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Hydrolysis and interactions of D-cellobiose with polycarboxylic acids

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ABSTRACT

The hydrolysis of cellulose model compound D-cellobiose was studied with a series of eight common polycarboxylic acids and two monocarboxylic acids in aqueous medium using 0.500 mmol -COOH/L at 170 °C. The maleic acid showed the highest catalytic activity with turnover frequency (TOF) of 29.5 h^{-1}. The interaction of carboxylic acids with D-cellobiose in DMSO-d_6 was studied by determination of the pseudo first-order rate constant k_H of anomeric -OH exchange rate in cellobiose using ^{1}H NMR spectroscopy. The maleic, oxalic and citric acids showed infinitely large k_H values indicating very strong interactions with D-cellobiose. The next highest interactions were found with phthalic acid (k_H = 248.8 Hz). The FT-IR studies showed significant carboxylic acid C=O stretching frequency shifts ($\Delta\nu_{C=O}$) of 12, 13 and 10 cm^{-1} for maleic, oxalic and acetic acids respectively in mixtures with D-cellobiose.

1. Introduction

The current interest in renewable carbon based fuels and chemical feedstocks has advanced the research on cellulose since this natural polymer is the most abundant carbon form and formed as a result of carbon dioxide sequestration by photosynthesis. However there are certain challenges in processing this rich natural resource and it is essential to depolymerize the high molecular weight linear polysaccharide to its monomer glucose for many applications like production of cellulosic ethanol and renewable feedstock chemicals. The depolymerization or hydrolysis of cellulose is a difficult task due to its complex molecular architecture with stiff polymeric chains and close packing *via* strong, inter and intra-molecular hydrogen bonds [1]. The currently used method for the cellulose hydrolysis is the high temperature-pressure dilute acid or steam pretreatment followed by the use of a cellulase enzymes in a biochemical process [1,2]. Nevertheless certain deficiencies in these biochemical technologies like the necessity of an energy intensive pretreatment and enzyme costs have motivated the research into simple enzyme mimics as well as alternative more efficient catalytic methods for the depolymerization of cellulose to glucose. The widely studied non enzymatic approaches include the use of dilute mineral acids like aqueous sulfuric acid [3], concentrated acids [4], solid acids [5–7] mineral acid in neutral ionic liquids [8], acidic ionic liquids [9,10], metal salts in mineral acid solutions and ionic liquid solutions [11,12]. Since these non-enzymatic cellulose hydrolysis can be achieved in relatively low yields, further improvements require a thorough understanding of catalysis mechanisms in the cellulose depolymerization process. Even though the active site of cellulase enzyme contains a carboxylic acid group as the acidic functionality there are only few studies on carboxylic acid based homogeneous catalysts in hydrolysis of cellulose [13–15] [1]. Mosier et al. has compared the cellulose hydrolysis with three organic acids: acetic, succinic and maleic and found that maleic acid is the most effective of the three carboxylic acids [15]. These experiments showed that the rate of Avicel cellulose hydrolysis is almost identical for both 5×10^{-2} M maleic and sulfuric acids. In addition they have found that the rate of glucose degradation is much lower for maleic acid when compared with sulfuric acid of the same acid concentration [15]. An example of the use of carboxylic acid sites generated on cellulose as the cellulose hydrolysis catalyst is also known [16]. In this case, air-oxidation of cellulose was used to oxidize -CH_2OH of cellulose to -CO_2H groups, and then the partially oxidized cellulose was hydrolyzed to glucose in hot water under pressure [16]. The cellulose hydrolysis by low concentrations of carboxylic acids is important in the high temperature hot water and steam pretreatment of cellulosic biomass for cellulosic ethanol process as well, since low concentrations of carboxylic acids such as acetic, formic, and levulinic acids are formed as cellulose degradation products during the pretreatment process causing some depolymerization as well [17].

