

Quantitative comparison of the effect of methyl D-glycopyranosides as cosolutes on the rates of base hydrolysis and aquation of some iron(II)–diimine Complexes†

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ABSTRACT: The kinetics of base hydrolysis and of aquation of some iron(II)–diimine complexes in the presence of stereoisomeric carbohydrates were monitored spectrophotometrically at 25.0 °C. In basic aqueous solution dissociation of both $\text{Fe(1,10-phenanthroline)}_3^{2+}$ and $\text{Fe(2,2'-bipyridine)}_3^{2+}$ is accelerated when methyl D-glycopyranosides are present. The aquation reaction of $\text{Fe(1,10-phenanthroline)}_3^{2+}$ in an aqueous EDTA medium is also accelerated in the presence of carbohydrates, but that of $\text{Fe(5-nitro-1,10-phenanthroline)}_3^{2+}$ is retarded. An equation obtained from a modification of the Savage–Wood additivity of groups principle applied to kinetics is used to quantify the kinetic medium effects observed. The magnitudes of these effects can be explained in terms of the hydration characteristics of the carbohydrates, which depend on their stereochemistry, and the change in the hydration environment of the iron(II)–diimine complexes during activation. Results and their interpretation for the aquation in acidic medium of the $\text{Fe(5-bromo-1,10-phenanthroline)}_3^{2+}$ and $\text{Fe(4,7-dimethyl-1,10-phenanthroline)}_3^{2+}$ complexes in highly aqueous methanol and ethanol solutions are also presented. The kinetic medium effects of the carbohydrates are consistent with those of simple alcohols. Copyright © John Wiley & Sons, Ltd.

KEYWORDS: iron(II)–diimine complexes; base hydrolysis; aquation; kinetics; methyl D-glycopyranoside cosolutes; stereoisomeric carbohydrates

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INTRODUCTION

Within the general context of efforts to understand solvent effects on reaction rates, one can envisage many possible approaches. It has been successfully shown that kinetic measurements using small quantities (typically no larger than 1 mol kg^{−1}) of cosolute or cosolvent can lead to a quantitative evaluation of the effect.¹ This treatment is derived from an extrapolation to kinetic studies of the additivity of groups principle which was developed essentially for equilibrium thermodynamic properties.² The model for this approach involves consideration of the interaction of the solvent spheres or solvent environments

of the initial state and the transition state with the solvent cosphere of the added substance. The extent of interaction can be expressed in terms of a $G(C)$ value, which can be determined making use of the following equation:^{1e,f}

$$\ln[k/k^0] = 2/RT[G(C)]m$$

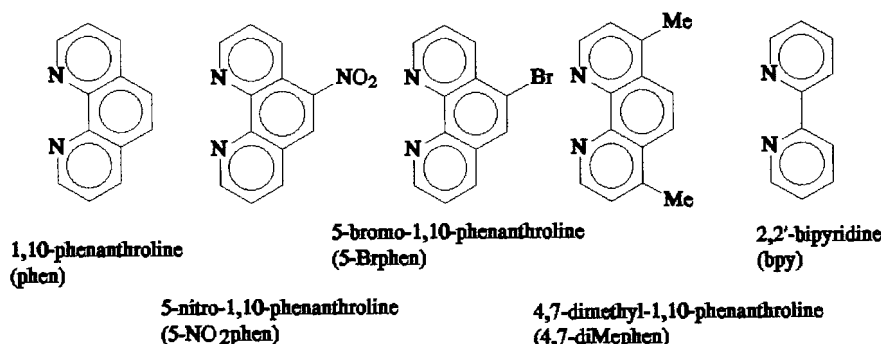
where k^0 is the rate constant for a reaction in a medium without any cosolute present ($m = 0$), k is the rate constant for the reaction at cosolute molality m , R is the gas constant and T is the temperature (K). $G(C)$ is the term, expressed in J kg mol^{−2}, which is based upon Gibbs energies, introduced into the treatment in terms of transition-state theory. Derivation of the equation can be found in the literature.^{1e,f} The value of $G(C)$ is a measure of the slope of the plot of $\ln(k/k^0)$ versus m and represents the difference sum of pairwise Gibbs energy interaction parameters describing the interactions of the particular cosolvent/cosolute C with the reactant(s) and the activated complex. The greater the $G(C)$ value, the greater is the kinetic medium effect, implying in principle

