

High efficiency of superacid HF–SbF₅ for the selective decrystallization–depolymerization of cellulose to glucose†Agnès Martin-Mingot,^a Karine De Oliveira Vigier,^{*b} François Jérôme^b and Sébastien Thibaudeau^{*a}

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Herein, we show that after polyprotonation, superacid HF–SbF₅ is able to selectively depolymerise cellulose to water-soluble carbohydrates with 68 wt% yield of glucose. This process is efficient at low temperature, thus avoiding the formation of side products as commonly observed with conventional acids.

Since the development of magic acid, fluoroantimonic acid and related conjugate superacids in the early 1960s,¹ superacid chemistry has emerged into a field of growing interest and importance.² In 1994, this topic received the Nobel prize attributed to Prof. G. A. Olah. Since then, the possibility of selectively accessing novel compounds starting from usually nonreactive substrates, *via* superacid-catalyzed reactions (*e.g.* fluorination,³ hydroxylation,⁴ Friedel–Crafts and other reactions)⁵ has been largely documented. The commercialization of the difluorinated anticancer agent vinflunine (Javlor®) synthesized in superacid HF–SbF₅ additionally demonstrates that this technology is already operational at an industrial scale.⁶ To the best of our knowledge, superacid (HF–SbF₅) has never been used for the conversion of biomass. With the depletion of fossil oil reserves,⁷ biomass, and specifically cellulose, has become an attractive source of renewable chemicals. The hydrolysis of cellulose to glucose is extensively developed in the literature since glucose is now used as a chemical platform.⁸ Although, significant advances have been made in this field,⁹ the direct conversion of cellulose to glucose in aqueous phase under mild conditions remains a major challenge due to the highly crystalline structure of cellulose.¹⁰ Hence, in order to increase the intrinsic reactivity of cellulose, pretreatments of cellulose are often used such as chemical treatments, ball milling, steam explosion, nonthermal atmospheric plasma, ionic liquids.¹¹ Among them, acid treatments (HCl, H₂SO₄, HF...) are the most reported way to

depolymerize cellulose to glucose because of their efficiency, especially when using HF–TFA mixtures.^{12,13} Under acidic conditions, the rate of hydrolysis seems to be governed by the pH rather than the acid type or shape.^{9b} In this context, we show here that the selective and efficient hydrolysis of cellulose can be performed in the presence of HF–SbF₅ superacid at only 0 °C. The advantages of this method are the (1) low temperature allowing the selective production of glucose and water-soluble cello-oligomers (formation of undesired side products was negligible) and (2) a low amount of HF–SbF₅ (4 mL *vs.* 100 mL for classical HF based cellulose hydrolysis)¹³ is required, thus facilitating the work-up procedure (convenient neutralization over industrially available anion exchange resins). We show here that the particular properties of superacid HF–SbF₅ such as (i) generation of long lived carbocations¹⁴ (ii) (poly)protonation of functionalized substrates (involvement of (poly)cationic superelectrophiles)¹⁵ and (iii) the very low nucleophilic character of the fluoride ions present in complexed forms Sb_nF_{5n+1}[–],¹⁶ offer efficient tools for the selective deconstruction of cellulose to glucose under mild conditions.

In a first set of experiments, 0.4 g of cellulose (PH AVICEL 105, degree of polymerization (DP) = 200) was added to 1 mL of HF at 0 °C and stirred for 1 min. Then, 3 mL of SbF₅ was added and stirred for 10 min (SbF₅ mol% = 1.9) prior to the addition of 20 mL of water. The mixture was then stirred at 0 °C for another 10 min (more details are provided in the ESI†). At the end of the reaction, the solution was neutralized over anion exchange resin Amberlyst 26 (OH[–] form). Under these conditions, the cellulose was totally converted to water-soluble carbohydrates (DP < 13, Fig. S1†) including the formation of 10 wt% glucose (Fig. 1a). It is noteworthy that the solution is colorless (Fig. 1b) suggesting that the carbohydrates were not degraded as usually observed with common acid treatments reported in the current literature. This was further supported by size exclusion chromatography (SEC) and HPLC analyses that revealed the quasi exclusive formation of water-soluble carbohydrates (purity > 98%, Fig. S2†).

