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Priority Communication

# Unexpected phosphate salt-catalyzed hydrolysis of glycosidic bonds in model disaccharides: Cellobiose and maltose

Alexandre Charmot, Alexander Katz *

*Department of Chemical and Biomolecular Engineering, University of California at Berkeley, Berkeley, CA 94720-1462, United States*

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ABSTRACT

Monobasic sodium phosphate salt is shown to unexpectedly catalyze cellobiose and maltose hydrolysis to glucose at temperatures between 90 °C and 120 °C and pH 4 in aqueous solution. A selectivity of up to 80% glucose is achieved, which increases with increasing disaccharide dilution. The catalytic role of the phosphate salt is evident in a comparison of the measured activation energy of the catalyzed process for cellobiose hydrolysis of 59 kJ $mol^{-1}$ versus that reported for the background reaction of 136 kJ $mol^{-1}$. The normalized rate of catalysis over background significantly increases further at higher pH. Zero-order dependence of hydrolysis rate on disaccharide concentration as well as a logarithmic dependence of hydrolysis rate on phosphate salt concentration is observed. A heterogeneous catalysis mechanism is proposed, which is supported by the presence of condensed phosphate in reaction solution via $^{31}P$ NMR spectroscopy. This mechanism involves disaccharide chemisorption and subsequent activation via interactions with surface acid/base sites.



## 1. Introduction

A central and ongoing challenge in the conversion of lignocellulosic biomass, the most readily available biomass on earth, to fuels and chemicals is catalytic cellulose depolymerization. The hydrolysis of the required glycosidic bonds under mild conditions of pH and temperature is usually associated with enzymes and not synthetic catalysts. In enzymes, acid–base bifunctional mechanisms are invoked for the active site of glycosidases [1], which are known to hydrolyze cellobiose at rate enhancements of over $10^{17}$-fold over background [2]. In stark contrast, when using synthetic catalysts for cellobiose hydrolysis, typically either strongly alkali or acidic media is necessary [3–6], and is often used in conjunction with high temperature hydrothermal conditions [7]. Such harsh conditions lead to specific acid/base catalysis mechanisms that inevitably synthesize undesired reaction by-products and lead to less favorable economics when dealing with energy requirements, process equipment corrosion, and catalyst recovery issues. A milder approach to synthetic catalysis involving hydrolysis of glycosidic bonds is desired to circumvent these challenges, and this requires moving away from systems that exhibit specific acid/base catalysis. Yet to-date, in synthetic systems, the belief has been that specific acid/base catalysis is required for glycosidic bond hydrolysis, when considering cellobiose as a relevant model disaccharide compound [8]. This is demonstrated with reported specific acid-catalyzed rates for cellobiose hydrolysis that increase logarithmically with decreasing pH values below 3 in aqueous solution and plateau to a minimum value within the pH range corresponding to mild conditions between 4 and 7 [8]. Indeed, in synthetic systems, the challenge of studying general acid-catalyzed acetal hydrolysis has required either the synthesis of acetals that form especially stable oxocarbonium cations [9,10] or acetals consisting of either sufficiently good leaving groups [11–13,14] or strained bonds [15,16]. Consistent with this, particular examples of phosphate-catalyzed hydrolysis of acetals consisting of glycosidic bonds require the incorporation of a good leaving group [17,18]. Other examples of phosphate-catalyzed reactions on an anomeric carbon center consisting of fluoroglycoside substitution also require a good leaving group [19,20]. All of these synthetic examples are departures from the types of molecules naturally present in biomass, and therefore represent impractical approaches for economically hydrolyzing biomass-derived carbohydrates to commodity chemicals and fuels.

The intramolecular general acid-catalyzed glycosidic bond hydrolysis discovered by Capon is remarkable because it demonstrates a several thousand-fold rate enhancement over background

* Corresponding author. Fax: +1 510 642 4778.
*E-mail address:* askatz@berkeley.edu (A. Katz).
*URL:* http://www.cchem.berkeley.edu/katzgrp/ (A. Katz).