In comparison to homogeneous catalysts a number of researchers have shown promising results in depolymerization of cellulose using heterogeneous solid acid catalysts with multiple carboxylic acid groups attached to a solid surface [18–21]. Kobayashi et al. has reported that carbons bearing weak acid sites are active for the hydrolysis of cellulose

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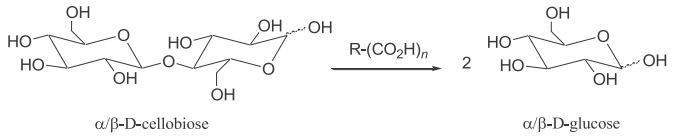

Fig. 1. Polycarboxylic acid catalyzed hydrolysis of D-cellobiose to D-glucose in water.

[19,22]. These catalysts with -COOH and -OH functionalized carbon and graphene type materials produced glucose up to 88% yield at relatively mild conditions in aqueous mediums. The facile hydrolysis of cellulose with many -COOH and -OH groups in proximity to the active site have been explained as a result of interactions or multiple hydrogen bonding with the carbohydrate -OH groups [19,22]. In addition, cellulose nanocrystals modified with natural di and tricarboxylic acids have also been used in the cellulose hydrolysis [23].

As a number of recent studies have shown the importance of having multiple carboxylic acid groups for the interaction of the catalyst with the cellulose structure, we have studied the hydrolysis of cellulose model compound D-cellobiose in dilute aqueous solutions using a series of common poly carboxylic acids as shown in Fig. 1. As a part of this study we have examined the interactions of D-cellobiose with carboxylic acids using ^{1}H NMR and FT-IR spectroscopy in an attempt to understand the role of multiple carboxylic acid and hydroxyl sites in proximity for cellulose hydrolysis. In this publication we present the hydrolysis and interaction of D-cellobiose with eight common polycarboxylic acids with two to three carboxylic acid groups and comparison with two monocarboxylic acids, acetic and lactic acids.

2. Results and discussion

2.1. Hydrolysis of D-cellobiose using carboxylic acids as catalysts

A series of ten carboxylic acids including eight polycarboxylic acids were selected for this study. A few of these compounds such as acetic acid are formed as cellulose degradation products during the steam pretreatment of biomass and some are naturally occurring carboxylic acids. Therefore studying the catalytic activities of these acids are important to explain their role in self hydrolysis of cellulose during the pretreatment as well. The turnover frequencies (TOF) for cellobiose hydrolysis using these carboxylic acid catalysts are shown in Table 1. The four acids: acetic, maleic, phthalic and tartaric showed noticeably high catalytic activities. Among all 10 acids studied the maleic acid with TOF of 29.5 h^{-1} showed the highest catalytic activity. The pKa values of the carboxylic acids are shown in the last column of Table 1. In comparison of four highly catalytically active carboxylic acids with the less active acids, apparently there is no direct co-relation with the pKa values. For instance highly active maleic acid (pKa = 1.90, 6.07) and tartaric acid (pKa = 2.89, 4.4) have higher pKa values or lower acidities when compared to less active oxalic acid (pKa = 1.25, 4.14). Thus the cellulose hydrolysis catalysis activity of polycarboxylic acids depends more on proximity and geometry of carboxylic acid groups, rather than the acidity of the catalyst. The most active maleic acid has a rigid structure with 1,2-carboxylic acid groups in the *cis*-geometry and the other two highly active phthalic and tartaric acids are also 1,2-dicarboxylic acids. However the correct geometry of carboxylic acids is particularly important; for example *cis*-1,2-cyclohexane dicarboxylic acid with two carboxylic acid groups in axial - equatorial geometry forcing the acid groups to be far apart from each other shows relatively poor catalytic activity. In comparison of maleic and phthalic acids both have rigidly held *cis*-carboxylic groups; nevertheless the aromatic acid is less acidic and the steric hindrance around carboxylic groups in phthalic acid may also contribute to somewhat lower activity in phthalic acid. The identification of maleic acid as the most active carboxylic acid out of ten acids studied is significant and further supports the limited study carried out by Mosier and co workers in 2001 using acetic, succinic and maleic acids [15].

Table 1
The turnover frequency (TOF) for D-cellobiose hydrolysis using carboxylic acid catalysts and the pKa values.

