

Efficient electrophilic catalysis of 1,5-anhydrocellobiitol hydrolysis by Al^{III}; implications for the conservation of “rosin-alum” sized paper

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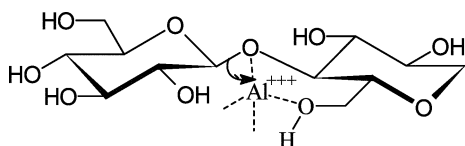
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Added Al₂SO₄ greatly accelerates the hydrolysis at 150.0 °C of 1,5-anhydrocellobiitol, a model for the β(1→4) linkages in cellulose, in succinate buffers of room temperature pH 3.05 and 3.35; E_a values for 20 mM Al^{III}- and H⁺-catalysed hydrolyses are 109 ± 3 and 140 ± 1 kJ mol⁻¹, respectively.

It is commonly found that the paper of eighteenth and early nineteenth century documents has much better mechanical properties than paper from the mid-nineteenth century up to the 1980s, which frequently is very friable, tears readily, and ruptures easily on folding. The culprit is “rosin-alum”[†] sizing (sizing with diterpene acids and aluminium sulfate), invented in 1807 and widespread by the 1840s;¹ earlier paper was sized with gelatine, which buffered it near neutrality. “Rosin-alum” sizing requires a change in the pH of the papermaking water system to 4–5 to maintain the aluminium in solution and introduces various hydrated aluminium species into the paper itself.[‡] Loss of paper strength is associated with a reduction in the degree of polymerisation of the cellulose in the fibres.⁴ As paper under ambient conditions is 4–9% water,² the reduction in the degree of polymerisation of cellulose in rosin-alum sized paper has hitherto been universally considered to arise by the usual mechanism of acid-catalysed hydrolysis of glycosides.⁵ Rosin-alum sized paper was thought to be labile both by virtue of the low pH under which it was made, and the presence of hydrated aluminium species, which buffered the paper at the low manufacturing pH. Conservation measures have therefore been based on ‘deacidification’ procedures⁶ and the permanence issue addressed by the use of acid-free papers.

Electrophilic catalysis of glycoside hydrolysis is, however, known.⁷ It is therefore a possibility that the rapid degradation of rosin-alum sized paper arises from direct action of Al^{III} as an electrophile: the 6-OH of the leaving group is well placed to act as a second ligand.

We therefore studied the effect of added aluminium sulfate on the rate of hydrolysis of 1,5-anhydrocellobiitol,⁸ a model for the β(1→4) glucan link in cellulose (Scheme 1). The coordination chemistry of Al^{III} is complex,^{1a} with polynuclear species variously written with 8 and 13 Al atoms predominating, even at sub-millimolar concentrations between pH 4 and 5, the pH of rosin-alum sized paper.^{1b} As we wished to examine much higher concentrations of Al^{III}, a lower pH was necessary to maintain homogeneity; moreover, it was necessary to buffer the solution strongly as the initial glucose product decomposed to an array of carboxylic acids.¹⁰



Scheme 1 Structure of 1,5-anhydrocellobiitol, showing a possible coordination pattern for Al^{III}. The intra-saccharide linkages are shown in the approximate conformation seen in cellulose. Coordination by O₆ is speculative, but has a possible precedent in the intramolecular conversion of lactose into allolactose by the *lacZ* β-galactosidase of *Escherichia coli*, where Mg^{II} may be the electrophile.⁹

Fig. 1 shows the effect of added aluminium and lanthanum sulfates on the pseudo-first order rate constant for hydrolysis of 1,5-anhydrocellobiitol (10 mM) at 150.0 °C in 100 mM succinate buffers with the room temperature pH values shown. § The much greater effect of Al^{III} compared to the La^{III} control establishes that the Al^{III} is indeed acting as an electrophile, rather than simply altering the ionic strength. The Al^{III} is likely to be essentially completely coordinated by the succinate buffer,^{1a} but a large kinetic effect is observed nonetheless. The apparent second-order rate constant is 0.8 s⁻¹ M⁻¹ at pH 3.05 and 0.4 s⁻¹ M⁻¹ at pH 3.35. Over this narrow pH range at least, approximate proportionality is observed between second-order rate constants and [H⁺], probably because protonation of the various Al^{III} species present increases their effectiveness as electrophiles. If the various Al^{III} species in rosin-alum sized paper likewise increase in effectiveness proportionally with [H⁺], then the relative importance of proton- and Al^{III}-catalysed depolymerisation of cellulose should be pH-independent.

In principle, the effect of added Al^{III} could arise not by the action of various >AlOH species as electrophiles, but by the kinetically equivalent pathway of nucleophilic attack of >AlO⁻ species on protonated 1,5-anhydrocellobiitol. Such a pathway is unlikely though, since even powerful nucleophiles accelerate cleavage of glycosides only very modestly; sodium azide (1.0 M) increases the rate of 2,4-dinitrophenolate production from 2,4-dinitrophenyl β-glucopyranoside by only 40%,¹¹ for example.