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under mild conditions of pH and temperature of 4.55 and 90 °C in aqueous solution [21–24]. This system critically relies on the precise positioning of the carboxylic acid functional group that acts as intramolecular acid catalyst: carboxylic acid functionality in the *ortho* position results in a 13,000-fold faster hydrolysis rate relative to a similar system in which the carboxylic acid functionality is in the *para* position [25]. Capon later demonstrated an additional rate enhancement of 20-fold over the intramolecular acid-catalyzed rate, by implementing a nearby pendant Lewis base functional group, wherein the system could be viewed as an intramolecular acid–base bifunctional catalyst [26].

Here, inspired by the results of Capon, in this manuscript, we describe an unusually mild and simple system for achieving hydrolysis of the type of glycosidic bond that comprises both cellulose and starch, using disaccharides cellobiose and maltose as relevant model reactants. Our approach to cellobiose and maltose hydrolysis is the first to use phosphate salts at a mild pH of 4 and relies on the unexpected catalytic activity of these salts for hydrolysis of the glycosidic bond in these compounds. The approach is hypothesized to circumvent the need for precise positioning of acid catalyst functional groups, as required in the Capon system, by essentially forming an acid-containing phosphate surface around the glycosidic bond. This surface contains many acid functional groups. Upon disaccharide adsorption, some of these acid functional groups are in the immediate vicinity of the glycosidic bond and close enough to activate this bond for hydrolysis. This concept of the inorganic oxide surface circumventing the need for precise acid group positioning as observed in intramolecular acid catalysis has been previously observed when dealing with bifunctional heterogeneous catalysts [27] and is itself inspired by the results of Hine using organic polymers [28]. This manuscript attempts to apply these concepts for the catalytic hydrolysis of glycosidic bonds.

## 2. Experimental

### 2.1. Chemicals

The reagents used for cellobiose and maltose hydrolysis experiments and HPLC (High Performance Liquid Chromatography) analysis were used as received and are as follows: D-(+)-cellobiose (99%, Fluka), maltose monohydrate (reagent grade, Fisher), D-(+)-glucose (99.5%, Sigma), HCl (37%, ACS reagent Sigma), sodium hydroxide solution (50% wt. in water, Fisher), phosphoric acid (85% wt. in water, 99.99%) $NaH_2PO_4$ monohydrate (98%, EMD).

### 2.2. Experimental apparatus and procedure

Experiments were conducted for cellobiose/maltose hydrolysis in a batch reactor (model 8648, 9 mL Ace glass Inc., Vineland, NJ, USA) at temperatures between 90 °C and 120 °C, under autogeneous pressure. Except for the initial point $t = 0$ min, which was taken at room temperature, the reactor was cooled prior to sampling. The buffer reactant solutions were prepared by diluting a solution of aqueous $NaH_2PO_4$ (40% wt., pH 4.00) with deionized acidified water ($H_3PO_4$, pH 4.00), so as to reach the desired composition: $NaH_2PO_4$/water (23.5/75.5 w/w). In cases where no buffer is used, a pH 4.0 solution of either HCl or $H_3PO_4$ was added, and on two runs, 4.4% mol and 7.4% mol of NaCl were also added to the HCl solution. At the required buffer concentration, the solution presents a slight excess of NaOH compared with $H_3PO_4$, in order to reach the target pH of 4. Every experiment was conducted with 1% wt. of carbohydrate. Concentrations were maintained below saturation levels in all experiments. The composition of the aqueous sample solution was diluted 10,000 fold in pure water before analysis with a Dionex HPAEC-PAD system Model ICS-3000 (High Performance Anion Exchange Chromatography with Pulsed Amperometric Detection). Conversion of cellobiose was calculated using HPLC. In addition, the glucose concentration was measured for each sample using a glucose analyzer YSI 2300 STAT Plus. The density was accurately measured in order to switch between molality and molarity (see Supplementary information). $^{31}P$ NMR spectra were recorded on a Bruker DRX-500 spectrometer using trimethylphosphate as external standard at the specified temperature. The pyrophosphate resonance was normalized with respect to the orthophosphate resonance for all systems.

