.0%. The large difference in $\Delta S^{\ddagger}$ suggests that the anomerization pathway is not the same for glucose and mannose.

Introduction

Saccharides and their derivatives are key compounds for life science. Saccharides play an important role not only in nucleic acids as the skeletal backbone, but also in tissues and organs as the osmolytes and cryoprotective agents [1]. In food sciences, polysaccharides are often used for controlling gelation processes. One of the most common, but important monosaccharide is glucose, which predominantly forms hexopyranose rings in aqueous solutions. Hexopyranose has two possible stereochemical isomers due to the position of OH group on the C1 carbon (see Fig. 1 for the chemical structures of glucose and mannose). These two isomers are called anomers. The stereostructure of the anomers is characterized by the orientation of the C1–O1 bond that can be axial (α) or equatorial (β) to the puckered six-membered ring [2].

Both the anomers can be found in biological systems. Glycogen and starch, which are made of α-D-glucose, are used for the energy resources of animals and plants. On the other hand, β-D-glucose is the monomer unit of cellulose that is a building block of plant cells and fiber. Human beings cannot digest cellulose, thus it is added to many kinds of diet foods as bulk. Living things properly use α- or β-D-glucose in accordance with the situation. Therefore, the anomerization of glucose in water had attracted keen interests of biochemists and life scientists.

It has been considered that in gas phase the α-anomer of glucose becomes stable as a result of the so-called "anomeric effect", which is often denoted when organic chemists explain the stability of stereoisomers after the substitution of the functional groups on the hexopyranose ring. In fact, a quantum chemical calculation revealed that the formation of α-D-glucose is energetically favorable in vacuo [3]. On the other hand, it was experimentally reported that β-D-glucose becomes more stable in aqueous media [4]. The increase in the stability of the β-anomer in water is considered as an important result of hydration effects on the

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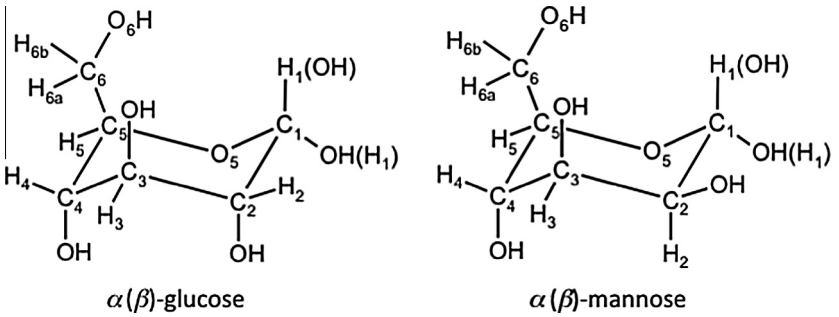

Fig. 1. The chemical structures of glucose and mannose.

anomerization. Karabulut and Leszczynski suggested by the use of quantum chemical calculation that the interaction between the water and the lone pairs of the anomeric oxygen atom in β-D-glucose is stronger than that for α-anomer because of the steric hindrance [3].

The anomerization of glucose in water occurs within a couple of hours [5–10]. This suggests that the activation energy of the anomerization (E_a) for glucose in water is relatively low so that the reaction can be investigated by the use of a conventional spectroscopic method such as infrared spectroscopy and NMR. However, there are only a limited number of reports available for E_a of glucose. Nagata et al. have determined that E_a of glucose is 72 kJ mol^{-1} by using the mutarotase–glucose oxidase method (mutarotase-GOD method) [11,12]. It is of note that they estimated the value of E_a by monitoring only the concentration of β-D-glucose. Lee et al. have measured the thermodynamic constants of anomerization of glucose and mannose by the use of optical rotation (OR) spectroscopy and gas liquid chromatography (GLC) [14]. The population ratio of α- and β-D-glucose in water at equilibrium has been found to be 36:64, and the activation enthalpy for the anomerization, $\Delta H^{\ddagger}$, is 67.3 kJ mol^{-1}. For the GLC study on the anomerization, trimethylsilylation of the isomers is required before the measurement. Although the OR and GLC techniques can provide the activation entropy of the anomerization ($\Delta S^{\ddagger}$), the value has still been controversial, because these techniques are not sensitive to the absolute concentration of each anomer.