Entry	Carboxylic acid	TOF (h^{-1})	pKa
1	Acetic	19.6	4.76
2	Lactic	15.2	3.86
3	Oxalic	14.7	1.25, 4.14
4	Malonic	11.6	2.83, 5.69
5	Succinic	14.8	4.2, 5.6
6	Maleic	29.5	1.9, 6.07
7	*cis*-Cyclohexane-1,2-dicarboxylic acid	15.4	–
8	Phthalic	19.6	2.89, 5.51
9	Citric	16.2	3.13, 4.76, 6.4
10	Tartaric	22.1	2.89, 4.4

TOF = [(mole of glucose produced in catalytic reaction) - (mole of glucose produced in blank test)]/(mole of catalyst)/time (h).

2.2. ^{1}H NMR study on interaction of D-cellobiose with carboxylic acids

During these experiments, first the baseline ^{1}H NMR spectrum of D-cellobiose was recorded in DMSO-d_6 and then a second spectrum was recorded under identical conditions after addition of an equivalent amount of carboxylic acid. The chemical shift and line shape changes due to the addition of the carboxylic acid was studied in order to get an insight into interaction of D-cellobiose with carboxylic acids. The interactions of carboxylic acids with D-cellobiose caused line broadening, and shifting of peaks in ^{1}H NMR and this effect is prominent in hydroxyl proton signals of D-cellobiose. The representative ^{1}H NMR spectra from pure D-cellobiose (**a**) and D-cellobiose - carboxylic acid mixtures with *cis*-cyclohexane-1,2-dicarboxylic acid (**b**), malonic acid (**c**) and oxalic acid (**d**) are shown in Fig. 2. The hydroxyl groups in α,β anomeric mixture of D-cellobiose can be assigned as shown in Fig. 2 (**a**) and the anomeric -OH groups of 1′α and 1′β protons appear as doublets at 6.27 and 6.62 ppm, while the other -OH protons are observed in the 4.4–5.3 ppm region [24]. The line broadening of -OH protons can be interpreted as a result of an increase in exchange rate of these protons. The weakly interacting *cis*-cyclohexane-1,2-dicarboxylic acid (**b**) shows broadening of all -OH peaks and malonic acid (**c**) with much stronger interaction shows significant broadening of these -OH peaks. The oxalic acid with the strongest interaction and fastest exchange of protons caused the -OH signals to completely disappear or burring into the baseline. We have used the exchange rate constants of the anomeric -OH of β-D-cellobiose as a quantitative indicator of the interaction between carboxylic acid and D-cellobiose, as this proton appear around 6.62 ppm with no interference from other signals and convenient in measuring the peak broadening. The exchange rate constant k_H was calculated using the formula $k_H = \pi.\Delta\nu$ where $\Delta\nu$ is the increase in half width of a proton signal upon addition of an acid [25–27]. The application of this formula to the 6.62 ppm peak in the spectra gave k_H values 3.8 and 73 Hz for *cis*-cyclohexane-1,2-dicarboxylic acid (b) and malonic acid (c) respectively. The oxalic acid with no peak at 6.62 ppm was assigned a very large or infinite k_H value. Similarly k_H values were calculated for the remaining series of carboxylic acids as well and these data are shown in Table 2. The very large k_H values were observed for oxalic, maleic, phthalic and citric acids. The three acids maleic, citric and tartaric which showed high k_H values showed high TOF values as well, showing the importance of acid-cellobiose interactions in hydrolysis. However, the oxalic and malonic acids with fairly high k_H values showed only low TOF values, indicating that besides the interaction with -OH groups, the stereochemistry of the carboxylic acid groups in poly acids is an important factor in determining the catalytic activity. In addition to calculation of k_H values, we have determined the change in the chemical shift of the acidic proton of -COOH group as well. The