### 2.3. Catalysis procedure

In a 9-mL glass tube, 32 mg of either cellobiose or maltose and 3 g of aqueous media at pH 4.0 (phosphate buffer or acidified water) were added, under stirring (350 rpm) in an oil bath at the desired temperature (90, 105, 120 °C), which was regulated by a thermocouple. The sample for zero point was taken after 12 h of stirring at room temperature, before introduction into an oil bath. The sampling process consisted of temporary cooling of the reactor tubes to decrease pressure and permitted sampling via pipetting approximately 150 μL of the solution and diluting it 10,000 fold before chromatographic analysis via HPLC at 4 °C. External standards consisting of 20 μg/L, 5 μg/L, and 0.5 μg/L cellobiose, maltose, and glucose were used to calibrate the HPLC instrument retention time.

## 3. Results and discussion

Results of phosphate salt-catalyzed cellobiose and maltose hydrolysis at various temperatures in aqueous solution are shown in Table 1. The pH is fixed at 4.0 for all catalytic studies. When using either HCl ($pK_a = -6$), $H_3PO_4$ ($pK_{a1} = 2.12$), or HCl/NaCl 4.4%, as expected at these mild pH conditions [6], there is minimal catalysis of glycosidic bond hydrolysis for either cellobiose or maltose, and this rate defines the background rate constant $k_0$ at all temperatures investigated.

The cellobiose and maltose rates when using $NaH_2PO_4$ as catalyst are at least 22-fold and 17-fold higher than background, respectively, at a temperature of 105 °C. Based on data in Table 1, the activation energy for phosphate salt-catalyzed hydrolysis of cellobiose and maltose at pH 4.0 is 59 kJ mol$^{-1}$ and 74 kJ mol$^{-1}$. The catalytic effect of the phosphate is unequivocal when considering background hydrolysis under identically mild pH conditions to have an activation energy of 136 kJ mol$^{-1}$ [23] for cellobiose and 138 kJ mol$^{-1}$ for maltose [29]. The selectivity of the phosphate

**Table 1**
Cellobiose and maltose consumption rates as measured using HPLC.

| Disaccharide | pH | Conditions Salt or acid/base | Reaction at 90 °C rate (selectivity) (nmol min−1) | Reaction at 105 °C rate (selectivity) (nmol min$^{-1}$) | Reaction at 120 °C rate (selectivity) (nmol min$^{-1}$) |
|---|---|---|---|---|---|
| Cellobiose | 4 | $NaH_2PO_4$[a] | 55 (47%) | 89 (45%) | 238 (31%) |
| | 4 | HCl | <4[b] | <4[b] | 45 |
| | 4 | $H_3PO_4$ | | | 44 |
| | 4 | HCl/ NaCl[a] | | | 26 |
| Maltose | 4 | $NaH_2PO_4$[a] | 42 (49%) | 68 (56%) | 281 (37%) |
| | 4 | HCl | n.d.[d] | <4[c] | 28 |
| | 4 | $H_3PO_4$ | n.d. | | 21 |

pH is corrected using HCl in the case of the NaCl solution, and using $H_3PO_4$ in the case of the phosphate salt solution. Rates are based on disaccharide consumption as measured by HPLC.

[a] 4.4 mole percent aqueous solution of either $NaH_2PO_4$ or NaCl.
[b] SD = ± 3 for HCl, $H_3PO_4$, and NaCl 4.4%.
[c] SD = ±1.5 for HCl and $H_3PO_4$.
[d] n.d. means not determined.

salt-catalyzed reaction is defined as the fraction of either cellobiose or maltose consumed that is observed as glucose hydrolysis product in solution and is shown for various temperatures in Fig. 1. At 105 °C, this selectivity is 45% for cellobiose and 55% for maltose, and it is observed to be independent of phosphate salt catalyst concentration and disaccharide conversion for conversions less than ~65%. At 120 °C, the selectivity drops to 31% for cellobiose and 37% for maltose; however, using a 100-fold lower initial concentration of cellobiose of 0.31 mM under otherwise identical conditions leads to a higher selectivity of 81% for cellobiose (see Supplementary information). Other by-products that remain uncharacterized include humins and glucose dehydratation by-products. Hydroxymethylfurfural (HMF) is not observed via HPLC for any of the phosphate salt-catalyzed reactions. Typically, in the phosphate salt-catalyzed reactions, the appearance of humins starts to become apparent as a pale brown coloration of the reaction mixture after a disaccharide conversion of ~10% (i.e. before this conversion the reaction solution remains clear).