The temperature dependence of the rate constants at pH 3.54 for 0 mM Al^{III} and pH 3.33 for 20 mM Al^{III} gave E_a values of 140 ± 1

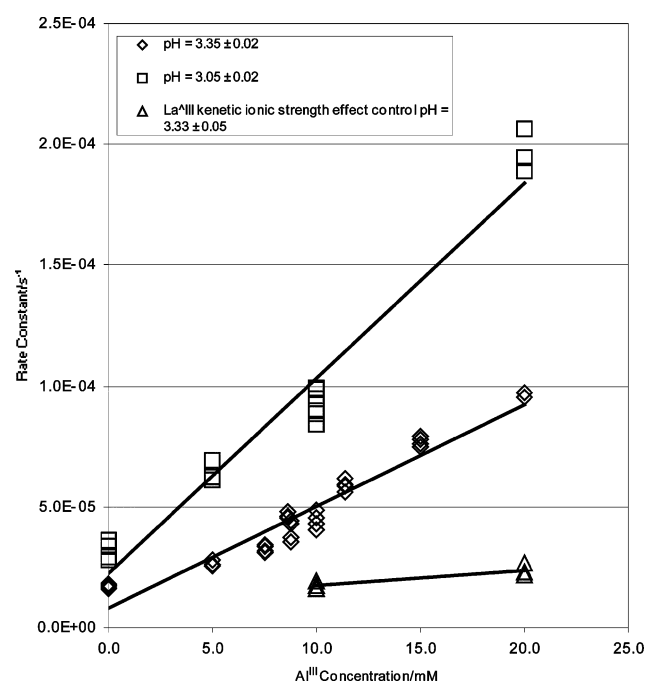


Fig. 1 First-order rate constant for hydrolysis of 1,5-anhydrocellobiitol at 150.0 °C as a function of added trivalent metal sulfates.

and $109 \pm 3 \text{ kJ mol}^{-1}$, respectively. Both values will be complex. The value for the proton-catalysed reaction, measured at constant buffer ratio, will include the heat of ionisation of the buffer, although this is likely to be small for an oxygen-based acid: 140 kJ mol^{-1} is close to those for the hydrolysis of simple alkyl glucosides, including sterically accelerated ones, in 0.5 M aqueous sulfuric acid.¹² The value of 109 kJ mol^{-1} derived from the first-order constant in 20 mM Al^{III} at 150.0 and 125.0 °C approximates to that for the Al^{III} -catalysed process: ~90% of the reaction is going through the electrophilic route at 150.0 °C.¶ The value will incorporate heats of Al^{III} complexation (to anhydrocellobiitol) and decomplexation (from the buffer). Nonetheless, it is significantly lower than E_a for the proton-catalysed reaction. Therefore, the importance of electrophilic catalysis relative to acidic catalysis will increase as the temperature decreases and approaches the ambient temperatures of document storage.

It is clear from these results that the effect of Al^{III} on cellulose degree of polymerisation in rosin-alum sized paper arises very largely because it acts as an electrophile, rather than a source of protons. 'Deacidification' programmes, such as that currently under way in the US Library of Congress,¹³ are only likely to have a positive effect by increasing the strength of the coordination of Al^{III} , rather than directly. Indeed, if they introduce electrophilic metal ions (such as the Cd^{II} from dimethylcadmium deacidification), they may even be counterproductive. Protocols to remove or mask the electrophile are needed, as well as more generic strategies such as routine low temperature storage.

Notes and references

† 'Papermakers' alum' is $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, rather than $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

‡ Paper properties such as pH and water content are measured under industry standard conditions. Thus, the water content of paper equilibrated under TAPPI standard conditions (50% relative humidity, 23 °C) is around 4–9%.² The pH of 40–60 year-old alum-sized paper, determined from the pH of aqueous extracts under standard conditions, is between 3.5 and 5 and the aluminium content [weight $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ /weight dry paper], determined by atomic absorption spectroscopy of acid extracts, ranges between 1.3 and 6.7% (average 3.8%).³ Much of this will be precipitated or absorbed, but if it is all dissolved in the water layer on the fibres, potential concentrations of Al^{III} in the molar range would be obtained. We see unambiguous effects in free solution at much lower concentrations.

§ Samples were sealed in melting point capillaries, immersed in a thermostatted oil bath, removed at intervals, and analysed by HPLC with

refractive index detection. Rate constants were calculated from the ratio of 1,5-anhydroglucitol to 1,5-anhydrocellobiitol, glucose giving an array of low MW products which did not give a signal after the solvent peak. Buffer solutions were brought back to their original pH by addition of NaOH after aluminium sulfate addition. The maximum pH change on Al^{III} addition was –0.3 (with 20 mM Al^{III}).

¶ The 10% of the reaction going through the proton-catalysed pathway at 150.0 °C will therefore be lower at 125.0 °C, so the E_a measurement will not be compromised by the minor, proton-catalysed pathway.

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