Several mechanisms of anomerization have been proposed based on the reaction energy experimentally estimated [10,13,15,16]. Two feasible pathways for the anomerization of glucose are illustrated in Fig. 2. One of them occurs in an acid aqueous solution through the formation of the free aldehyde form, aldose [10,13,15]. The other is the pathway through the carbocation intermediate [16]. In this scenario, a H_3O^+ ion in solution transfers a proton to the OH group attached to C1, and then the protonated OH (OH_2^+) is eliminated from the hexopyranose ring so that C1 forms carbocation.

In this study, we reexamine the reaction rate and the activation energy of the anomerization for two monosaccharides, glucose and mannose, by using NMR spectroscopy. The NMR spectroscopy is used for monitoring the population and conformation of anomers. The systematic studies on two different monosaccharides may give us a new insight into the anomerization process in water.

Experimental section

The α-glucose, β-glucose, and D-(+)-mannose were purchased from Sigma Aldrich and TCI and used without further purification. D_2O (Cambridge Isotope Laboratories Inc., 99.9%) was used as received. The concentration of monosaccharides in D_2O was 1 wt%. All NMR spectra were measured on JEOL ECA 500 MHz at a temperature from 10 to 40 °C.

Results and discussion

^{1}H NMR spectrum of α- and β- glucose in D_2O

Fig. 3 shows the ^{1}H NMR spectra of α- and β-glucose in D_2O at 25.0 °C. The ^{1}H NMR spectra of these two anomers are different from each other. The assignments of the ^{1}H NMR signals for glucose proposed by Roslund et al. [17] are summarized in Table 1. The chemical structures of glucose with the definition of

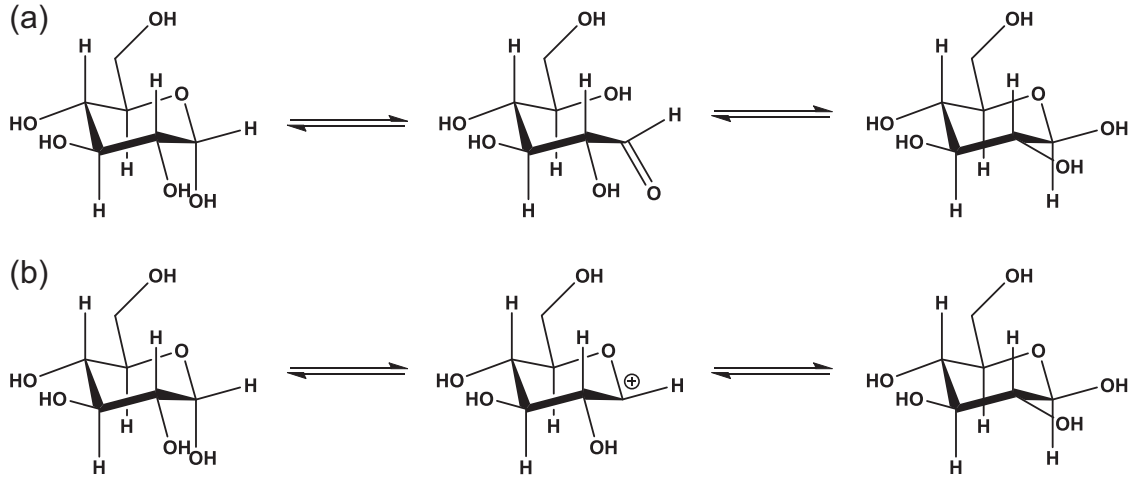

Fig. 2. Reaction pathways for the anomerization of glucose (a) through aldehyde intermediate and (b) through the carbocation intermediate.

