

## Interaction of potassium fluoride with $\alpha$ -D-glucose

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### Abstract

Addition of KF to solutions of  $\alpha$ -D-glucose ( $\alpha$ DG) in DMSO- $d_6$  and D<sub>2</sub>O alters the <sup>1</sup>H NMR spectra, which is attributed to an interaction of the hydrogen atoms of the –OH groups with the basic F<sup>–</sup> anions of the salt. It is shown that K<sup>+</sup> cations do not interact with the oxygen atoms of the –OH groups of the  $\alpha$ DG. Mutarotation rates of  $\alpha$ DG in D<sub>2</sub>O in the presence of potassium halides and alkaline chlorides were measured from the integrated <sup>13</sup>C NMR signal of the anomeric protons. The mutarotation rates were higher with KF than other potassium halides. In order to shed light on the interactions of KF with the  $\alpha$ DG, the mutarotation of  $\alpha$ DG in the presence of KF and KOH were also studied using polarimetric measurements. At similar pH values, the effect of KF on the mutarotation rate is about five times that observed for KOH, indicating a major affinity for the F<sup>–</sup> anion by the anomeric proton as compared with OH<sup>–</sup>. The acceleration of the mutarotation process of  $\alpha$ DG is evidence for KF– $\alpha$ DG interactions, since NMR spectra of  $\beta$  conformer are also altered by the presence of KF. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Potassium fluoride (KF);  $\alpha$ -D-Glucose; Proton NMR; Mutarotation

### 1. Introduction

The interaction of metallic cations with carbohydrates is a subject of growing interest in recent years due to the importance of the complexes in chemistry [1–3] and biology [4–8]. Most of the work has been carried out in aqueous solutions. The models used for the analysis of the interaction are based in the structure of the sugars and the properties of the cations (charge, size, polarizability) with practically no reference to the role of the anions [9].

Recently, it has been reported on the interaction in the solid state of alkali fluorides with acidic substances where the stability of the acid fluoride anion, HF<sub>2</sub><sup>–</sup>, determines the course of the mechanochemical reactions [10]. A strong interaction is also observed between KF and D-xylose, both in solid state and from methanolic solutions, with formation of a KF–xylose complex [11]. According to IR and NMR spectra, the driving force of the complex formation is the interaction of F<sup>–</sup> with the –OH protons.

Mutarotation of all reducing sugars are catalyzed by acids and bases [12], with a same value of the mutarotation

constant for  $\alpha$ - and  $\beta$ -D-glucose over a wide temperature range, from 0 to 40°C [13]. Also, the reaction constant is independent of the concentration of sugar over a wide range. Later work revealed that catalysis of mutarotation is not an exclusive property of hydrogen and hydroxyl ions [13]. It has been reported [14] that the determination of the catalytic activity of anions of weak acids requires adjustment of the pH of the solution in order to keep the concentration of hydroxyl ion low, because the catalytic activity of the hydroxyl ions resulting from hydrolysis of the salt is so great that it masks the smaller catalytic effect of the anion. Evaluation of the catalytic activity of the hydroxyl ion is difficult, because the mutarotation becomes too rapid to allow an accurate measurement. Small variations in the hydroxyl ion concentration cause large differences in the reaction rates. It has been reported that the mutarotation process of  $\alpha$ DG follows kinetics of pseudo-first-order [13].

The aim of the present paper is to shed light on the nature of  $\alpha$ DG–KF interactions using NMR spectroscopy and polarimetric measurements. According to the obtained evidence, the main role is played by the F<sup>–</sup> ion and not by the K<sup>+</sup> ion. In order to discard the effect of the salt hydrolysis in the observed interactions, parallel polarimetric experiments were carried out adding KOH to the  $\alpha$ DG aqueous solution instead of KF.

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