THE HYDROLYSIS OF COTTON CELLULOSE BY HYDROCHLORIC ACID IN BENZENE*

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ABSTRACT

The partial hydrolysis of cotton cellulose by hydrogen chloride in benzene containing various proportions of water has been studied by measurements of fluidity, loss of weight, and copper number. Both the rate and site of hydrolysis are strongly dependent on the amount of water present. The determining factors are the partition of the hydrogen chloride between the water in the benzene and that adsorbed by the cellulose, and the relative accessibility of glycosidic linkages near the ends of chains and those far removed from chain ends. With little water present, hydrolysis tends to be confined to the ends of the cellulose chains.

INTRODUCTION

The hydrolysis of glycosidic linkages in fibrous cellulose by dilute, aqueous acids is generally believed to begin in randomly placed, accessible regions in the fibres and thereafter to proceed at the ends of crystallites, the lengths of which are exponentially distributed[1]. Less is known about the action of acids in non-aqueous, protic solvents, but alcoholysis, although more rapid, appears to be completely analogous to hydrolysis[2]. No reaction at all would be expected in dry, aprotic solvents; according to Girard[3], dry hydrogen chloride gas has no effect on cellulose. However, as long ago as 1923, it was reported[4] that dry cotton fabric suffered a much more-rapid loss of strength in dry solutions of hydrogen chloride in ethanol or benzene than in aqueous solutions of similar or even greater concentration. The suggestion that hydrogen chloride can degrade cellulose in the complete absence of water (because of its enhanced "reactivity" in non-aqueous solvents) is untenable and we have therefore reinvestigated the phenomenon. We have not succeeded in eliminating the last traces of water from suspensions of cellulose in solutions of hydrogen chloride in benzene, but we have shown that, when small, known amounts of water are added, they are preferentially adsorbed by the cellulose, taking hydrogen chloride with them

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and thereby creating conditions under which severe degradation is to be expected. We have also found that hydrolysis at sites near the ends of the cellulose chain molecules predominates under dry, or nearly dry, conditions, whereas under moist conditions, the cellulose structure is sufficiently opened-up to allow hydrolysis to occur along the whole length of accessible chains.

EXPERIMENTAL

Materials. — A long-staple, Sudanese cotton was mechanically cleaned and 300-g lots in sliver form were boiled twice with 2% aqueous sodium hydroxide containing Lissapol N (0.2%) under an excess pressure of ∼35 p.s.i. (giving a temperature of 130–140°). Care was taken to exclude air from the pressure vessel, and the cotton was washed successively with cold water, 0.2M hydrochloric acid, and cold water after each boiling. The final washing was continued until B.D.H. Universal indicator showed that all the acid had been extracted, and the cotton was then dried by centrifugation and exposure to the air.

Benzene (AnalaR) was dried by refluxing with calcium hydride for ∼1 week and distilling (b.p. 80.0–80.2°). It was transferred to the vessel in which it was to be used by distillation in a closed system to prevent contact with the laboratory atmosphere at any time.

Hydrogen chloride (Honeywill and Stein Ltd.) was dried by bubbling through conc. sulphuric acid contained in two Dreschel bottles having inlet tubes with sintered-glass ends and protected on each side by empty Dreschel bottles. The dry gas was then bubbled for 2–3 days through benzene in a round-bottomed flask in a dry box through which air containing less than 2 p.p.m. of water (as determined by the frost point) was circulating at a rate of 25 l. min^{-1}. The air was dried by passing it through Laporte's molecular sieve T4A. In this way, ∼0.4M solutions were obtained. Excess hydrogen chloride was passed through more bottles containing sulphuric acid, before being allowed to escape into a fume cupboard, in order to prevent any back diffusion of water vapour from the atmosphere into the benzene. In two experiments, known amounts of water were added to the solution, from a micrometer syringe, inside the dry box. In all other experiments where water was present, it was adsorbed on the cotton before this material was added to the hydrogen chloride solution. All glassware used in the preparation of the solutions of hydrogen chloride in benzene was heated in an oven at 150° for several days before use.

The concentration of hydrogen chloride in the benzene was determined by adding known amounts from a weight-pipette to an excess of M sodium hydroxide and back-titrating with M hydrochloric acid.