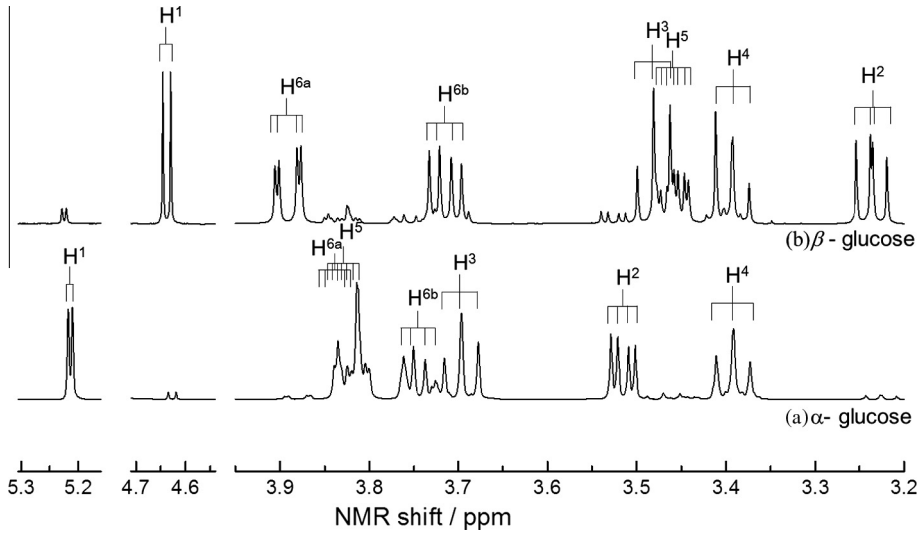

Fig. 3. ^{1}H NMR chart of (a) α-glucose and (b) β-glucose in D_2O.

Table 1
Chemical shift of the ^{1}H signals for α- and β-glucose.

Assignment	Chemical shift/ppm					
	α-glucose			β-glucose		
	Literature [16]	This study	Splitting	Literature [16]	This study	Splitting
H1	5.214	5.21	*d*	4.627	4.63	*d*
H2	3.516	3.52	*dd*	3.226	3.23	*dd*
H3	3.696	3.70	*dd*	3.469	3.46	*dd*
H4	3.393	3.39	*dd*	3.385	3.38	*dd*
H5	3.817	3.81	*ddd*	3.447	3.44	*ddd*
H6a	3.823	3.84	*dd*	3.879	3.89	*dd*
H6b	3.745	3.75	*dd*	3.704	3.70	*dd*

atoms are given in the left panel of Fig. 1. As shown in Table 1, the chemical shifts of the protons obtained here are in good agreement with the reported ones. By comparing the proton signals for α- and β-glucose, a large difference in the chemical shift on H1, H2, H3, and H5 are found. These shifts should arise from the change in the magnetic shielding of each proton by the anomerization. On the contrary, the chemical shifts of H4 for both anomers are similar. This is expected because H4 is attached to the farthest carbon from C1, at which the anomerization occurs. It is worthy of note that the shifts in H6a and H6b arising from the anomerization are larger than that in H4, even though H6a and H6b are far from C1. This indicates that the hydrogen bonding of the hydroxyl (O6–H) group is affected by the anomerization and/or the orientation of the O6–H group in α- and β-glucose is different.

The glucose has several conformers concerned with the rotation of the C5–C6 and C6–O6 bonds. The rotamers due to the C6–O6 rotation may not be identified on the spectrum, because the rotation of the C6–O6 bond is generally faster than the proton relaxation time. On the other hand, it is possible to evaluate the C5–C6 rotamers by the use of Karplus equation if those conformers are stable enough. The vicinal coupling constant between H5 and H6b protons ($^3J_{H5H6b}$) is correlated with the dihedral angle of O5–C5–C6–O6 (ϕ) by the following Karplus-type equation [18].

$$J_{H5H6b} = 5.06 + 0.45\cos\phi - 0.90\cos 2\phi + 0.80\sin\phi + 4.65\sin 2\phi \quad (1)$$

The splitting of H5 and H6b signals are *ddd* and *dd*, respectively, which are caused by the vicinal and geminal couplings. As seen in Fig. 3, the coupling constants observed for H6b signals in α- and β-glucose are well-isolated from the others. Although the H5 signals of β-glucose overlap with H3, the coupling constant can be obtained with a reasonable precision because the relative intensities of the signals are obviously different. As a result, we determined the vicinal coupling constant for β-glucose as $^3J_{H5H6b}$ = 5.7 Hz, indicating that the dihedral angle of O5–C5–C6–O6 (ϕ) for β-glucose estimated by Eq. (1) is one of the following: ca. 6°, 93°, 167°, or 93°. Note that ϕ = 6° is not realistic according to the torsional potential energy profile reported in Ref. [18].

For α-glucose, $^3J_{H5H6b}$ = 5.4 Hz is obtained, indicating that ϕ of α-glucose is similar to that for β-glucose. It implies that the orientation of the O6–H group to hexopyranose ring between α- and β-glucose is not so different. Thus, the change in the chemical shifts of H6a and H6b due to the anomerization is possibly ascribed to the difference in the hydration state of O6–H group between α- and β-glucose.