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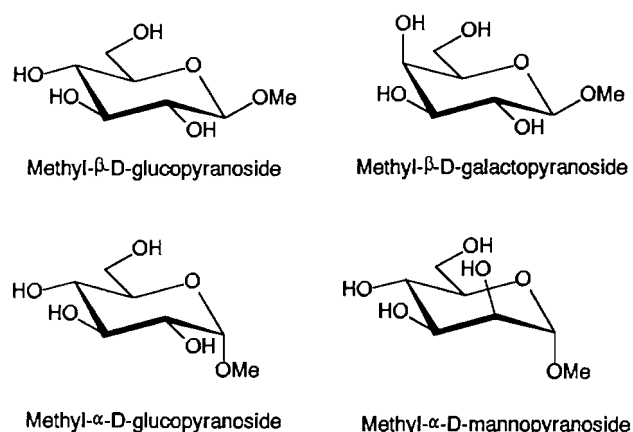
Scheme 1. Bidentate ligands used to form tris-iron(II) complexes

a greater number of interacting moieties or stronger interaction of the reactants and transition state with the cosolute. $G(C)$ may be thought of as the sum of the constituent Gibbs energies arising from such interactions, which result in either a lowering of or an increase in the Gibbs energy of activation, relative to that for a reference solvent (water), for a 1 mol kg⁻¹ cosolute concentration.

This approach can be exploited in two ways, as follows. (1) As a vehicle for examining the effect of solvation cospheres which differ based on stereochemistry differences of a series of otherwise identical or very similar molecules. For example, the hydration characteristics of several carbohydrates could be determined by such an investigation using the hydrolysis of the activated amide 1-benzoyl-3-phenyl-1,2,4-triazole.³ Interestingly, the extent of interaction could be related to the hydration characteristics of the carbohydrates.^{3,4} Furthermore, the pattern of interactions reflected the stereochemistry of the carbohydrates: a carbohydrate with a better fit into the three dimensional hydrogen-bonded network of water has a greater apparent hydrophobicity as gauged from its interaction parameter. (2) As a vehicle for studying the reaction mechanism of selected reactions in aqueous solution; for example the mechanism of the neutral hydrolysis of *p*-nitrophenyl methylsulfonyl perchlorate could be further elucidated.^{1m}

In the present study, we used the kinetics of base hydrolysis of the Fe(phen)₃²⁺ and Fe(bpy)₃²⁺ ions (the ligands are displayed and named in Scheme 1) and aquation of the former complex ion and of Fe(5-NO₂phen)₃²⁺ to probe the hydration characteristics of several carbohydrates. In addition, the influences of methanol and ethanol on the rate constants for aquation, in acidic medium, of Fe(5-Brphen)₃²⁺ and of Fe(4,7-diMephen)₃²⁺ have been studied.⁵ The carbohydrates in question are methyl D-glycopyranosides (illustrated in Scheme 2); mutarotation is prevented and therefore they occur in only one anomeric form. They have been shown to be extremely slowly hydrolysed, if at all, in the media used.⁶

The rate laws and mechanisms of reactions of iron(II)–tris-phen and iron(II)–tris-bpy complexes are well established,⁷ and indeed along with several other



Scheme 2. Carbohydrates used as cosolutes for kinetic medium effects

iron(II)–tris-diimine and related complexes have been the focus of several atmospheric and elevated pressure kinetic studies^{8–10} in water and in aqueous solvent mixtures, using in some cases cosolvent mole fractions up to 0.5 (where the additivity of group treatment² is not valid). Supporting transfer chemical potential data have allowed a thorough, but mostly qualitative, analysis of cosolvent effects for low molecular weight mono-ols, a diol, a triol, acetone and DMSO.^{9,10}

Hence this work represents an extension of a study of kinetic solvent effects, but here the emphasis is on low concentrations of cosolvent/cosolute. This study also marks a further investigation of hydration characteristics of carbohydrates.

EXPERIMENTAL

Materials. The iron(II) salts of phen and bpy were prepared as the perchlorates by standard methods and had the literature molar absorptivities.^{11,12} **WARNING!** Perchlorate-containing compounds are potentially explosive and should be handled only in small quantities and with caution.

