

Study of the interaction of KF with carbohydrates in DMSO-d₆ by ¹H and ¹³C NMR spectroscopy

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Abstract

The interaction of KF with sugars (D-glucose, D-xylose, D-galactose, D-ribose, D-mannose, D-lyxose, cellobiose, maltose, maltotriose, amylose, saccharose and γ -cyclodextrin) were studied by ¹H and ¹³C NMR spectroscopies in DMSO-d₆. The main interactions are of the hydrogen bonding type between the sugar hydroxyl protons and the F[−] anions of KF. The shifts in mutarotation toward the β anomers are due to the breaking of the (OH)₁⋯(OH)₂ intramolecular hydrogen bonds by F[−], which destabilizes the α form in glucose, xylose, galactose and ribose. KF also attacks and breaks intermolecular hydrogen bond bridges as those observed between (OH)₂ and (OH)₃ groups of neighboring hexose units in amylose. © 2002 Published by Elsevier Science B.V.

Keywords: Potassium fluoride; Sugars; Mutarotation; Hydrogen bonding; ¹H and ¹³C NMR

1. Introduction

The interactions of sugars and salts is a field of active interest due to the role of carbohydrate-cation complexes in chemistry and biology [1–4]. The formation of the complexes is explained in terms of the interactions of the cations with the hydroxyl oxygens in the sugar [2,5]. The stability of the complexes increases with: (a) increase of the charge Zⁿ⁺ of the cation and the decrease of its ionic radii; (b) the configuration of the sugar, the most effective being that which has three vicinal OH groups in axial–equatorial–axial positions in pyranose rings.

The role of the anion has always been disregarded. We have recently studied the interactions of KF with D-glucose in DMSO-d₆ and found a large broadening of the ¹H hydroxyl signals and a large acceleration of the mutarotation of the α and β pyranose forms [6]. We have interpreted the D-glucose–KF interactions as due to the formation of strong hydrogen bonds between the hydroxyl protons and the fluoride anions. To test this hypothesis in other sugars we now present a study by ¹H and ¹³C NMR of 12 sugars in DMSO-d₆ solutions with KF. This solvent has been selected

since in it the mutarotation process is slow compared to the NMR time scale [7,8].

The effect of KF on the ¹H and ¹³C NMR spectra together with the calculation of the population of the molecular species α -pyranose (α p), β -pyranose (β p), α -furanose (α f) and β -furanose (β f) give clear evidence of the existence of the hydroxyl protons interactions with the F[−] anions, which leads to a destabilization of the α forms.

2. Experimental

The sugars employed were analytical grade reagents from Sigma, and the KF and the DMSO-d₆ (99.5% deuteration) were from Merck. The solvent came in sealed capsules of 1 ml and the dissolution of KF and sugars was done immediately after breaking the bulb, to minimize the adsorption of atmospheric water. The NMR experiments were run in a pulse Fourier Transform spectrometer Jeol Eclipse⁺ 270 operated at 270 MHz (¹H) and at 67.5 MHz (¹³C). All the experiments were run at 293 K.

The IR spectra of the sugar samples and of sugars milled with KF, KCl and KBr were run in a Fourier Transform spectrophotometer model Equinox (from Bruker) using the KBr pressed disks technique.

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