^{1}H NMR spectrum of α- and β- mannose in D_2O

Fig. 4 shows the ^{1}H NMR spectra of α- and β-mannose in D_2O at 25.0 °C. The complete assignments of the ^{1}H signals for mannose are listed in Table 2 [19]. By comparing the chemical shifts between the two anomers of mannose, it is found that the differences for H1, H3, H4, and H5 are significant. On the contrary, the chemical shifts of H2 for both anomers are similar. As described in the previous section, these shifts should arise from the change in the magnetic shielding of each proton by the anomerization. However, the shifts in H2 and H4 of mannose are different from those for glucose. Interestingly, the H2 signal of mannose does not show a large shift with anomerization, even though the H2 is attached to the carbon next to C1.

If the magnetic shielding of the H2 proton is influenced not only by the through-bond effect but also by the through-space one, it is possible that the apparent insensitivity of the chemical shift is concerned with the fact that the H2 proton is axial to the hexopyranose ring. In this case, the chemical shift of H2 may be sensitive to the orientation of the hydroxyl group on C1. Indeed, the chemical shift of H2 for glucose is significantly different from that for mannose, implying the orientation of the H2 proton to the hexopyranose ring is crucial to determine the chemical shift. The shift in H4 by the anomerization is possibly explained by the 1,3-diaxial

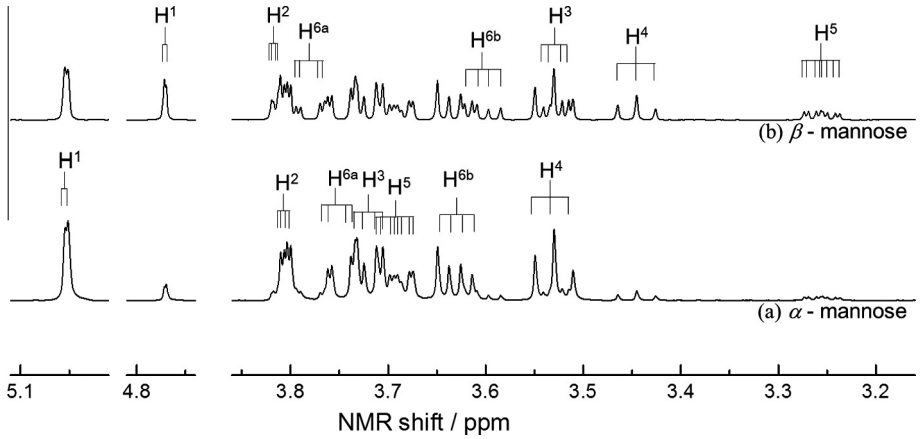

Fig. 4. ^{1}H NMR chart of (a) α-mannose and (b) β-mannose in D_2O.

Table 2
Chemical shift of the ^{1}H signals for α- and β-mannose.

Assignment	Chemical shift/ppm					
	α-mannose			β-mannose		
	Literature [18]	This study	Splitting	Literature [18]	This study	Splitting
H1	5.05	5.05	*d*	4.77	4.77	*d*
H2	3.79	3.80	*dd*	3.85	3.82	*dd*
H3	3.72	3.71	*dd*	3.53	3.53	*dd*
H4	3.52	3.52	*dd*	3.44	3.45	*dd*
H5	3.70	3.68	*ddd*	3.25	3.26	*ddd*
H6a	3.74	3.74	*dd*	3.74	3.78	*dd*
H6b	3.63	3.62	*dd*	3.60	3.60	*dd*

interaction between H2 and H4. That is, the orientational change in the C2–H2 may affect the chemical shift of H4.

In order to investigate the C5–C6 rotamers of α- and β-mannose, the coupling constant between H5 and H6b for mannose has to be determined. The peaks of H5 and H6b split into *ddd* and *dd*, respectively. The coupling constant between H5 and H6b for both the anomers is obtained from the ^{1}H NMR spectra shown in Fig. 4. The value of J_{H5H6b} is 5.9 Hz, indicating that the O5–C5–C6–O6 dihedral angle is one of the following: ca. 8°, 95°, 165°, or 96°. Again, the calculation result [18] implies that $\phi = 8°$ is unrealistic. Note that the quantity of $^3J_{H5H6a}$ is 1.9 Hz in consistency with the $^3J_{H5H6b}$ quantity. For β-mannose, $^3J_{H5H6b}$ of 6.3 Hz is obtained. Although these values are not so far from those observed for α-mannose, it is suggested that the O5–C5–C6–O6 dihedral angle of α-mannose is slightly larger than that of β-mannose.