Methods. — Weighed samples of cotton (2 g) were either dried over phosphorus pentaoxide for 2 weeks in an evacuated desiccator in a dry box at room temperature, or exposed to atmospheres of known relative humidity (obtained by means of aqueous solutions of sulphuric acid) for 1 week at room temperature. In the latter cases, samples (1 g) were simultaneously treated in the same way and their moisture contents

determined by weighing before and after being heated to 110° for 3 h. The reaction samples were weighed in stoppered bottles and transferred rapidly to 100-cm^3 conical reaction flasks. With the completely dry sample, this transfer was done in the dry box. The solution of hydrogen chloride in benzene (80 cm^3) was introduced into the reaction flasks inside the dry box. The flasks were stoppered immediately and placed in a thermostat at 25.00 $\pm$0.02°. The correct volume of benzene was obtained by means of a mark on the reaction flask. After the required length of time, the samples were filtered off into weighed sintered-glass crucibles and washed with several portions of benzene, followed by several portions of ethanol, and finally with numerous portions of distilled water until no change in the pH of the wash water was observed (B.D.H. Universal indicator) over a period of 16 h. The samples were then dried to constant weight over phosphorus pentaoxide in an evacuated desiccator, so that the loss of weight during the total process of hydrolysis and washing could be calculated.

In a comparative experiment, cotton was treated with 0.45M aqueous hydrochloric acid.

In order to determine the partition of hydrogen chloride between benzene and cotton of known initial moisture content, samples of cotton (1 g) were treated as already described; on being removed from the reaction flask, they were rapidly squeezed free of excess benzene and dropped immediately into weighed conical flasks (250 cm^3) containing M sodium hydroxide (25 cm^3). After shaking and reweighing, the excess of sodium hydroxide was titrated with M hydrochloric acid. In order to calculate the amount of hydrogen chloride associated with the cotton, it was assumed, that the concentration in the benzene not removed from the cotton was the same as in the original solution.

The products of degradation were characterised by their copper numbers and fluidities in cuprammonium hydroxide, both of which are directly related to the extent of reaction. Copper numbers were measured by the Braidy method[5] and fluidities were measured with 0.5% solutions at 20° in the special viscometers described by Calvert and Clibbens[6].

RESULTS AND DISCUSSION

Partition of hydrogen chloride between benzene and moist cotton. The rates of adsorption of hydrogen chloride from 0.4M solutions in benzene at 25° by cotton having various moisture regains are shown in Fig. 1. At regains of 4.7% and 6.0% (Curve 1), the amount of hydrogen chloride adsorbed rises rapidly to an equilibrium value of $\sim$5.5%. The amount required to give a saturated solution (42.7% by weight) in the water present would be 2.0% and 2.55% at regains of 4.7% and 6%, respectively. Similarly, at 3.4% regain (Curve 2), 1.45% of hydrogen chloride would be required for saturation; however, an equilibrium value of 4.5% was observed, although this was attained more slowly than with the moister samples. With only 1.1% moisture regain (Curve 3), 0.45% of hydrogen chloride would be required for a
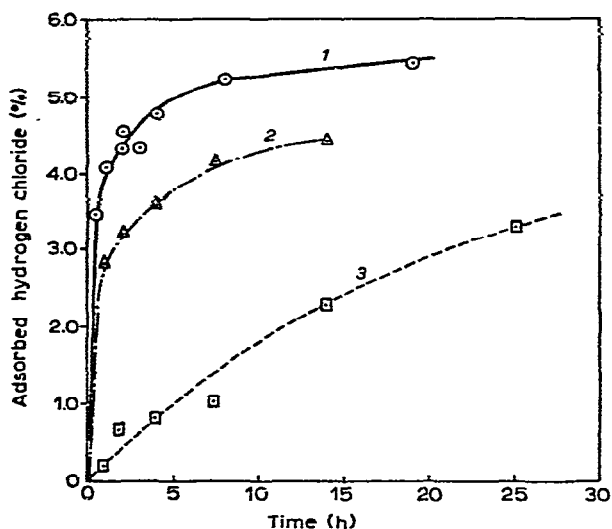
Fig. 1. Adsorption of hydrogen chloride from 0.4M solution in benzene at 25° on to cotton having the following moisture regains: (*1*) 4.7% and 6.0%; (*2*) 3.4%; (*3*) 1.1%.
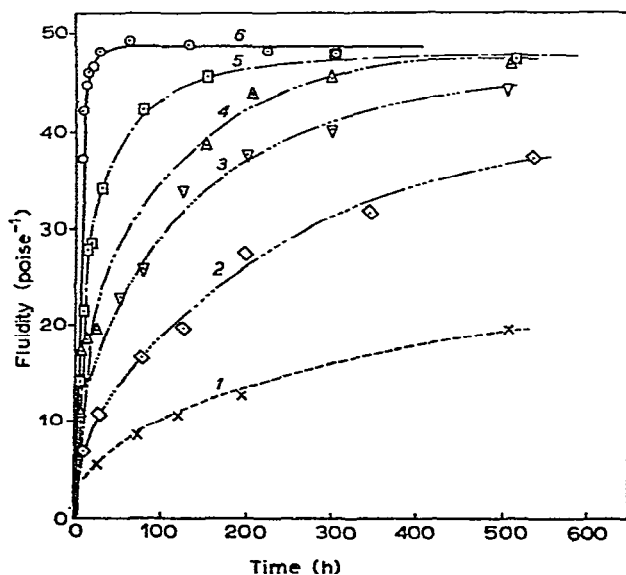