Commercially available 0.025 mol dm⁻³ solutions of iron(II) tris-1,10-phenanthroline sulfate (Fisher Scienti-

fic) and iron(II) tris-5-nitro-1,10-phenanthroline sulfate (GFS Chemicals) were also employed. The 5-bromo- and 4,7-dimethyl-phen ligands and their iron(II) complexes were samples reported earlier.^{5,9d} The carbohydrates methyl α -D-glucopyranoside, methyl α -D-galactopyranoside (Sigma), methyl β -D-glucopyranoside and methyl α -D-mannopyranoside (Aldrich) were used as received.

Sodium hydroxide solutions were prepared from commercially available concentrates (Titrisol) in vials by dilution with distilled water. Acid solutions were made from stock concentrated ACS reagent-grade acid solutions and distilled water. EDTA was of analytical reagent grade from Mallinckrodt.

Methods. Solutions were prepared by weight. Reaction was initiated by the addition of a few microliters of moderately concentrated iron(II)–diimine complex ion to 3 ml quantities of a thermostated solution containing the other components. The reference kinetic measurement in each case was performed using an identical solution except for the presence of the carbohydrate or alcohol. The kinetics were followed, in triplicate, by monitoring the loss of the absorbance peaks at 511 nm (Fe(phen)_3^{2+} and $\text{Fe(5-NO}_2\text{phen)}_3^{2+}$) or 522 nm (Fe(bpy)_3^{2+}) using iron(II) complex ion concentrations of 7.5×10^{-5} mol dm^{-3} in 1 cm cuvettes on a Cary Model 219 spectrophotometer, or the loss of absorbance peaks at 510 nm ($\text{Fe(5-Brphen)}_3^{2+}$ and $\text{Fe(4,7-diMephen)}_3^{2+}$), in 1 cm cuvettes on a Unicam 1800 spectrophotometer or a Hewlett-Packard Model 8451A diode-array spectrophotometer, using iron(II) complex ion concentrations of $ca\ 1 \times 10^{-4}$ mol dm^{-3} . Temperature control of solutions ($25.0 \pm 0.1^\circ\text{C}$) was maintained by circulating fluid from a thermostated bath. All reactions were strictly first order for at least three half-lives, and the rate constants were obtained using either the Varian Advanced Kinetics Calculation program on an Apple IIe computer or standard in-house software as described previously.¹³

RESULTS AND DISCUSSION

Reaction kinetics and mechanism

Base hydrolysis. The kinetics of base hydrolysis of Fe(phen)_3^{2+} and Fe(bpy)_3^{2+} and related complex ions have been thoroughly investigated.⁷ The rate law for base hydrolysis has been established^{7a} as

$$-d[\text{Fe(phen)}_3^{2+}]/dt = [\text{Fe(phen)}_3^{2+}](k_1 + k_2[\text{OH}^-] + k_3[\text{OH}^-]^2 + \dots)$$

Provided that the concentration of hydroxide ion does not exceed a certain level, the term that is second order in hydroxide ion concentration (with rate constant k_3)

assumes no significance in the rate law. The solvolysis term (k_1) would assume importance only if the hydroxide ion concentrations were much lower than used here. Thus, by studying the reaction in moderate excess of hydroxide ion (typically $[\text{OH}^-] = 0.01$ mol dm^{-3} for a given series), pseudo first-order kinetics are expected, and were found, in the presence or absence of carbohydrate cosolute. To ascertain whether the rate law would be affected by the presence of carbohydrates, the kinetics of the base hydrolysis of Fe(phen)_3^{2+} in varying OH^- concentrations up to 0.02 mol dm^{-3} (maintaining a constant ionic strength of 0.02 mol dm^{-3} with sodium chloride), for a fixed methyl α -D-glucopyranoside concentration (0.20 mol kg^{-1}), were monitored. First-order kinetics were observed at each OH^- concentration, and the measured first-order rate constants depended linearly on OH^- . Hence the added cosolute has no influence on the rate law.