To investigate the possibility of a scenario wherein lower pH synthesized in situ during reaction could lead to specific acid catalysis and cause the observed disaccharide consumption, the pH after reaction is measured. A decreased pH could indeed be consistent with oxidative degradation of carbohydrate, which is known to synthesize carboxylic acid functionality [8]. However, the pH of the solution after reaction does not change and is measured to be 4.2 ± 0.2, effectively ruling out such a scenario; however, this does not preclude carbohydrate oxidative degradation during reaction, because the buffering capacity of the solution could in principle avoid pH variations even if this reaction occurs. We also investigate whether the effect of ionic strength has a dominant role in the observed disaccharide conversion, since, for acetal hydrolysis [14], ionic strength can enhance catalytic activity. However, comparison of experiments conducted at pH 4.0 using HCl in the presence of 4.4% NaCl and absence of NaCl in Table 1 demonstrate a lack of rate enhancement. This demonstrates that ionic strength in the range used for the phosphate salt catalysis experiments does not play a significant role. The effect of phosphate source on catalysis is also investigated. Using Sigma TraceSelect $NaH_2PO_4$ as phosphate source results in 60% of the catalytic activity relative to using ACS $NaH_2PO_4{\cdot}H_2O$ as phosphate source, at otherwise identical conditions of 120 °C (SI). Levels of reported cationic impurities are at least 20-fold lower in Sigma TraceSelect $NaH_2PO_4$ relative to ACS $NaH_2PO_4{\cdot}H_2O$. This observation suggests that though phosphate source has an effect on catalysis, it is not directly correlatable with a single impurity. Also, various grades of purified water do not change catalyst activity or selectivity within experimental error (see Supplementary information).

The rate of disaccharide conversion in Fig. 1 appears to be independent of disaccharide concentration and follows a zero-order kinetic dependence. This is different from previously reported buffer-catalyzed reactions, which typically follow a first-order kinetic dependence in reactant [13,17–20]. Buffer-catalyzed reactions also usually follow a first-order kinetic dependence on buffer concentration in solution [13,17–20]. In contrast, despite using a similar salt concentration to that used in prior buffer-catalyzed systems [13,17–20], a highly nonlinear kinetic dependence of disaccharide hydrolysis rate on phosphate catalyst concentration is observed. This kinetic dependence can be described more precisely as a logarithmic dependence than a typical power law and is shown in Fig. 2.

The data in Figs. 1 and 2 together suggest a heterogeneous mechanism for phosphate salt-catalyzed disaccharide hydrolysis. Such saturation of sites cannot occur if homogeneous $NaH_2PO_4$ is the catalytically active species, because it is present in excess relative to disaccharide. Because the $[HPO_4^{2-}]/[H_2PO_4^-]$ ratio is fixed by the Henderson–Hasselbach equation, the lack of linearity between rate and phosphate concentration for phosphate concentrations below 0.5 M in Fig. 2 (see inset) also precludes $HPO_4^{2-}$ as the catalytically active species (i.e. if $HPO_4^{2-}$ was the catalytically active species, then a linear relation between rate and phosphate concentration would be expected). Saturation of binding sites could explain the observed zero-order kinetic dependence on disaccharide concentration, and