In order to get more insight into the reaction mechanism, a few counter experiments were performed. The first experiment was carried out in neat HF at 0 °C with 0.4 g of cellulose. Then, water was added and the hydrolysis was performed as described above (0 °C, 10 min). At the end of the reaction, the mixture was neutralized with sodium hydroxide. XRD analyses showed a

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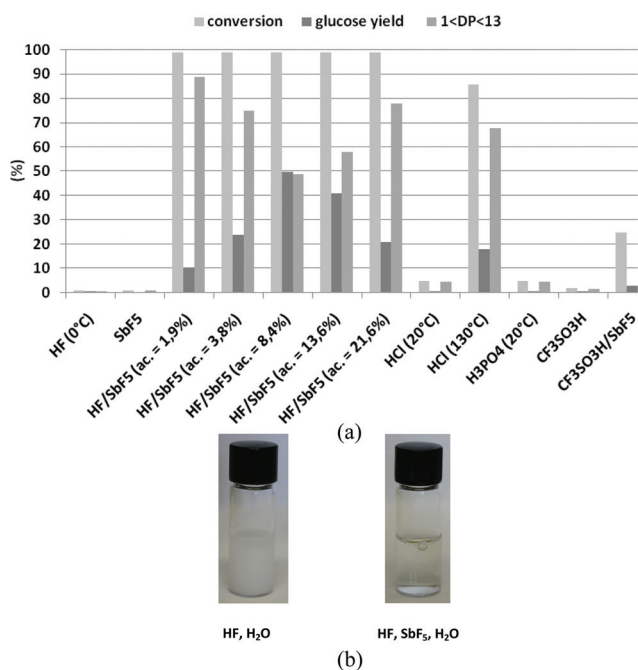
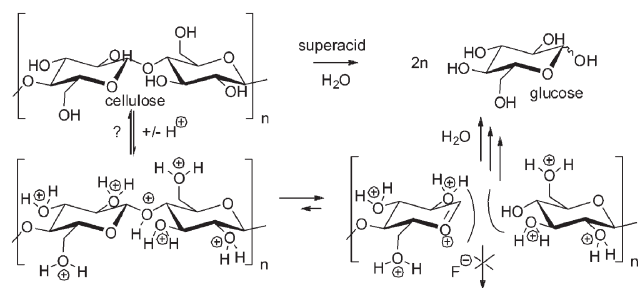


Fig. 1 Acid and superacid hydrolysis of cellulose.



Scheme 1 Proposed mechanism to account for the behaviour of cellulose in superacid HF-SbF₅.

total decrystallization of cellulose (Fig. S3†). When the same reaction was conducted in aqueous NaOH, the crystallinity of cellulose remained unaltered demonstrating that, in our conditions, HF is capable of decrystallizing cellulose. Although cellulose was totally decrystallized in neat HF, no formation of water-soluble carbohydrate was observed upon addition of water showing that, at 0 °C, HF cannot hydrolyze cellulose. The second experiment was carried out in neat SbF₅ at 0 °C with 0.4 g of cellulose prior to the addition of water. No glucose was formed which shows that cellulose can be only converted in the presence of a HF-SbF₅ mixture (Fig. 1a). Note that when cellulose was first treated in HF-SbF₅ and then hydrolyzed, no depolymerization of cellulose occurred. This indicates that cellulose is first decrystallized by HF followed by a superacid polyprotonation (Scheme 1).