Thermodynamic parameters of the anomerization for glucose and mannose

The difference in the standard Gibbs energy of the anomerization from α- to β-anomer $\Delta_r G_{\alpha\to\beta}$ can be calculated from the equilibrium constant $K = [\beta]/[\alpha]$ by using the following equation.

$$[\beta]/[\alpha] = \exp(-\Delta_r G_{\alpha\to\beta}/kT) \quad (2)$$

where k is the Boltzmann constant, T is the absolute temperature, $[\alpha]$ is the mol fraction of the α-anomer at the equilibrium, and $[\beta]$ is that for the β-anomer. As a result, $\Delta_r G_{\alpha\to\beta} = -1.3$ kJ mol^{-1} is obtained for glucose, suggesting that the β-glucose is more stable in the aqueous solution. The $\Delta_r G_{\alpha\to\beta}$ quantity obtained here is in good agreement with that previously reported by the use of GLC and OR [14]. On the other hand, $\Delta_r G_{\alpha\to\beta}$ of 1.8 kJ mol^1 for mannose indicates that the α-anomer is more stable in aqueous solution, which is also consistent with the value of 1.84–2.01 kJ mol^{-1} determined by GLC and OR [14]. Quantum chemical calculations have suggested that in the gas phase the α-anomer of both glucose and mannose is more stable than the β-anomer, in which the O–H groups forms the intramolecular hydrogen-bond [20]. In water, the OH groups of glucose and mannose may change their orientations because of the hydration, implying that the stability of β-glucose is owing to the hydration. The hydration effects on the stability of the anomers may be different for glucose and mannose.

The ^{1}H NMR spectra of α- and β-glucose show the time-dependent changes caused by anomerization. To monitor the population of both monomers, we chose the H1 proton of α-glucose and H2 of β-glucose, because they are well isolated from the other proton signals as shown in Fig. 3. Note that the H1 proton signal of β-glucose is not used, because the peak is located at the lower slope of the proton signal of the residual H_2O. Fig. 5(A) shows the time-dependent change in the mole fraction of the α-glucose $x_{\alpha-g}(t)$ during the anomerization starting from the α-anomer. The value of $x_{\alpha-g}(t)$ monotonically decreases as a function of time. Fig. 5(B) represents the time-dependent change in the mole fraction of the β-glucose $x_{\beta-g}(t)$ during the anomerization starting from the β-anomer, and a monotonic decrement is also found. The decrement of $x_{\alpha-g}(t)$ and $x_{\beta-g}(t)$ becomes steep when the temperature increases as shown in Fig. 5, indicating that the reaction rate gets high. The reaction rate constant, k, can be evaluated by the least square fitting with using the following single exponential equation,

$$x(t) = (x_0 - x_{eq})\exp(-kt) + x_{eq} \quad (3)$$

where x_0 is the initial mol fraction of anomer and x_{eq} is the mole fraction at equilibrium. In the anomerization process of mannose, we used the integral intensity of the H1 proton of α-mannose and that of H5 of β-mannose to monitor the population change. The time-dependent change in the mole fraction of the α-mannose $x_{\alpha-m}(t)$ is recorded at a different temperature as shown in Fig. 6. All the time profiles can also be fitted by Eq. (3) and the quantities of k are determined.

In order to estimate thermodynamic properties, we employ the Arrhenius and Eyring plots. Since the reaction rate is possibly affected by surrounding aqueous media, we must consider that the parameters determined here may contain the influence from the hydration of compounds. At the same time, however, we can also expect that the hydration state of compounds does not significantly change because of the temperature range. First, the activation energy of anomerization (E_a) for glucose and mannose is estimated by the Arrhenius Plots. As shown in Fig. 7(A), a linear relationship between $\ln(k)$ and $1/T$ fits quite well for both