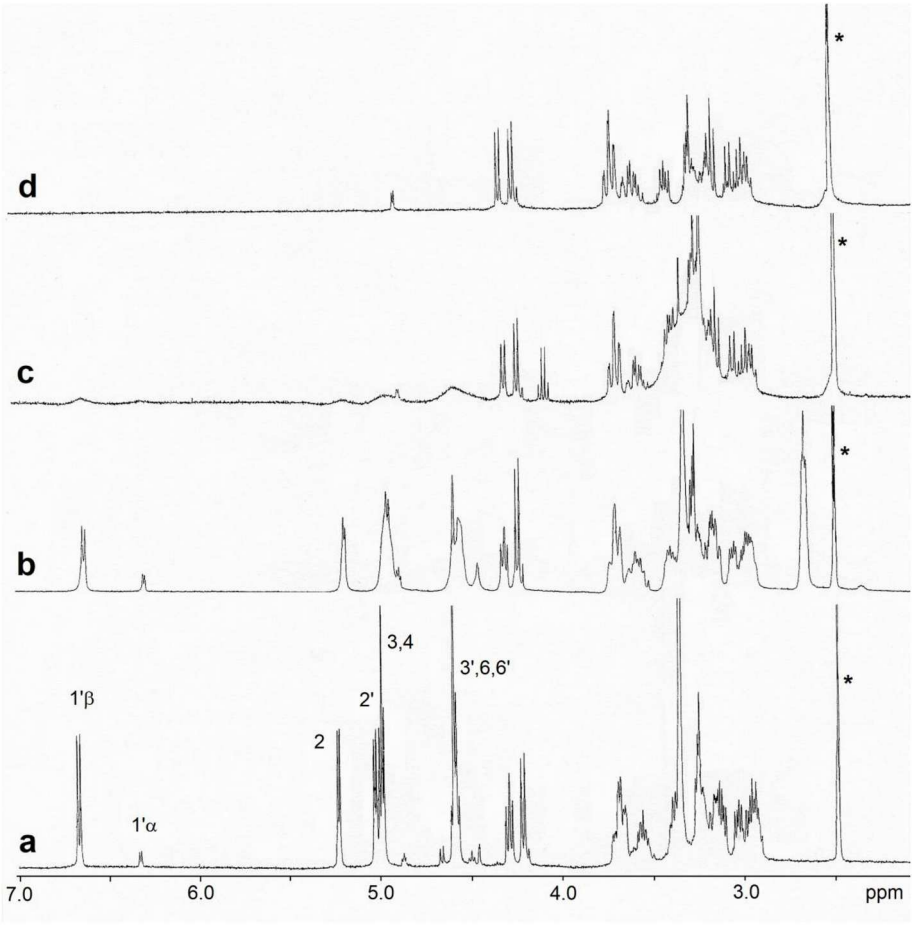

Fig. 2. Representative ^{1}H NMR spectra (DMSO-d_6) from D-cellobiose - carboxylic acid interaction study. **a**. D-cellobiose; **b**. D-cellobiose + *cis*-cyclohexane-1,2-dicarboxylic acid (k_H = 3.8 Hz); **c**. D-cellobiose + malonic acid (k_H = 73 Hz); **d**. D-cellobiose + oxalic acid (k_H = ∞ Hz). * solvent.

-COOH peak was not observed in acid - D-cellobiose mixtures of very strongly interacting acids like oxalic and maleic acids with high exchange rates. In other acids a small shift towards high field was observed in mixing with D-cellobiose.

The changes in acidity of dicarboxylic acids due to complexation with compounds such as phenanthridine and imidazoles are known as a result of X-ray crystallography studies of their co-crystals with dicarboxylic acids [28,29]. Therefore similar changes in acidity is possible in the case of strong interactions between the carbohydrate -OH groups and polycarboxylic acids as well. As mentioned earlier, there is no direct co-relation between pKa values of free acids and turnover frequency (TOF) for D-cellobiose hydrolysis. Therefore possible change

Table 2
The D-cellobiose (CB), carboxylic acid mole ratios used, calculated D-cellobiose -OH exchange rates (k_H), -COOH ^{1}H NMR chemical shifts of pure carboxylic acid and acid - cellobiose mixtures and pKa values of carboxylic acids. All ^{1}H NMR were recorded at 400 MHz in DMSO-d_6 at 23 °C.