Fig. 2. Rate of increase of fluidity for cotton treated with hydrogen chloride in benzene at 25°: (*1*) 0.45M (aqueous acid), ~6% moisture regain; (*2*) 0.38M (benzene–HCl), "0.0%"; (*3*) 0.38M, 0.5%; (*4*) 0.42M, 1.7%; (*5*) 0.39M, 2.7%; (*6*) 0.41M, 3.4%.

saturated solution; however, over 3% was adsorbed during 25 h, although the rate of adsorption was very low. Thus, it appears that considerable quantities of hydrogen chloride are adsorbed by the cotton by a mechanism additional to dissolution in the water present, which, in all four cases, produces very concentrated solutions of hydrochloric acid within the fibres. The additional process is much slower than hydrochloric acid formation, but its rate increases as the amount of water in the fibres increases. It will be assumed in subsequent discussion that the effective degrading-agent in the systems studied is hydrochloric acid of a concentration approaching that of a saturated solution ($\sim$12M).

Fluidity measurements. The rate of increase of fluidity of cotton having various moisture regains in $\sim$0.4M hydrogen chloride in dry benzene at 25° is shown in Fig. 2; the rate for aqueous hydrolysis is shown for comparison (Curve 1). At all regains, including a nominal zero value (Curve 2), although it is much greater in benzene than in water, it increases with increasing moisture regain. This implies that the hydrolysis sites become progressively more randomly distributed as the amount of water increases either on a chain-molecular basis, or on a micromorphological basis, or possibly on both. The levelling-off fluidity at the higher regains (Curves 5 and 6) is $\sim$50, which is the limit to which Curve 1 must ultimately tend[7]. Whether or not the curves for the lower regains would reach the same limit after a long enough time is not evident, but it is probable that there is insufficient water present for them to do so.

Since no degradation is to be expected under absolutely dry conditions, that represented by Curve 2 must be attributed to a small, but undetermined, amount of water left in the system in spite of the efforts made to remove it. This water is most probably associated with the cotton; displacement with ethanol was not attempted, because ethanol might have been retained at least as strongly as water and ethanolysis occurs more rapidly than hydrolysis[2]. Furthermore, since ethanolysis produces no reducing end-groups, its extent cannot be assessed by measurements of copper number.

