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Mechanism of the transition-metal-catalyzed mutarotation reaction of *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine in methanol☆

Kazimiera Smiataczowa, Jarosław Kosmalski, Teresa Widernik, Zygmunt Warnke*

Faculty of Chemistry, University of Gdańsk, Sobieskiego 18, PL-80-952 Gdańsk, Poland

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Abstract

Rate constants for the mutarotation reaction of *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine (NGlc) in methanol have been determined in the presence of transition metal chlorides (MCl_2), at 25 °C. The activity of the metal ions catalyzing the α-pyranoside↔β-pyranoside interconversion has been found to increase in the following series: $Mn^{2+} < Co^{2+} < Ni^{2+} < Zn^{2+} < Cu^{2+}$. The pHs of the methanolic solutions of the chlorides were measured and acidity constants of the $[MCl(CH_3OH)_5]^+$ ions and NGlc were determined in this solvent. Addition of NGlc to the salt solutions resulted in lowering their pH. Raising the methyloxonium ion concentration in the solutions resulted in rapid increase in the rate of mutarotation in the presence of MCl_2. It is suggested that in solutions of NGlc and MCl_2, the $CH_3OH_2^+$ ions are generated by solvolysis of the salts and additionally by dissociation of the hydroxyl group at C-6 of the glucosylamine molecule taking place during complexation of the metal ions. A scheme has been derived for interaction of deprotonated NGlc molecules with the transition metal ions.

Keywords: *N*-(*p*-Chlorophenyl)-β-D-glucopyranosylamine; Methanol; Metal chlorides

1. Introduction

The α-pyranoside↔β-pyranoside interconversion is a characteristic feature of glycopyranosylamines. The rate of attaining equilibrium of this reaction is strongly catalyzed by acids and proceeds through an acyclic immonium ion[1–3] intermediate as schematically shown in Scheme 1. In addition the rate of a weak-acid-catalyzed mutarotation reaction has been found to be affected by salts. Neutral salts, such as alkali metal chlorides enhance the reaction rate by virtue of the secondary salt effect.[4] Salts of weak acids, for instance, sodium benzoate, slow down the rate on account of the Law of Mass Action effect resulting in suppressing methyloxonium ion concentration in solution.[5,6] The influence of the transition metal salts on the mutarotation of glycosylamines has not been studied to date.

This type of interactions in the area of mutarotation of sugars has been surveyed by Mitzner and Behrendwald. They studied the kinetics of mutarotation of β-D-mannose in water in the presence of the cobalt(II) and copper(II)[7] and also iron(II), zinc(II) and manganese(II) ions.[8] Based on the results of further investigations, they derived the following rank order of catalytic activity of metal ions:[9] $Cu^{2+} > Zn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$. Moreover, they found that catalytic activity of $Ni(NO_3)_2$ in the mutarotation reaction depended on the nature of sugar.[10] They also found that the initial and final optical rotations of sugar solutions were identical in the presence and absence of a salt and did not depend on salt concentration, thus excluding the formation of stable complexes in solution. According to the authors, only labile transition products are formed whose composition was determined on the basis of a relationship between activation parameters and salt concentration. Generally, the results have shown that the metal ion is attached to the ring oxygen atom of the sugar molecule and to the oxygen of the $-CH_2OH$ group to form a five-membered ring.[10] The formation of compounds of this type apparently accelerates the mutarotation of monosaccharides and explains the en-

☆ The experiments were partly carried out by Katarzyna Maj and Anna Urbańczyk.

* Corresponding author. Fax: +48-58-3410357
E-mail address: warnke@chemik.univ.gda.pl (Z. Warnke).