Entry	Carboxylic acid	CB: Acid	k_H (Hz)	δ (COOH) in mixture	δ (COOH) Pure	Δδ (COOH)	pKa
1	Acetic	1: 2	47.8	11.90	11.85	0.05	4.76
2	Lactic	1: 2	85.5	12.33	12.40	0.07	3.86
3	Oxalic	1: 1	∞	No peak	11.25	–	1.25, 4.14
4	Malonic	1: 1	73.0	12.56	11.50	0.06	2.83, 5.69
5	Succinic	1: 1	2.5	12.10	12.20	0.10	4.2, 5.6
6	Maleic	1: 1	∞	No peak	11.00	–	1.9, 6.07
7	*cis*-Cyclohexane-1,2-dicarboxylic	1: 1	3.8	11.99	12.04	0.05	–
8	Phthalic	1: 1	248.8	13.03	13.00	0.03	2.89, 5.51
9	Citric	1: 1	∞	12.36	12.38	0.05	3.13, 4.76, 6.4
10	Tartaric	1: 1	47.8	12.71	12.82	0.11	2.89, 4.4

Table 3
The D-cellobiose (CB), carboxylic acid mole ratios used, C=O absorption frequencies of pure carboxylic acid, carboxylic acid - cellobiose mixtures and change in -COOH group C=O frequencies ($\Delta\nu$) of carboxylic acids. All FT-IR were recorded in KBr pellets.

Entry	Carboxylic acid	CB: Acid	ν(C=O) acid (cm^{-1})	ν(C=O) acid + cellobiose (cm^{-1})	$\Delta\nu$(C=O) (cm^{-1})
1	Acetic	1: 2	1718	1728	10
2	Lactic	1: 2	1734	1735	1
3	Oxalic	1: 1	1705	1718	13
4	Malonic	1: 1	1719	1720	1
5	Succinic	1: 1	1700	1692	−8
6	Maleic	1: 1	1706	1718	12
7	*cis*-Cyclohexane-1,2-dicarboxylic	1: 1	1692	1692	0
8	Phthalic	1: 1	1686	1686	0
9	Citric	1: 1	1734	1728	−6
10	Tartaric	1: 1	1735	1741	6

in acidity due to interactions can also contribute to different catalytic activities of the carboxylic acids.

2.3. FT-IR study

The IR absorption frequencies of the carboxylic acid C=O group in pure carboxylic acid, carboxylic acid - cellobiose mixtures and change in C=O absorption frequencies ($\Delta\nu$) are shown in Table 3. The two acids oxalic and maleic, which showed high cellobiose -OH proton exchange rates (k_H) in NMR study showed high $\Delta\nu$ values 13 and 12 cm^{-1} respectively. The citric acid with a k_H value of infinity in ^1H NMR study showed $\Delta\nu$ of −6 cm^{-1} in the FT-IR study, this is probably due to the fact that citric acid is a tricarboxylic acid and not comparable to other dicarboxylic acids in the series. The hydroxy acids: lactic, citric and tartaric can have intramolecular hydrogen bonding as well, in addition to the interactions with the carbohydrate hydroxyl groups.

3. Conclusion

In conclusion the maleic acid with a turnover frequency (TOF) of 29.5 h^{-1} showed the highest catalytic activity among the ten carboxylic acids studied for the D-cellobiose hydrolysis in water at 170 °C. The ^1H NMR study on D-cellobiose proton exchange rate k_H determination as well as FT-IR study on carboxylic acid C=O stretching frequency shift ($\Delta\nu_{C=O}$) measurements showed that strong interactions are present between carbohydrate -OH groups and polycarboxylic acid functions in the acids showing high catalytic activity. However, in addition to the carbohydrate -OH, acid -COOH interactions, the geometry of the carboxylic acid groups play an important role in the catalytic activity in D-cellobiose hydrolysis.

4. Experimental

4.1. Instrumentation and materials

D-cellobiose (99.9%), DMSO-d_6 (99.9% atom D), analytical grade (> 99.9%) carboxylic acids: acetic, oxalic, malonic, succinic, maleic, *cis*-cyclohexane-1,2-dicarboxylic acid, phthalic, lactic, citric and tartaric were purchased from Aldrich Chemical Co and were used without further purification. Cellobiose hydrolysis experiments were carried out in 25 mL stainless steel solvothermal reaction kettles with Teflon inner sleeves, purchased from Lonsino Medical Products Co. Ltd. Jingsu, China. The reaction kettles were heated in a preheated laboratory oven (Precision Scientific model-28) with temperature accuracy ± 1 °C. Glucose concentrations in D-cellobiose hydrolyzate solutions were determined using the glucose oxidase/peroxidase enzymatic assay as described in our earlier work [30]. A Thermo Scientific GENESYS 10S UV–Vis spectrophotometer and 1 cm quartz cells were used in the colorimetric glucose measurements. ^1H NMR Spectra in DMSO-d_6 were recorded on a Varian Mercury plus spectrometer operating at 400 MHz, rd = 1s, spectral width of 6398 Hz, and typically 16 scans were collected for spectra. All NMR spectra were collected at room temperature, 23 °C. FT-IR spectra were recorded on a Thermo Nicolet IR 200 using KBr pellets at 1.0 cm^{-1} resolution.