Two other features of the effect of hydrogen chloride in benzene on the fluidity of cotton are illustrated in Figs. 3 and 4. Fig. 3 shows that the rate of hydrolysis increases with increasing concentration of hydrogen chloride, even when differences in moisture regain might be expected to lead to the opposite result. Fig. 4 illustrates the effect of introducing water directly into the benzene instead of by way of the cotton. Curve 1 (the same as Curve 3 in Fig. 2) represents the introduction of cotton with a regain of 0.5% into dry benzene, and Curve 2 the introduction of dry cotton into benzene containing 0.02% by weight of water (an amount equivalent to a regain of 0.7% by the cotton). The rate of fluidity rise is lower when the water is initially present in the benzene than when it is in the cotton; in fact, the rate curve for initially wet benzene is almost the same as that for nominally, absolutely dry conditions (Curve 3, the same as Curve 2 in Fig. 2). The controlling factor is probably the state of aggregation of the cellulose fibrils, which depends more on the moisture regain at the start of the reaction than on the total amount of water present.
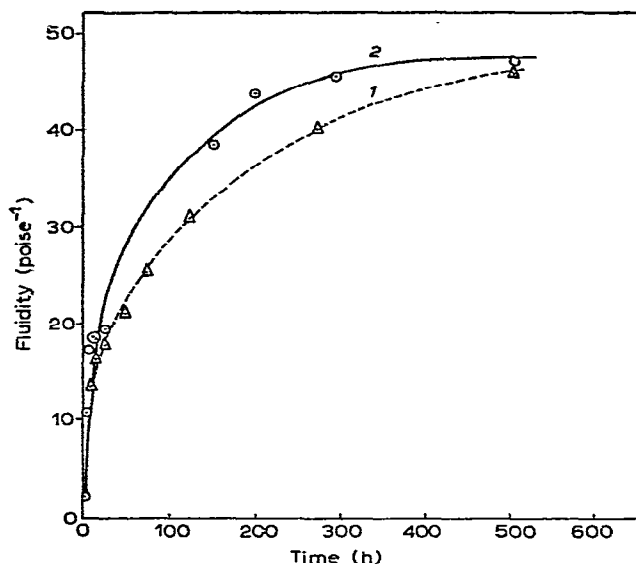
Fig. 3. Effect of hydrogen chloride concentration in benzene at 25° on the rate of fluidity change: (1) 0.35M acid, 1.9% moisture regain; (2) 0.42M, 1.7%.
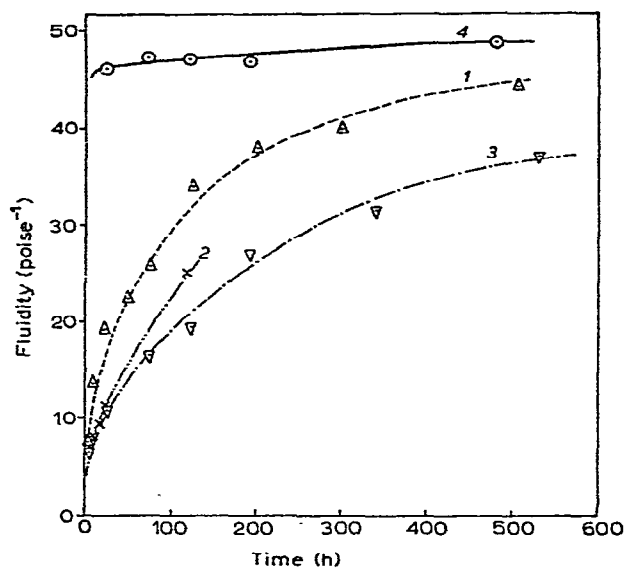

Fig. 4. Effect of method of introducing water on rate of fluidity increase of cotton treated with hydrogen chloride in benzene at 25°: (1) 0.38M acid, 0.0% of water, 0.5% moisture regain of cotton; (2) 0.38M, 0.02%, "0.0%"; (3) 0.38M, 0.0%, "0.0%"; (4) 0.43M, 0.05%, 6.0%.

Finally, an experiment (Curve 4) in which air-dry cotton (regain, ~6%) was added to 0.43M hydrogen chloride in benzene containing 0.05% of water showed that the levelling-off fluidity is attained roughly as quickly as in 10M hydrochloric acid in water[7] (~24 h), thus reinforcing the conclusion drawn in the last paragraph.