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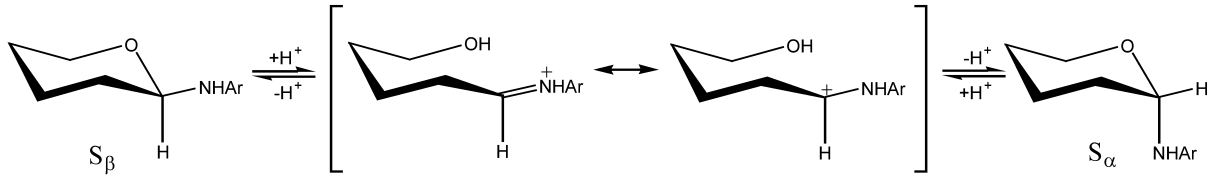


Scheme 1. Mechanism of anomerization of glycopyranosylamines.

hanced acidity of solutions, because it facilitates the release of proton from the anomeric –OH group responsible for the acidity of sugars.

The influence of transition metal ions on the mutarotation of α-D-glucose in water has also been investigated.[11,12] An extremely strong catalytic activity of copper(II) salts has been attributed to small amounts of binuclear $[Cu(OH)_2Cu]^{2+}$ ions present in the solutions. Just these ions, apart from the OH^- ones, have been recognized as the strongest catalysts of the mutarotation reaction of α-D-glucose.

All in all, the metal–sugar interactions in aqueous solutions are weak, because metal ions co-ordinate water molecules more strongly than alcoholic hydroxyls. Stability constants of the metal complexes of sugars are invariably small.[13,14] Stronger electron-donating properties are exhibited by sugars after deprotonation of the hydroxyl groups.[13,15,16] The associations of metal ions with sugars are freely soluble in water and it is difficult to obtain them in the solid state. Nonetheless, a number of sugar complexes with transition metal ions have recently been isolated from strongly alkaline solutions. Products precipitated from aqueous solutions after addition of methanol contained also the sodium and potassium ions.[15–17] Additional obstacles in studying metal–sugar interactions arise from the finding that in solutions of monosaccharides, different anomeric and conformational species occur at equilibrium. Further, sugar isomers, depending on the sequence of hydroxyl groups, can bind metal ions in different ways. Metal ions can co-ordinate one, two or even three sugar molecules.[13,14,18] The numerous hydroxyls can also form chelate-like structures. In more concentrated solutions also polynuclear species can emerge.[12,13]

The stability of complexes is considerably enhanced after substitution of a carboxyl, phosphate, amine and other groups to the sugar molecule. Extremely strong tendency towards complexation of diamines, in particular ethylenediamine, has been utilized to the synthesis of solid nickel(II) and cobalt(III) complexes in which glycosylamine products of condensation of diamines with monosaccharides were used as ligands. These products were characterized by crystallography.[19]

In continuation of our studies concerned with the influence of acids and salts on the rate of mutarotation of D-glucosylamines and bearing in mind the foregoing literature reports, we embarked on investigation of catalytic activity of selected transition metal chlorides. Further, the purpose of this contribution was to elucidate the mechanism of interaction of the transition metal ions with the molecule of glycosylamine during its mutarotation in methanol.

Table 1
Rate constants, k, of the mutarotation of a 0.02 M methanolic NGlc solution catalyzed with 3.3×10^{-6} M transition metal chlorides and rate constants, k_b, of this reaction determined in the benzoate buffer (2:1)

Compound	$pK_{a(H_2O)}$[22]	k (10^{-3} min^{-1})	k_b (10^{-3} min^{-1})
$CuCl_2$	7.29 [a]	41.3 ± 0.2	8.80 ± 0.15
$ZnCl_2$	8.96	9.73 ± 0.11	8.97 ± 0.17
$NiCl_2$	9.86	4.39 ± 0.06	9.07 ± 0.10
$CoCl_2$	10.00 [a]	3.93 ± 0.06	8.95 ± 0.16
$MnCl_2$	10.59	2.39 ± 0.02	8.90 ± 0.15
$[Cu(acac)_2]$		1.89 ± 0.04	
Methanol		1.78 ± 0.05	8.91 ± 0.17

[a] Data obtained in this work.