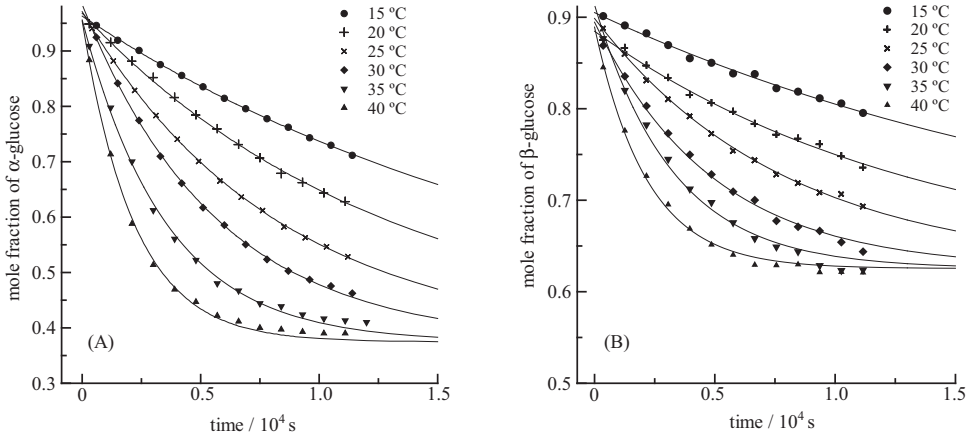

Fig. 5. (A) Time dependent changes in the mole fraction of α-glucose during the anomerization from α- to β-anomer, and (B) that of β-glucose during the anomerization from β- to α-anomer.

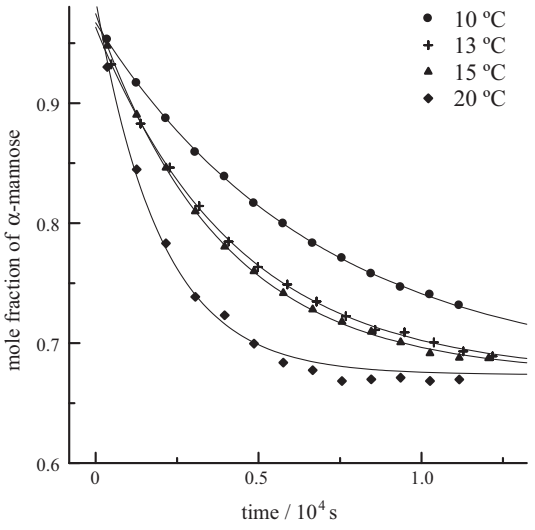

Fig. 6. Time dependent changes in the mole fraction of α-mannose in the anomerization from α- to β-anomer.

monosaccharides. As a result, E_a of glucose is determined to be 69.3 kJ mol^{-1} for anomerization from α- to β-anomer, and the E_a of glucose from β to α is 70.9 kJ mol^{-1}. The 1.6 kJ mol^{-1} difference of E_a is in good agreement with $\Delta_r G_{\alpha\rightarrow\beta}$ of −1.3 kJ mol^{-1}. For mannose, E_a from α- to β-anomer is estimated to be 83.4 kJ mol^{-1}. The quantity of E_a from α- to β-anomer for mannose is larger by ca. 12 kJ mol^{-1} than that of glucose. The tendency is in good agreement the result reported previously [14].

The temperature-dependence of k obtained here can also be analyzed by means of the Eyring plots. By plotting $\ln(k/T)$ as a function of $1/T$, we evaluate the activation enthalpy ($\Delta H^{\ddagger}$), the activation entropy ($\Delta S^{\ddagger}$), and the activation Gibbs energy ($\Delta G^{\ddagger}$). The obtained values are listed in Table 3. For glucose the value of $\Delta H^{\ddagger}$ from α- to β-anomer is estimated to be 65.2 kJ mol^{-1} (68.3 kJ mol^{-1} from β to α), while for mannose $\Delta H^{\ddagger}$ from α to β is 81.0 kJ mol^{-1}. The difference in the $\Delta H^{\ddagger}$ values between glucose and mannose suggests that the recombination energies of the chemical bonds concerned with the anomerization of the two monosaccharides is different. The recombination may occur around the O5C1 bond when the reaction passes through the aldehyde intermediate, whereas if the reaction pathway is related to the carbocation intermediate the C1O1 bond is recombined. Although the $\Delta G^{\ddagger}$ values for both monosaccharides are similar to those reported previously [14], $\Delta S^{\ddagger}$ from α to β obtained here shows a large deviation from those. The $\Delta S^{\ddagger}$ of about