4.2. General experimental procedures for the hydrolysis of D-cellobiose using carboxylic acids as catalysts

The stock solutions of ten carboxylic acids were prepared by dissolving appropriate amounts of these acids in deionized water to give acid concentrations of 0.500 mmol -COOH/L in each. The accuracy of the concentrations were checked by titration with standardized aqueous NaOH solution using phenolphthalein as the indicator. D-cellobiose (0.030 g, 0.0876 mmol) was weighed into the Teflon container with a lid and stainless steel jacket capable of withstanding the high pressure. To this 10.0 mL of the aqueous acid was added and the contents were thoroughly mixed with a spatula and tightly sealed. The reaction kettle was heated in a thermostated oven maintained at 170 ± 1 °C for 2.0 h. Then reactor was removed from the oven and immediately cooled in ice-cold water to quench the reaction. The contents were transferred into a centrifuge tube, neutralized by drop wise addition of 0.5 M aq. Sodium hydroxide and centrifuged at 1,700 *g* for 6 min To remove any unreacted cellulose and solids. The clear supernatant was used for the glucose analysis using glucose oxidase/peroxidase enzymatic assay as described in our earlier work [30]. A similar experiment using 10.0 mL of deionized water as the reaction medium was carried out as the blank experiment. The glucose yields from these experiments were applied in calculating turnover frequencies (TOF) using the formula:

TOF = [(mole of glucose produced in catalytic reaction) - (mole of glucose produced in blank test)]/(mole of catalyst)/time (h).

4.3. General procedure: interaction of D-cellobiose with carboxylic acids - ^1H NMR study

A solution of D-cellobiose (15.0 mg, 0.146 mmol) in 0.50 mL of DMSO-d_6 was prepared in a 5 mm NMR tube. The sample was allowed to stabilize at room temperature for 4 h, then ^1H NMR (rd = 1 s, NS = 16) spectrum was recorded as the initial baseline data. Afterward, carboxylic acid (1–2 equivalents) was added and thoroughly mixed using EW-04726-01 Cole-Parmer Vortex Mixer for 2.0 min, allowed to stabilize at room temperature for 4 h. Then ^1H NMR spectrum was recorded using the conditions identical to the pure D-cellobiose spectrum. The representative spectra from pure D-cellobiose, mixtures with *cis*-cyclohexane-1,2-dicarboxylic, malonic and oxalic acids are shown in Fig. 2. The half width of 6.62 ppm peak in D-cellobiose, before and after the addition of carboxylic acid was used in calculating k_H, employing the formula: $k_H = \pi.\Delta\nu$ where $\Delta\nu$ is the increase in half width of a proton signal upon addition of an acid [25–27]. The calculated k_H values for the series of carboxylic acids is shown in Table 2.

4.4. General procedure: interaction of D-cellobiose with carboxylic acids - FT-IR study

A mixture of D-cellobiose (15.0 mg, 0.146 mmol) and carboxylic acid (1–2 equivalents) was prepared and ground together for 2.0 min in a pestle and mortar. Then a 5 mg portion of the mixture was thoroughly mixed with 100 mg of dry KBr and was used in making the KBr pellet for recording the spectrum. All spectra were collected with 32 scans and 1.0 cm^{-1} resolution. The FT-IR spectra of pure carboxylic acids recorded under identical conditions were used as the reference spectra

and all FT-IR spectra are included in the supplementary material. The shifts in carboxylic acid C = O absorptions ($\Delta\nu_{C=O}$) due to mixing with D-cellobiose are shown in Table 3.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carres.2019.02.002.

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