In order to establish the kinetic medium effect for each cosolute, the standard approach of maintaining the reactant concentration(s) constant [hydroxide ion and iron(II) complex ion in this case] for a given series of varying cosolute concentrations (carbohydrates in this context) was adopted. In the absence of carbohydrate the initial reaction products are $\text{Fe}^{2+}(\text{aq})$ ions and three phen molecules per iron(II) species. Ultimately, except with the rigorous exclusion of oxygen, iron(III) hydroxide will be formed, although this occurs only after the relevant reaction is essentially complete. In thoroughly purged (by nitrogen) solutions, no kinetic differences were observed from solutions which were not purged. Scavenging of released iron(II) by carbohydrates that may occur in competition with hydroxide ions does not cause a deviation from first-order kinetics, and would occur subsequent to the rate-determining attack of the hydroxide ion on the first iron–nitrogen bond of the complex to be broken. The kinetics of the base hydrolysis of Fe(bpy)_3^{2+} in the presence of carbohydrates were studied in an analogous manner.

Aquation. The rate of the dissociation of iron(II)–tris-phen complexes in acidic medium is first order in complex ion concentration and is independent of acid concentration in the range 10^{-3} – 1 mol dm^{-3} . The fact that the first-order rate constant is virtually identical with that in acidic medium when the acid is replaced by a solution of 10^{-2} mol dm^{-3} EDTA^{9d} supports the idea that the first iron–nitrogen bond extension or cleavage is rate determining, followed by rapid protonation of the ligand or by EDTA scavenging the iron end of the bond. Thus in aquation studies the products are either $\text{Fe}^{2+}(\text{aq})$ and protonated forms of phen or phen derivatives, or Fe(edta)^{2-} and phen or a substituted phen. Acid aquation of Fe(bpy)_3^{2+} is characterized by a rate law in which there is a complex acid concentration dependence^{7c} which precludes this reaction from being studied by the approach adopted here.

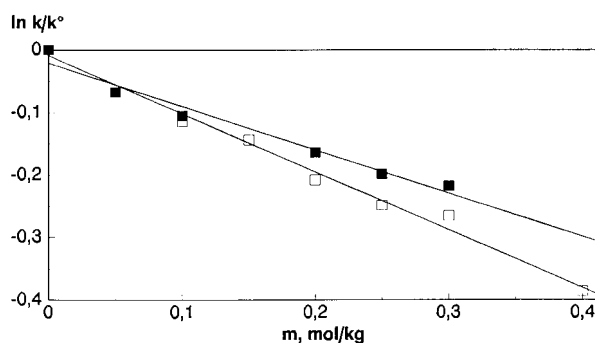


Figure 1. $\ln k/k^0$ at 25°C versus molality of methyl D-glycopyranosides for the base hydrolysis of iron(II)-bpy complexes in the presence of OH^- : \square , methyl α -D-mannopyranoside; \blacksquare , methyl α -D-glucopyranoside

Influence of carbohydrates on base hydrolysis. The adaptation of the additivity of groups principle of Savage and Wood to kinetics¹ indicates that the value of $\ln(k/k^0)$ will depend linearly on the molality (m) of added solute providing the molality is below that where triplet or higher order solute cosphere interactions occur.^{1e} For organic reactions this is typically when $m < 1 \text{ mol kg}^{-1}$. For the iron complexes studied here, the appropriate plots are not ideally linear; two examples are shown in Fig. 1. It is not obvious why the primary data show better correlations for organic reactions;¹ it may be a consequence of the larger charge density changes occurring in this investigation. Table 1 is a compilation of the $G(C)$ values derived from the slopes of the plots, assuming linearity, for each base hydrolysis reaction in the presence of carbohydrate. The primary results from which the parameters reported in Table 1 are derived, are assembled in Supplementary Tables S1–S5, (available from the epoc website at <http://www.wiley.com/epoc>).

For dissociation of phen, the $G(C)$ values are not significantly different for methyl α -D-glucopyranoside and methyl α -D-mannopyranoside, but both exhibit a pronounced retardation effect on the reaction rate. The magnitude of the effect is much greater than that in many other cosolute studies and illustrates the extent to which the solvent shells of these two cosolutes interact with the reactants and transition state to increase the Gibbs energy of activation, i.e. indicative of how strongly these iron(II) complexes interact with the solvation environment of the sugar cosolutes employed. However, even these large