Taking into account the exceedingly acidic nature of superacids (HF-SbF₅), substrates should undergo (poly)protonation. After the break of the glycosidic bond, polyprotonated carbohydrate species should be formed. As a consequence, the formation of side products^{13b} and unwanted polymerization should

be strongly unfavoured due to the charge repulsions in superacid (Scheme 1).¹⁷

In order to show the higher efficiency of HF-SbF₅ as compared to other acids, several acids and superacids (going from *H*₀ values of -14 for CF₃SO₃H to less than -21 values for HF-SbF₅ mixtures)² have been tested (Fig. 1a). With mineral acids, conversion of cellulose was very low (below 2%) and no water-soluble carbohydrate was observed. Note that cellulose can only be converted to glucose (20 wt%) after increasing the hydrolysis temperature to 130 °C. In agreement with previous existing reports, at 130 °C, the reaction is not selective and formation of black soluble materials was observed. The crystallinity of cellulose was studied by XRD analyses. Even though cellulose was totally decrystallized at 0 °C in the presence of HF and TFA (Fig. S3 and S4,† Fig. 1b), no depolymerization of cellulose occurred using such acids, showing the remarkable contribution of HF-SbF₅.

Considering that the polyprotonation of cellulose in superacid plays a pivotal role in the reaction mechanism, the effect of the acidity was investigated by varying the Bronsted-Lewis acid ratio.¹⁶ To this end, the molar percentage of SbF₅ was increased from 1.9 to 21.6 mol%. It was interesting to see that cellulose was totally converted independently of the medium acidity. The yield of glucose gradually increased from 10 wt% to 54 wt% when the amount of SbF₅ was increased from 1.9 mol% to 8.4 mol%. Over this percentage, the yield of glucose decreased due to the side repolymerization of glucose to cello-oligomers indicating that 8.4 mol% of SbF₅ is optimal (Fig. 1a). It should be noted that the possible reversion of the reaction, according to the amount of SbF₅, is of particular interest since it provides a straightforward access to valuable water-soluble cello-oligomers with high yields. All these results are in accordance with a polyprotonation of both cellulose and formed carboxonium intermediates in superacid.

To further evaluate this hypothesis, cellobiose was tested as a model substrate, dissolved in superacid HF-SbF₅ and characterized by low temperature ¹H NMR spectroscopy (Fig. S5†). A clean ¹H NMR spectrum could be obtained. The observed strongly deshielded signals at 10 ppm were consistent with the proposed (poly)protonation of the cellobiose in these conditions. Interestingly, the observed ratio between anomeric protons, signals at 5.25–5.05 ppm, and the protons coming from the protonation of the alcohols, signals at 10.12–9.93 ppm, was in accordance with the involvement of a (poly)protonated cellobiose as a reaction intermediate. These observations combined with the obtained results from cellulose could account for the contribution of (poly)protonated cellulose in the process.

With the aim of increasing the efficiency of the superacid treatment, reaction time, hydrolysis time and temperature were varied (Fig. 2). First, the effect of the hydrolysis time was investigated. When time of hydrolysis was increased over 10 min after the cellulose treatment by HF-SbF₅ at 0 °C, a dramatic decrease of the yield of glucose from 53 wt% to 10 wt% was observed mainly due to the dominant repolymerization of glucose (Fig. 2a). In such conditions, the solution remained colorless which still suggests the absence of degradation products. Remarkably, when the time of the hydrolysis step was decreased from 10 min to only 1 min a similar yield of glucose was obtained. Additionally, treatment time of cellulose with SbF₅ can

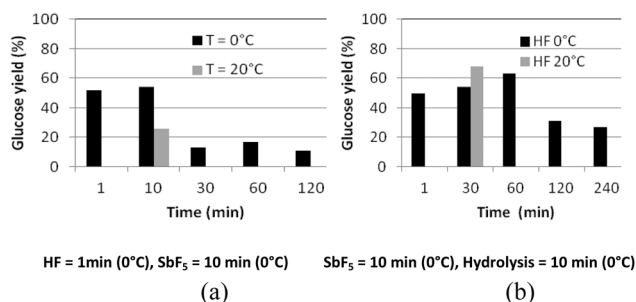


Fig. 2 Effect of (a) hydrolysis time and temperature; (b) HF time and temperature.