2. Results and discussion

The rate of the mutarotation reaction of glucosylamines has been found to depend on the strength and concentration of the acid catalyst.[1–3] The strongest catalyst in methanolic solutions is the methyloxonium ion, $CH_3OH_2^+$ (referred to as the H^+ ion). Divalent transition metal chlorides are weak Brönsted acids as shown by their acidity constants listed in Table 1. They are, however, much stronger catalysts of the mutarotation reaction as compared with other weak acids.[20] For instance, $CuCl_2$ gives almost instantaneous attainment of equilibrium of the reaction. For this reason, very dilute (3.3×10^{-6} M) salt solutions were used for the kinetic experiments. The reaction proceeds according to the first kinetic order. The rate constants, k, listed in Table 1 show that $MnCl_2$ accelerates the rate of mutarotation only slightly as compared to the reaction proceeding in methanol. The effectiveness of $CoCl_2$ matches that of $NiCl_2$, both enhancing the rate almost twofold, whereas $ZnCl_2$ more than fivefold and $CuCl_2$ more than 20-fold. The catalytic influence of the transi-

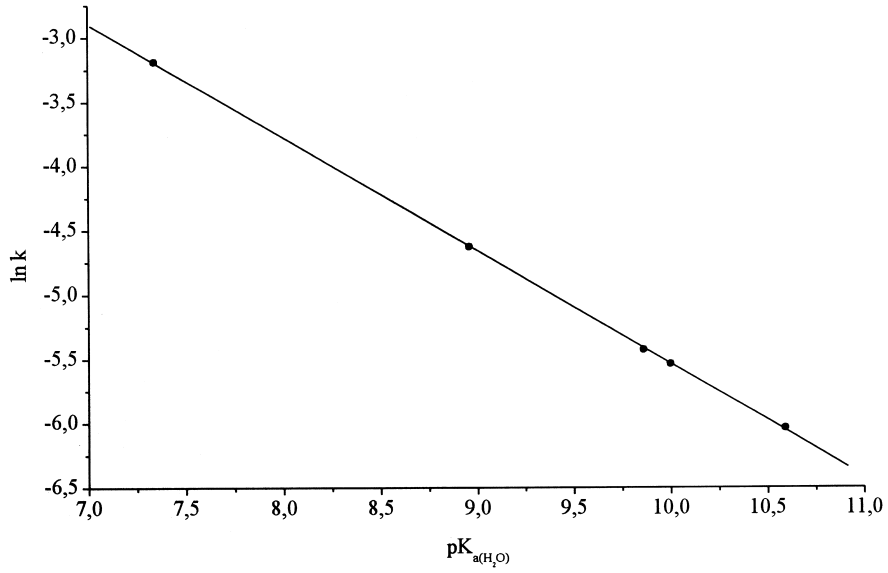


Fig. 1. Plot of the logarithm of the mutarotation rate constant of NGlc vs. $pK_{a(H_2O)}$ of the transition metal chlorides.

tion metal chlorides on the mutarotation of the glucosylamine can be due to the presence of H^+ ions in solutions of the transition metal salts. In order to check whether the reaction is catalyzed solely by the H^+ ions derived from solvolysis of the salts, or by the metal ions themselves, the rate measurements were run in a methanolic benzoate buffer solution. The rate constants, k_b, (Table 1) oscillated around 9×10^{-3} min^{-1} and were independent of the kind of cation, this showing that the H^+ ions were the sole catalysts of this reaction.

Table 1 lists also the rate constant of the mutarotation catalyzed by copper(II) acetylacetonate. This is almost identical with that determined in methanol and shows that the very stable complex ($\log \beta_{(H_2O)} = 18.40$)[21] does not undergo solvolysis and does not generate H^+ ions catalyzing the reaction.

It is also remarkable that there is a linear relationship between $\ln k$ and the literature acidity constants, $pK_{a(H_2O)}$.[22] With manganese(II), nickel(II) and zinc chlorides it is so accurate that the acidity constants of the hydrated Cu^{2+} and Co^{2+} ions (7.29 and 10.00, respectively) for which the literature quantities vary within broad limits[23] can be determined more accurately from the equation: $\ln k = -0.866\ pK_{a(H_2O)} + 3.12$ ($r = -0.9999$). The relationship is presented graphically in Fig. 1.