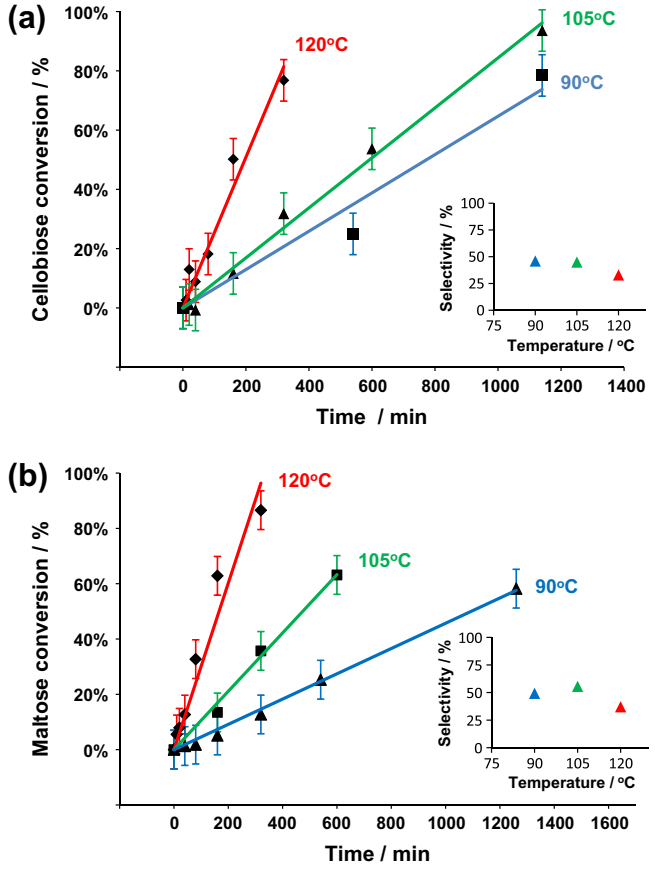


**Fig. 1.** (a) Cellobiose conversion as a function of reaction time at pH 4 in a phosphate buffer solution (4.4% mol phosphate) at different temperatures. (b) Maltose conversion as a function of reaction time at pH 4 in a phosphate buffer solution (4.4% mol phosphate) at different temperatures, as measured using HPLC.

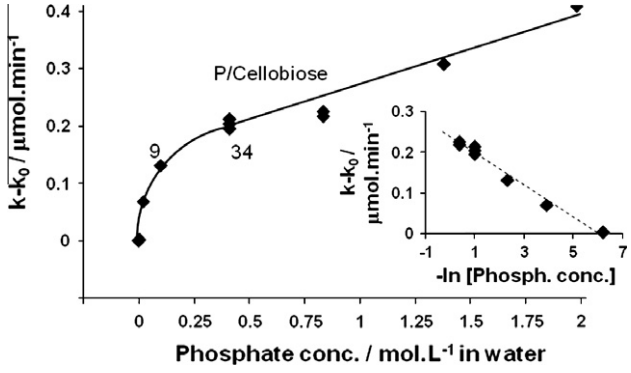


**Fig. 2.** Specific rate of cellobiose conversion as calculated by subtracting the background rate ($k0$) from the actual total measured rate for cellobiose consumption via HPLC ($k$), at various phosphate salt concentrations at a fixed pH of 4.0 and 120 °C. The solubility limit for phosphate salt at these conditions is 12% mol (2 M). Selected points are labeled with P/cellobiose molar ratio. Inset: specific rate of cellobiose conversion versus natural logarithm of the phosphate salt concentration (line represents best fit to experimental data points).