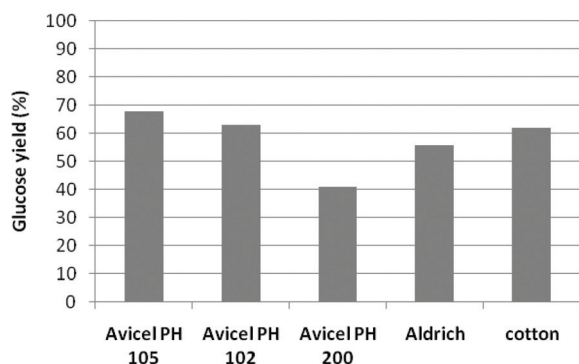


Fig. 3 Glucose production from different cellulose sources in superacid.

be decreased to less than 1 min without significant change of the yield of glucose showing that the *in situ* formed polyprotonated species are stable in our conditions. Taken together, these results show that the deconstruction of cellulose is quasi instantaneous using HF–SbF₅ superacid. Next, we investigated the influence of the reaction temperature in the hydrolysis step. For the sake of clarity, the time of hydrolysis was kept to 10 min in the following set of experiments. When the temperature was raised from 0 °C to 20 °C, the yield of glucose decreased from 53 wt% to 26 wt%. As observed above, with the increase of the hydrolysis time, the repolymerization of glucose was favored by an increase in the temperature. Finally, the stirring time in HF (decrystallization step of cellulose) was also studied. As shown in Fig. 2b, an optimum time of 60 min was required to get the highest yield of glucose. Note that when the temperature was raised from 0 °C to 20 °C, the optimum stirring time in HF was decreased to 30 min with a glucose yield of 68 wt%. From these results, we may conclude that optimum reaction parameters are: (step 1) 30 min of stirring in HF at 20 °C, (step 2) 8.4 mol% of SbF₅ at 0 °C and (step 3) hydrolysis at 0 °C.

This superacid-based process can be also successfully applied to other type of cellulose with different particle sizes (Fig. 3). Indeed, independently of the particle size (AVICEL PH 105 < 38 μm, AVICEL PH 102 < 75 μm), similar yields of glucose were obtained (>60 wt%). Additionally, cotton can be directly used leading to the formation of glucose with 62 wt% yield increasing the interest of this methodology (Fig. 3).

Conclusion

In conclusion, we reported here that cellulose can be conveniently decrystallized–depolymerized to glucose with up to 68 wt% yield in the presence of superacid HF–SbF₅. Such treatment is highly selective since only water-soluble carbohydrates (DP < 13) were detected. Remarkably, depending on the amount of SbF₅ used, the DP distribution of cello-oligomers could be adjusted. As compared to known acid treatments of cellulose, superacid HF–SbF₅ allows the selective deconstruction of cellulose to glucose (1) at low temperature (<20 °C vs. >120 °C for other acids), thus avoiding the formation of side products and post-bleaching treatment, (2) with short reaction time (<30 min) and (3) with a low cellulose–superacid mass ratio (1 : 10 vs. 1 : 500 with HF), hence facilitating the work-up procedure. In addition, by using low temperature NMR spectroscopy experiments, we showed that the (poly)protonation of the raw material is crucial. The process is highly selective, opening a promising route for the conversion of other biomass resources to high valued organic compounds.

Experimental section

Hydrolysis of cellulose was performed in superacid medium as follows: cellulose (0.4 g) was first stirred with 3 mL of HF at 0 °C at the required time prior to add SbF₅. Next, 20 mL of water were added to promote the hydrolysis of cellulose to water-soluble carbohydrates. At the end of the reaction, 40 g of Amberlyst 26 (–OH form) were added not only to neutralize the superacid but also to remove the antimony salts. The antimony content of recovered carbohydrates was lower than 35 ppm in all experiments. After filtration of the Amberlyst 26 resin and distillation of water under vacuum, products were quantified by SEC and HPLC calibrated with standards. More details regarding analysis are provided in the ESI.†

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