Anhydrous transition metal chlorides undergo dissociation in methanol, and in dilute solutions an equilibrium $CoCl_2 \leftrightarrow CoCl^+ + Cl^-$ is set up.[24] Cations of the remaining metals also retain the chloride ion in the co-ordination sphere and after solvation assume usually an octahedral symmetry.[15–17] Solvolysis of these complexes results in acidification of the solution due to the following equilibrium:

$$[MCl(CH_3OH)_5]^+ + CH_3OH \leftrightarrow [MCl(CH_3O)(CH_3OH)_4] + CH_3OH_2^+$$

The H^+ ion concentration in methanolic solutions of the transition metal chlorides was determined by pH measurements using salicylate and succinate buffer solutions as standards.[25] To achieve better accuracy of results of the pH metric measurements, solutions of higher concentrations were used than those prepared for kinetic measurements. Table 2 lists results of the pH measurements of the 4.0×10^{-5} M methanolic solutions of the transition metal chlorides. There is a strictly linear relationship between H^+ ion concentration and the rate of mutarotation of NGlc which can be expressed as:

$$k = 1.71 \times 10^6[H^+] + 1.94 \times 10^{-4} \quad (r = 0.9997)$$

Table 2
Acidity constants of the transition metal chlorides, $pK_{a(CH_3OH)}$, determined from pH measurements in two batches of methanol ($pH_{(I)}$ and $pH_{(II)}$)

Compound	$pH_{(I)}$	$pH_{(II)}$	$pK_{a(CH_3OH)}$
$CuCl_2$	7.62	7.72	10.94 ± 0.14
$ZnCl_2$	8.24	8.60	12.46 ± 0.50
$NiCl_2$	8.62	8.66	12.96 ± 0.02
$CoCl_2$	8.73	8.82	13.29 ± 0.03
$MnCl_2$	8.82	8.94	13.62 ± 0.13
Methanol	8.91	9.42	
NGlc	8.19		
O-Ac-NGlc	8.92	9.41	

Salt concentration, $c_s = 4 \times 10^{-5}$ M.

Table 3
pH values of 3.3×10^{-6} M salt solutions with and without 0.02 M NGlc in methanol

Compound	$pH_{(s)}$		$pH_{(NGlc+s)}$	
	Found	Calcd	Found	Calcd
$CuCl_2$	8.18	8.20	6.70	8.05
$ZnCl_2$	8.26	8.79	7.60	8.18
$NiCl_2$	8.45	8.86	7.83	8.20
$CoCl_2$	8.86	8.89	7.99	8.19
$MnCl_2$	8.75	8.90	8.24	8.19

The differences in pH between the two runs of the measurements (I and II) are due to different pH values of two batches of the solvent used (8.91 and 9.42). The different and slightly higher than the literature pH values of absolute methanol (8.35)[24] can be due to trace amounts of water in both batches of the solvent.[26]

The dissociation constant of $CoCl_2$ in methanol is 0.1.[24] It has been assumed that the remaining metal chlorides are equally well dissociated, and consequently it can be assumed that in the 4.0×10^{-5} M solutions the concentration of MCl^+ is equal to the salt concentration. Having in hand the measured pHs and taking into account the concentration of the $CH_3OH_2^+$ ions derived from autodissociation of methanol, the acidity constants of the transition metal chlorides in methanol were calculated from the equation:

$$[H^+] = [(K_a \times c)_{MCl_2} + K_i]^{1/2}$$

The calculations were performed separately for either of the two batches of the solvent. In Table 2 collected are average $pK_{a(CH_3OH)}$ quantities for particular salts. With $CuCl_2$, $CoCl_2$, $NiCl_2$ and $MnCl_2$ the deviations from the average value do not exceed 1.5%. The acidity constant of $ZnCl_2$ is burdened with the greatest error probably due to very strong hygroscopicity of the salt.