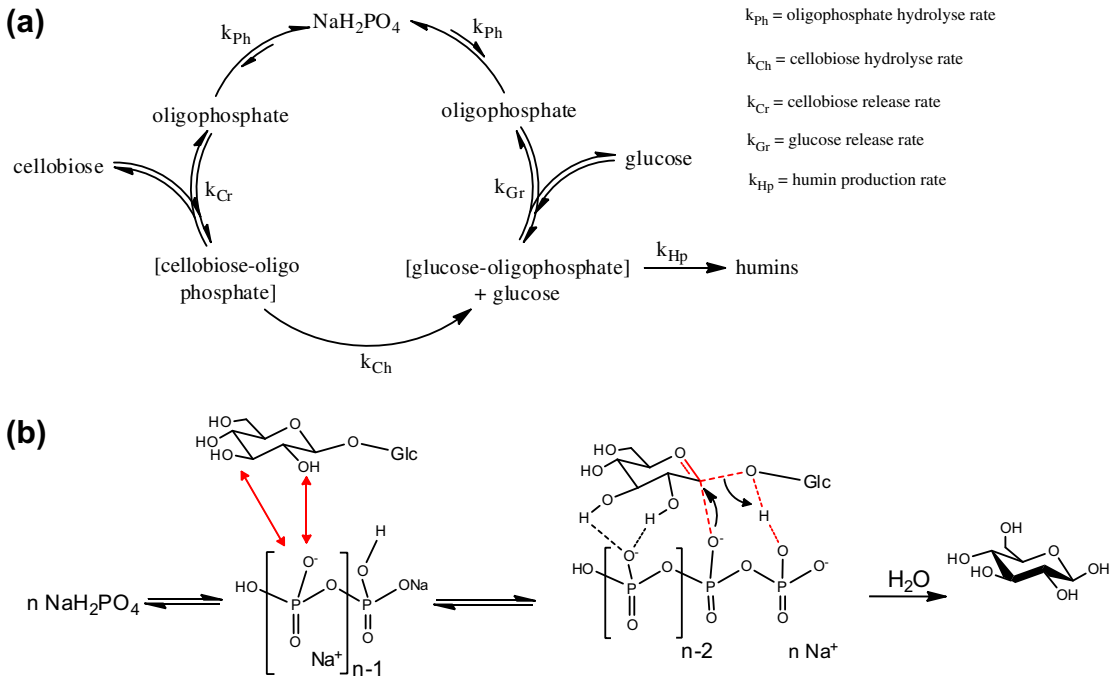


**Fig. 3.** (a) Proposed reaction steps involved in phosphate salt-catalyzed hydrolysis of cellobiose. (b) Schematic illustration of oligophosphate active site, which presents a combinatorial distribution of distances between the acid site and reactant, among them the one allowing the optimal activation of the reactant for hydrolysis after binding.

if phosphate condensation processes are involved in the synthesis of these binding sites in solution, this would lead to a highly nonlinear phosphate concentration dependence on the rate (i.e. a small increase in phosphate concentration could lead to a large increase in amount of condensation products at low concentrations). This could in turn explain the unusual logarithmic kinetic dependence on phosphate salt concentration.

We hypothesize the mechanism of disaccharide hydrolysis to follow the sequence of steps schematically outlined in Fig. 3a. This mechanism involves synthesis of oligophosphates, which act as nanoscale surfaces to chemisorb disaccharide reactant, and thereby activate it for hydrolysis. Such active catalytic roles for oligophosphates are common in biological catalysts, which use them as co-enzymes [30], but they have been exploited to a lesser degree in synthetic catalyst systems. The formation and hydrolysis of such oligophosphates should be quasi-equilibrated at the high temperatures and pH used during catalysis [31–34]. The first step of the mechanism is binding of the disaccharide to form a glycophosphate ester to the oligophosphate surface. This positions the glycosidic bond within an array of Bronsted acid sites defined by the oligophosphate surface and thereby activates it for hydrolysis according to similar intramolecular mechanisms demonstrated previously by Capon [26]. Arrays of mild acid sites on silica have been previously shown to act as potent acid catalysts when reactant is chemisorbed to the surface [27,28]. The role of an inorganic phosphate surface as an entity that overcomes stringent acid functional group positioning requirements of the Capon system is enabled by the surface presenting a large number of acid groups in the immediate vicinity of the glycosidic bond. This role of the surface is similar to that recently demonstrated for silanol-rich silica surfaces, in activating β-glycosidic bond hydrolysis in grafted poly(1 → 4-β-glucan) strands, under the similarly mild conditions of temperature and aqueous solution pH as used in this manuscript [35]. In addition, an oligophosphate surface can in principle act as a bifunctional acid–base catalyst wherein, in addition to acid catalysis via P–OH functionality, there can be stabilization of positive charge on the oxocarbenium ion intermediate by Lewis basic $P–O^-$ functionality. The resulting system is then representative of the intramolecular acid–base bifunctionally catalyzed hydrolysis of a glycosidic bond, which was demonstrated by Capon previously [26], except that now catalytic cooperativity between acid and base functionalities is enforced by the surface array of both P–OH and $P–O^-$ sites (i.e. one or more of the many combinations of P–OH and $P–O^-$ is in the right organization for catalysis to occur with the bound disaccharide). Similar acid–base bifunctional catalysts consisting of an inorganic oxide surface have been previously described and demonstrated as versatile catalysts in which the acid and base components act cooperatively within the mechanism [27]. An example of this type of acid–base bifunctional catalysis scenario for cellobiose hydrolysis is shown in Fig. 3b.