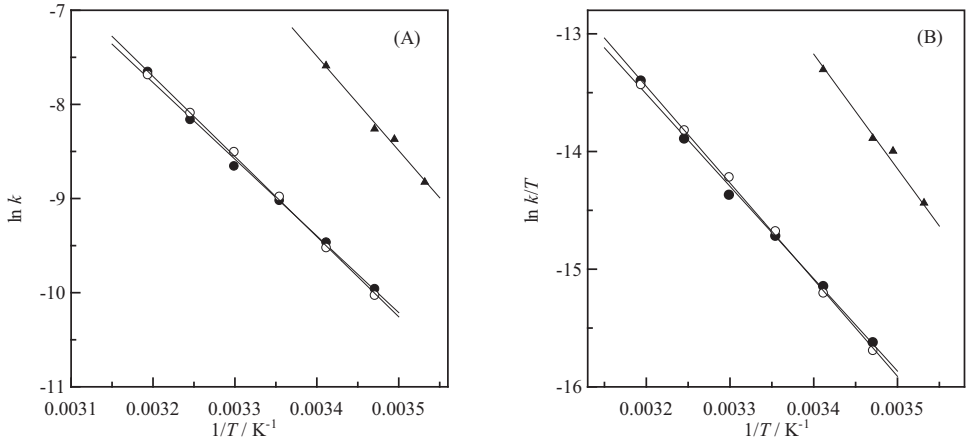

Fig. 7. (A) Arrhenius plots for anomerization (the filled circle: α- to β-glucose, the open circle: β- to α-glucose, and the filled triangle: α- to ββ- mannose) and (B) Eyring plots of anomerization (the filled circle: α- to β-glucose, the open circle: β- to α-glucose, and the filled triangle: α- to β-mannose).

Table 3
Thermodynamic parameters for anomerization of glucose and mannose.

	$\Delta G^{\ddagger}$/kJ mol^{-1}			$\Delta H^{\ddagger}$/kJ mol^{-1}			$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}		
	^{1}H NMR	GLC [14]	O.R. [14]	^{1}H NMR	GLC [14]	O.R. [14]	^{1}H NMR	GLC [14]	O.R. [14]
Glucose									
α to β	95.3 ± 2.5	92.51	92.38	65.2 ± 1.0			−101.1 ± 7.8	−56.48	−82.84
β to α	95.5 ± 2.6	95.31	95.31	68.3 ± 1.1			−90.8 ± 8.1	−71.55	−82.01
Mannose									
α to β	90.3 ± 1.3	91.59	91.71	81.0 ± 0.8			−24.8 ± 3.7	−68.99	−59.50
β to α		89.70	89.66					−65.52	−57.15

100 J K^{-1} mol^{-1} for glucose is larger than the reported one, while the $\Delta S^{\ddagger}$ of about 25 J K^{-1} mol^{-1} for mannose is much smaller.

Both monosaccharides show the similar $\Delta G^{\ddagger}$ at 298 K. However, the contribution of $\Delta S^{\ddagger}$ to $\Delta G^{\ddagger}$ is different from each other. The contribution of $\Delta S^{\ddagger}$ to $\Delta G^{\ddagger}$ at 298 K for glucose is ca. 30%, while that for mannose is only 8%. At the moment, we cannot explain how the difference in the configuration of the O–H group on C2 affects $\Delta S^{\ddagger}$ of anomerization. Anyway, the $\Delta S^{\ddagger}$ quantities imply that the reaction pathway of anomerization is different for glucose and mannose. In the case that the anomerization process passes through an aldehyde intermediate [10,13,15], the flexibility of the chain structures after the ring opening may contribute the quantity of $\Delta S^{\ddagger}$. If a carbocation process takes place in the anomerization [16], the conformational entropy of the ring is not likely different for glucose and mannose. In this case, the differences in $\Delta S^{\ddagger}$ is possibly owing to the hydration structure of the intermediates.

Conclusion

For glucose and mannose, we reexamined the thermodynamic parameters of the anomerization by the use of ^{1}H NMR spectra. The $\Delta S^{\ddagger}$ of about 100 J K^{-1} mol^{-1} for glucose is much larger than that for mannose, which is evaluated to be about 25 J K^{-1} mol^{-1}. These $\Delta S^{\ddagger}$ values are significantly deviated from the values found in the literatures. The contribution of $\Delta S^{\ddagger}$ to $\Delta G^{\ddagger}$ for glucose in water is estimated to be ca. 30%, while that for mannose is 8.0%. The large difference in $\Delta S^{\ddagger}$ suggests that the anomerization pathway is not the same for glucose and mannose.

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