Similar to other weak acids of this same type, there is a linear relationship between $pK_{a(H_2O)}$ and $pK_{a(CH_3OH)}$[20] with the slope of 0.81 and correlation coefficient, $r = 0.995$.

N-(*p*-Chlorophenyl)-β-D-glucopyranosylamine is a very weak base in methanol with $pK_{b(CH_3OH)}$ of 14.65 as determined by titration with hydrochloric acid.[27] During these experiments, it has unexpectedly been found that the pH of a 0.02 M solution of the base in methanol is lower (8.19) than that of methanol (8.91) (run I, Table 2). This means that NGlc is a very weak acid with $pK_{a(CH_3OH)}$ of 14.70 as determined by us. Monosaccharides in water are also very weak acids with the protolysis constants of the order of 10^{-13}.[28] The H^+ ions in solutions of NGlc are derived from deprotonation of one of the hydroxyl groups, as is the case with free sugars. This assumption is supported by the pH of a tetra-*O*-acetylated NGlc equal to 8.92 (run I), a value identical with that of the methanol used in this run.

Similar results were obtained in run II. These results reveal that NGlc is an amphiprotolyte, because on one hand the ring oxygen atom readily attracts the proton[3,29] and on the other hand, at least one of the four hydroxyl groups undergoes deprotonation. The pK_a and pK_b quantities of the glucosylamine in methanol indicate that its acid and basic properties are almost equal.

In the presence of the transition metal chlorides, the pH of the NGlc solutions is further depressed. In Table 3 presented are the pH values of 3.3×10^{-6} M solutions of the salts (pH_s) used for the kinetic measurements and those containing also 0.02 M NGlc ($pH_{(NGlc+s)}$). The H^+ ion concentration in a solution containing weak acids ($NGlc + MCl_2$) in a solvent of autoprotolysis constant K_i can be calculated from the equation:

$$[H^+] = [(K_a \times c)_{MCl_2} + (K_a \times c)_{NGlc} + K_i]^{1/2}$$

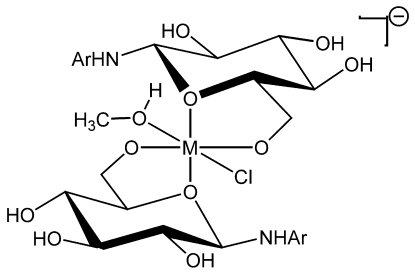
Hence, for instance, the pH of a methanolic $CuCl_2$ and NGlc solution at the concentrations indicated above is 8.05, while the measured value is 6.70 (Table 3). With the remaining salts, the measured pHs are also lower than those calculated. It can be suggested that the increase in acidity of the metal chloride solutions following addition of NGlc can be due to the influence of the cationic forms of the metals on deprotonation of the glucosylamine molecule.

The rank order of the rate constants of mutarotation of NGlc in methanol in the presence of the transition metal chlorides, associated with acidity of the NGlc–MCl_2 system, can be useful for estimation of the relative stability of compounds being formed. The transition metal ions, arranged in this rank order, form the following series: $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$ consistent with the Irving–Williams series. The values for Cu^{2+} distinctly stand out. The stability constants of the $CuCl^+$, $NiCl^+$ and $CoCl^+$ ions in methanol, determined by Khan and Bouet,[30] arrange themselves in the same sequence, the stability constants for $CuCl^+$ being much higher than for the remaining ones. This is compatible with our results and reveals the stronger complexation capacity of the Cu^{2+} ion.

As mentioned above, the literature reports show that interactions between metals and sugars are weak and depend much on the structure of a sugar molecule. Among six-membered monosaccharides, the most convenient ligands are conformers containing either axial–equatorial–axial or 1,3,5-triaxial hydroxyl groups.[18] Just these groups form complexes with metal ions.