Evidence for the presence of condensed phosphate species in solution under reaction conditions is provided by $^{31}P$ NMR spectroscopy. This data is shown by the resonance in the vicinity of −10 ppm in Fig. 4, which represents a pyrophosphate species [36–38]. Each aqueous solution investigated in Fig. 4 corresponds to the same pH and range of phosphate/disaccharide concentrations as used in reaction studies and is equilibrated for a period of 2 h at 90 °C prior to NMR spectroscopic investigation. There is no overwhelming effect of either temperature or concentration on the pyrophosphate species concentration, in the range investigated. It is unclear at this time whether pyrophosphate versus higher phosphate oligomers present at even lower concentration are the catalytically relevant active site.

There are clear and obvious implications of the results above toward the optimization of this catalyst system, which can involve among other factors, changing the pH and cation to improve catalyst performance. Preliminary investigations demonstrate an increase in catalyst activity over background at 120 °C to be ~67 at pH 7, relative to its value reported above at pH 4 of 5.3. Future work will also involve extending these results to the depolymerization and release of sugars using complex feedstocks that are more representative of raw biomass, such as starch, cellulose, and lignin. These results will be reported in due course.

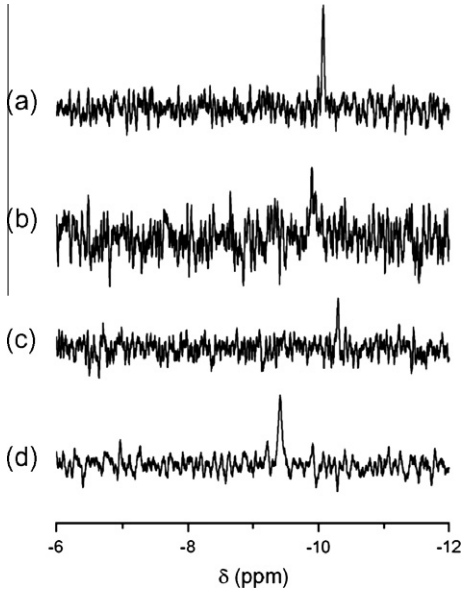


**Fig. 4.** $^{31}$P NMR spectroscopy of aqueous solutions of $NaH_2PO_4$ at pH 4 and specified temperature, containing 32 mg of disaccharide corresponding to: (a) maltose, $[PO_4^-] = 0.2$ M, 25 °C, (b) maltose, $[PO_4^-] = 0.2$ M, 75 °C, (c) cellobiose, $[PO_4^-] = 0.2$ M, 25 °C, (d) cellobiose, $[PO_4^-] = 0.2$ M, 75 °C. All spectra are normalized to the same orthophosphate resonance, and chemical shift (ppm) is referenced to trimethylphosphate as external standard.

## 4. Conclusion

This study is to the best of our knowledge the first demonstration of cellobiose and maltose hydrolysis at pH 4.0 in aqueous media. These mild conditions are in stark contrast to the conventionally held viewpoint that specific acid catalysis and/or use of strong mineral acids is required in synthetic systems to accomplish this transformation. On the basis of the observed zero-order dependence of hydrolysis rate on disaccharide concentration as well as the nonlinear dependence (logarithmic at low phosphate salt concentrations) of hydrolysis rate on phosphate salt concentration, the catalytically active species is proposed to consist of oligophosphate that forms and breaks up in a quasi-equilibrated fashion under reaction conditions. This oligomer is proposed to form an acid-functionalized surface onto which disaccharides can chemisorb and become activated for hydrolysis. The observed catalysis of O-glycosidic bond hydrolysis could serve an important role in pretreatment technology for biomass conversion as well as the release of soluble sugars/depolymerized products from starch, cellulose, and lignin.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2010.08.006.

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