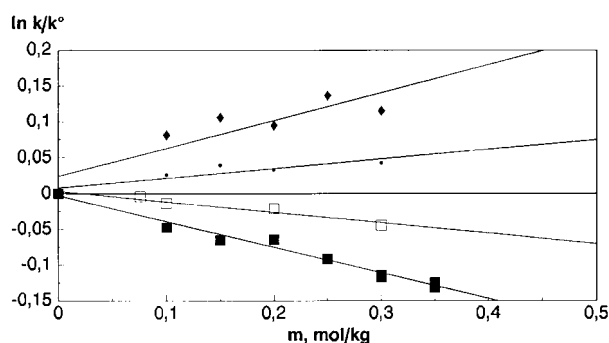


Figure 2. $\ln k/k^0$ at 25°C versus molality of methyl D-glycopyranosides for the dissociation of iron(II)-phenanthroline complexes in the presence of EDTA: \square , phen/methyl α -D-galactopyranoside; \blacksquare , phen/methyl α -D-glucopyranoside; \bullet , 5NO₂phen/methyl α -D-galactopyranoside; \blacklozenge , 5NO₂phen/methyl β -D-glucopyranoside

effects [$G(C)$ values in the -1200 to $1300 \text{ J kg mol}^{-2}$ range] are dwarfed by the value, close to $-2000 \text{ J kg mol}^{-2}$, determined for methyl β -D-glucopyranoside, differing from its α -isomer only in the stereochemistry of the anomeric methoxy group.

Rate retardations are slightly less for methyl α -D-glucopyranoside and methyl α -D-mannopyranoside when the ligands are bpy, perhaps reflecting the ability of the cosolvent sphere of the iron(II) ion in this case to adjust to the impact of the cosolute and its environment since the bpy ligand has some flexibility compared with the rigid phen ligand. Alternatively, the small difference between the two complex ions may reflect a different effect on reactant and cosolute solvation structure due to the charge density difference of the two ions.

Influence of carbohydrates on aquation. The kinetic results for the acid-mediated dissociation are less satisfactory than those obtained in the presence of EDTA (examples of plots for EDTA are shown in Fig. 2). Invariably the precision of the rate constants of a given set is less than for the base hydrolysis experiments and in some cases in acid solution a rate retardation at low cosolute concentrations changes to a rate acceleration at higher cosolute concentration. There is concern that the carbohydrates themselves are subject to reaction with acid. However, at the acid concentrations usually used ($0.050 \text{ mol dm}^{-3}$), we found no evidence from

Table 1. Values of $G(C)$ (J kg mol^{-2}) for base hydrolysis of Fe(phen)_3^{2+} and Fe(bpy)_3^{2+} in $0.01 \text{ mol dm}^{-3} \text{ OH}^-$ in the presence of methyl D-glycopyranosides at 25.0°C

Methyl D-glycopyranoside ^a	Fe(phen)_3^{2+}	r^b	Fe(bpy)_3^{2+}	r^b
Methyl α -D-glucopyranoside	-1183	0.9783	-952	0.9867
Methyl β -D-glucopyranoside	-1993	0.9454	—	—
Methyl α -D-mannopyranoside	-1362	0.9649	-1282	0.9891

^a Concentrations 0–0.5 mol kg^{-1} .

^b Correlation coefficient.

Table 2. Values of $G(C)$ (J kg mol^{-2}) for the aquation of iron(II)–tris-phen complexes in 0.01 mol dm^{-3} EDTA in the presence of methyl D-glycopyranosides at 25.0°C

Methyl D-glycopyranoside ^a	Fe(phen)_3^{2+}	r^b	$\text{Fe(5NO}_2\text{phen)}_3^{2+}$	r^b
Methyl α -D-glucopyranoside	–433	0.971	+318	0.836
Methyl β -D-glucopyranoside	–424	0.860	+501	0.770
Methyl α -D-mannopyranoside	–515	0.904	+404	0.928
Methyl α -D-galactopyranoside	–170	0.951	+165	0.779

^a Concentrations $0\text{--}0.5 \text{ mol kg}^{-1}$.^b Correlation coefficient.

polarimetry⁶ that any interfering reaction gave rise to complications that would render the carbohydrates as other than inert cosolutes. A solution of 1 mol dm^{-3} methyl α -D-glucopyranoside in 1 mol dm^{-3} DCl showed no difference in its ^1H NMR spectrum after a 10 h period; this acid concentration is much higher than that used (0.05 mol dm^{-3}) in the kinetic experiments. Despite these findings, the acid-mediated aquation results are not reported and further investigations are warranted.

The correlation coefficients are less satisfactory for the EDTA-mediated aquation than for base hydrolysis, although the trends of variation of rate constant with cosolute concentration are all systematic. The $G(C)$ values are given in Table 2.