The sugar residue of NGlc has all hydroxyls arranged equatorially and thus it does not obey any of the foregoing conditions. By analogy to the finding that in

acid solutions solvated proton is readily bound to the ring oxygen atom of the NGlc molecule,[1–3] it can be assumed that also a metal cation would co-ordinate to the oxygen. Subsequently, following simultaneous involvement of the –OH group at C-6 a chelate is formed whose five-membered ring has a structure similar to that suggested by Mitzner and Behrenwald[10] which facilitates deprotonation of the $-CH_2OH$ group. Both



Scheme 2. Suggested structure of the complex formed.

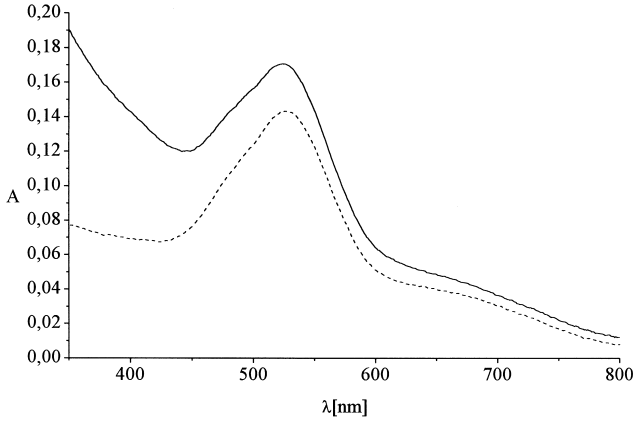


Fig. 2. Absorption spectra of methanolic solutions of 0.01 M cobalt(II) chloride (----) and 0.01 M cobalt(II) chloride after addition of a 0.02 M NGlc solution (—).

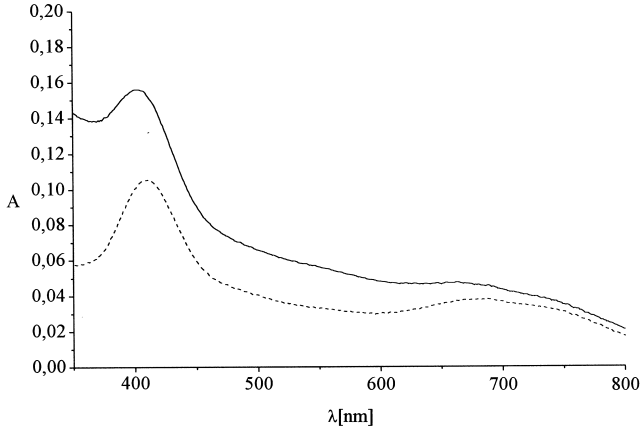


Fig. 3. Absorption spectra of methanolic solutions of 0.01 M nickel(II) chloride (----) and 0.01 M nickel(II) chloride after addition of a 0.02 M NGlc solution (—).

the literature evidence[31] and an approximately 6000-fold excess of NGlc in respect to the transition metal chlorides used allow to conclude that in the solutions considered a complex is formed with involvement of two deprotonated glucosylamine molecules as shown in Scheme 2.

Interactions taking place during complex formation with involvement of the sugar residue of NGlc manifest themselves in the absorption spectra presented in Figs. 2 and 3. In both figures there is an increase in absorption intensity of solutions containing $CoCl_2$ or $NiCl_2$ and NGlc relative to that of salt solutions without NGlc. Both the shape of the spectra and location of the absorption bands reveal complexes of a distorted octahedral symmetry. Only a slight displacement of the bands towards shorter wavelengths, noted after addition of NGlc to the methanolic solution of the metal chlorides, shows that both in the case of methanol and the deprotonated NGlc molecules, the oxygen atoms are electron donors. The nitrogen atom of the amino group of NGlc is virtually not involved in complexation, this being consistent with our previous calculations[3] revealing much higher electron density on the oxygen atom of the pyranoside ring as compared to that of the amine nitrogen. An increase in the absorption bands can be explained in terms of chelate formation of with deprotonated NGlc molecules exhibiting much lower symmetry as compared to that of the $MCl(CH_3OH)_5^+$ ions.

