



# 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<sub>2</sub>O.
- 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  $\alpha$ - and  $\beta$ -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 <sup>1</sup>H NMR spectroscopy for monitoring the population of both  $\alpha$ - and  $\beta$ -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.

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## 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 ( $\alpha$ ) or equatorial ( $\beta$ ) to the puckered six-membered ring [2].

Both the anomers can be found in biological systems. Glycogen and starch, which are made of  $\alpha$ -D-glucose, are used for the energy resources of animals and plants. On the other hand,  $\beta$ -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  $\alpha$ - or  $\beta$ -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  $\alpha$ -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  $\alpha$ -D-glucose is energetically favorable in vacuo [3]. On the other hand, it was experimentally reported that  $\beta$ -D-glucose becomes more stable in aqueous media [4]. The increase in the stability of the  $\beta$ -anomer in water is considered as an important result of hydration effects on the

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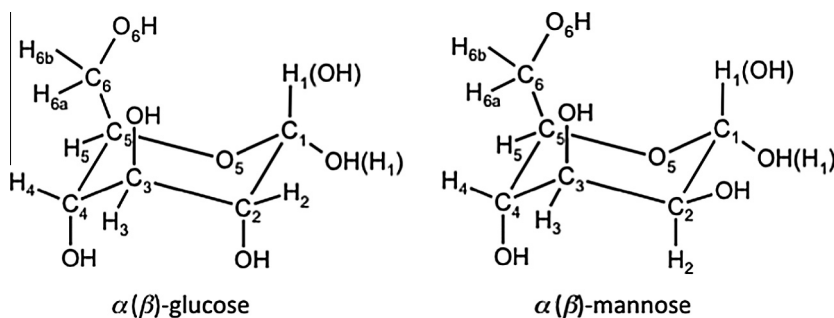


Fig. 1. The chemical structures of glucose and mannose.

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  $\beta$ -D-glucose is stronger than that for  $\alpha$ -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  $72 \text{ kJ mol}^{-1}$  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  $\beta$ -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  $\alpha$ - and  $\beta$ -D-glucose in water at equilibrium has been found to be 36:64, and the activation enthalpy for the anomerization,  $\Delta H^\ddagger$ , is  $67.3 \text{ kJ mol}^{-1}$ . 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  $\text{H}_3\text{O}^+$  ion in solution transfers a proton to the OH group attached to C1, and then the protonated OH ( $\text{OH}_2^+$ ) 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  $\alpha$ -glucose,  $\beta$ -glucose, and D-(+)-mannose were purchased from Sigma Aldrich and TCI and used without further purification.  $\text{D}_2\text{O}$  (Cambridge Isotope Laboratories Inc., 99.9%) was used as received. The concentration of monosaccharides in  $\text{D}_2\text{O}$  was 1 wt%. All NMR spectra were measured on JEOL ECA 500 MHz at a temperature from 10 to  $40^\circ\text{C}$ .

## Results and discussion

### $^1\text{H}$ NMR spectrum of $\alpha$ - and $\beta$ - glucose in $\text{D}_2\text{O}$

Fig. 3 shows the  $^1\text{H}$  NMR spectra of  $\alpha$ - and  $\beta$ -glucose in  $\text{D}_2\text{O}$  at  $25.0^\circ\text{C}$ . The  $^1\text{H}$  NMR spectra of these two anomers are different from each other. The assignments of the  $^1\text{H}$  NMR signals for glucose proposed by Roslund et al. [17] are summarized in Table 1. The chemical structures of glucose with the definition of

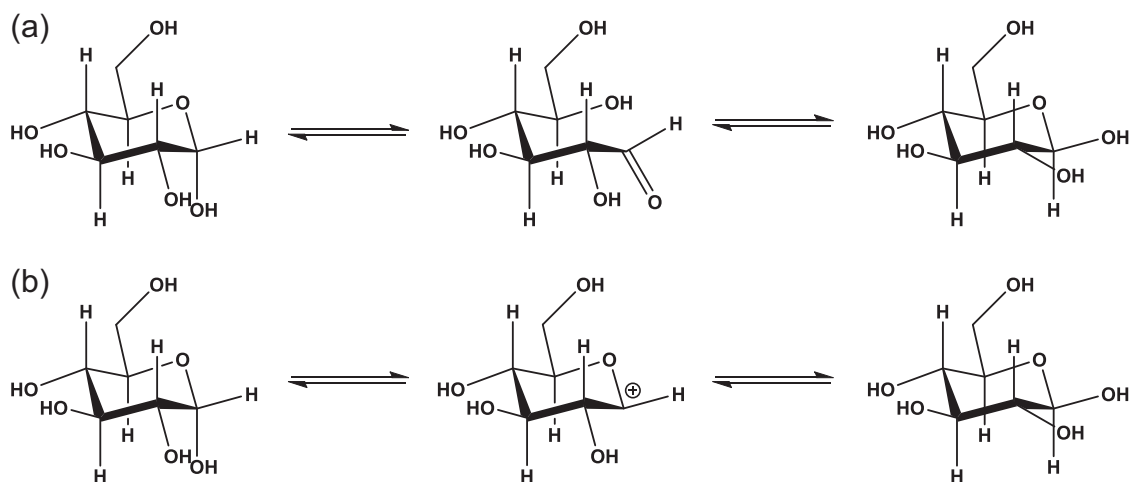


Fig. 2. Reaction pathways for the anomerization of glucose (a) through aldehyde intermediate and (b) through the carbocation intermediate.

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