The results for EDTA-mediated aquation show the interesting feature of decreasing rate constant with increasing molality of carbohydrate for the phen complex, but the opposite trend for the 5-nitro-phen complex, indicating the significant effect of a polar substituent, on the kinetic medium effect.

Comparison of carbohydrate cosolute effects for different reactions. From the results assembled in Table 2 and illustrated in Fig. 2, it is clear that the solvent effects of the methyl D-glycopyranosides operate in opposite directions for both iron(II) complexes studied in the presence of EDTA. For the 5- NO_2 phen complex the reaction rate is accelerated but for the phen complex the rate of dissociation is retarded in the presence of the

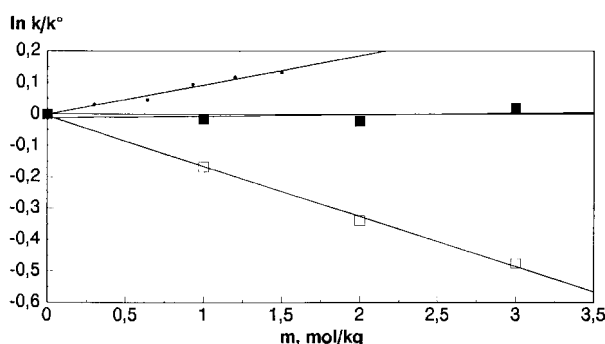
cosolutes. A parallel effect has been observed previously, for the solvent effects of alcohols on the aquation of different iron(II) complexes⁵ (see also Fig. 3). It has been established⁸ that the 5- NO_2 phen complex becomes more hydrophobic upon activation. Hence the rate of dissociation will be enhanced by the presence of the carbohydrates as they exert their apparent hydrophobicity.³

The activation mechanism of the 1,10-phen complex is most likely to be similar to that of the 4,7-dimethylphen complex, which becomes less hydrophobic upon activation.

Probably for the aquation reaction the rate-determining step involves not only ligand extension into the bulk solvent but also to some extent (depending on the character of the ligand substituent) it is accompanied by water attack at the iron(II) center of the latter complex.

It is our view that this possible difference in activation mechanism between the 5- NO_2 phen and phen complexes could explain why in fact a rate decrease in the dissociation of Fe(phen)_3^{2+} is observed in the presence of the methyl D-glycopyranosides, whereas the opposite effect has been observed for 5- NO_2 phen.

Differences in kinetic medium effects of carbohydrates for the different complexes. As shown by the $G(C)$ values, the influence of the methyl D-glycopyranosides on the rates of dissociation is variable, which indicates that the kinetic medium effects of the carbohydrates in question are governed by the hydration characteristics of the methylglycopyranosides. Overall, only methyl- α -D-galactopyranoside has a different kinetic medium effect in comparison with the other cosolutes studied (methyl- β -D-glucopyranoside, methyl-D-glucopyranoside and methyl- α -D-mannopyranoside). This is in accordance with the hypothesis that the camouflage effect^{3,4} influences the hydration characteristics of the carbohydrates. Previous studies have shown the galactose derivative exerts the smallest camouflage and exerts the smallest kinetic medium effect.

**Figure 3.** $\ln k/k^0$ at 25°C versus molality of ethanol for the aquation of three iron(II)–diimine complexes in the presence of 0.1 mol kg^{-1} H_2SO_4 : \square , 4,7-diMephen; \blacksquare , 5-Brphen; \blacklozenge , 5- NO_2 phen

CONCLUSION

We have demonstrated that the quantitative analysis of kinetic medium effects as described previously for

organic reactions in aqueous media and recently for an electron transfer reaction can also be applied to the base hydrolysis and aquation of iron(II) complexes. The magnitude of the effect and higher order interactions than pairwise interactions necessitate the use of concentrations of cosolute or cosolvent which are lower than the concentrations used for the studies of organic reactions in aqueous media.

Two conclusions are apparent from this study: the kinetic medium effect of carbohydrates seems to be governed by the stereochemistry of the carbohydrate, which results in methyl- α -D-galactopyranoside demonstrating a smaller kinetic medium effect in comparison with the other stereoisomers studied; and the differences in kinetic medium effects for the different substituted phen or bpy complexes, observed for both carbohydrates and for alcohols, indicate that the approach employed here shows promise for other mechanistic studies.

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