3. Experimental

3.1. Reagents

Methanol was first dried over Na_2SO_4, then with iodine-activated magnesium metal and distilled. To remove basic impurities, the tartaric acid was added to the solvent and distillation was repeated. Finally, the solvent was distilled through a Widmer column and a fraction boiling strictly at the bp of pure MeOH, i.e., 65 °C/1013 hPa[32] was collected. The pHs of the two batches of MeOH were 8.91 and 9.42. Zinc chloride was dried at 180 °C. The remaining chlorides were dried at 130 °C for 3 h. The salts were stored over P_4O_{10} in a desiccator. The *N*-glucosyl-*p*-chloroaniline was synthesized by methanolic method,[32] whereby 0.06 mol of glucose and 0.066 mol of *p*-chloroaniline were dissolved in 70 cm^3 of freshly purified MeOH and refluxed for several hours. The reaction was monitored by thin-layer chromatography (TLC) using aluminium-supported plates coated with Silica Gel 60 (0.2 mm, E. Merck, Darmstadt, Germany) in a CCl_4–acetone solvent system 3:1 (v/v). The crude product was purified by crystalization from 96% EtOH; mp 147–148 °C (Ref. 32 146 °C); initial specific rotation $[\alpha]_{546}^{25} = -130°$ ($c =$

0.579, MeOH) (Ref. 32 $[\alpha]_{546}^{25} = -137°$); ^{1}H NMR ($CD_3OD$): δ 4.49 (d, 1 H, $J_{1,2}$ 8.8 Hz, H-1), 3.45 (t, 1 H, $J_{4,5}$ 8.8 Hz, H-4), 3.36–3.28 (m, 2 H, H-2, H-3), 3.37 (m, 1 H, $J_{5,6}$ 2.4 Hz, H-5), 3.85 (dd, 1 H, $J_{6,6'}$ 12 Hz, H-6), 3.66 (dd, 1 H, $J_{5,6'}$ 5.2 Hz, H-6′).

3.2. Measurements of the rate constants

The rate constants of mutarotation of *N*-glucosyl-*p*-chloroaniline were determined polarimetrically by measuring the angle of rotation of the plane of polarized light at 546 nm over time with an accuracy of $\pm 0.01°$. The measurements were carried out at 25 °C. Solutions were placed in 2 dm long water-jacketed polarimetric tubes thermostated to ± 0.1 °C. The concentration of the *N*-glucoside in MeOH was 2×10^{-2} M. The concentration of the salts was 3.3×10^{-6} M. The reaction started immediately after addition of a metal chloride. The rates were also measured in a benzoate buffer of pH 8.38 obtained by mixing together 0.2 M benzoic acid with 0.1 M sodium benzoate solutions.[6]

3.3. pH measurements

The pH of the solutions were measured at 25 °C using a prototype of an in house designed high quality pH controller linked to a PC running Windows operating system. The pH unit consisted of a high impedance input circuitry, precision ± 18 bit ADC, a microcomputer and a standard RS232C interface. Results of the measurements could be presented either graphically (on the screen or paper) or transferred into other programmes for further processing. A combination pH electrode filled with a satd methanolic KCl solution was used. For calibration of the instrument, buffer solutions were used, whose pHs in MeOH were: 7.53 (0.01 M salicylic acid + 0.01 M sodium salicylate) and 8.75 (0.01 M succinic acid + 0.01 M lithium hydrogen succinate).[25] The pH measurements were run over the salt concentration ranges of 4×10^{-5} and 3.3×10^{-6} M and for a 3.3×10^{-6} M salt solution containing 2×10^{-2} M NGlc.

3.4. Spectra

The NMR spectra were taken on a Varian Unity Plus 500 spectrometer at 500 MHz in CD_3OD, and the UV–Vis spectra on a Perkin–Elmer Lambda 18 instrument.

Acknowledgements

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