Formation of water-soluble material. The loss of weight suffered by cellulose during hydrolysis by aqueous acids takes place in two stages, a rapid, initial loss being followed by a much slower reaction[7,9]. It has been found that no loss of weight occurs when cotton (moisture regain, 2.4%) is treated with 0.41M hydrogen chloride in dry benzene for 10 days at 25°. Losses are sustained, however, at all moisture regains on subsequent washing with ethanol and water (Fig. 5). The rate at which
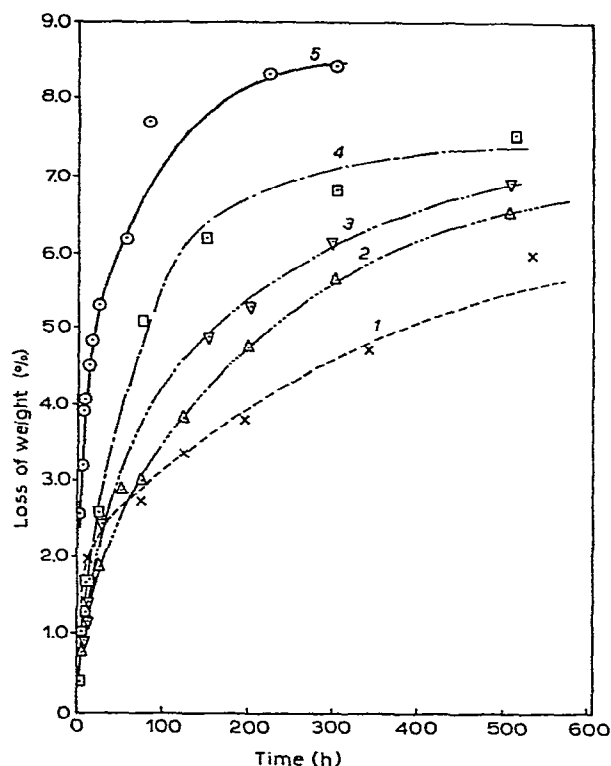

Fig. 5. Rate of loss of weight of cotton treated with hydrogen chloride in benzene at 25° and washed with ethanol and water: (*1*) 0.38M acid, "0.0%" moisture regain; (*2*) 0.38M, 0.5%; (*3*) 0.42M, 1.7%; (*4*) 0.39M, 2.7%; (*5*) 0.41M, 3.4%.

the losses occur increases as the amount of water in the system increases, but, in every case, becomes very slow as the reaction proceeds. The reaction must cease altogether when all the water has been consumed.

The formation of water-soluble material can result only from hydrolysis of glycosidic linkages near the chain ends, although the simultaneous, rapid rises in

fluidity show that appreciable amounts of reaction at sites far from chain ends must also take place. If all the water present were consumed in removing single D-glucose residues from the chain ends in the experiments illustrated in Fig. 5, the losses of weight would be as shown in Table I. The actual losses at 500 h (300 h in Expt. 5) are also shown and, whilst these appear to have reached a maximum in Expts. 4 and 5, they have clearly not done so in Expts. 2 and 3. Nevertheless, the ratio of the actual to the calculated weight-loss decreases as the amount of water increases. This can only mean that the more water there is associated with the cotton, the more intermediate glycosidic linkages are hydrolysed in preference to those near chain ends. The loss of weight at a nominal moisture regain of zero is anomalous and is only explicable on the assumption that some water was in fact present.

TABLE I

WEIGHT LOSSES DURING HYDROLYSIS OF CELLULOSE

Experiment (as in Fig. 5)	Water on cotton (%)	Loss of weight (%)		W_a/W_c
		Calc. (W_c)	Actual (W_a)	
1	"0.0"	—	5.5	—
2	0.5	4.5	6.5	1.44
3	1.7	15.3	6.9	0.45
4	2.7	24.3	7.4	0.30
5	3.4	30.6	8.5	0.28

The effect of water on the relative importance of hydrolysis at intermediate and chain-end glycosidic linkages is further clarified by considering the relation between fluidity and loss of weight. In Fig. 6, values of these two properties, read at a series of arbitrarily chosen times from the smoothed curves in Figs. 2 and 5, are plotted against one another. Hydrolysis in water and hydrolysis in benzene are clearly distinguished. In water (Curve 1), the fluidity rises to quite high values before any appreciable loss of weight is observed, thus confirming the preponderance of reaction at sites far from the ends of chains. In benzene, under the driest conditions obtained (Curve 2), the fluidity reaches only 10 at a weight loss of 2%, thus showing that the proportion of chain scissions at sites far from chain ends must be very small. At higher extents of reaction, the rate of fluidity rise relative to weight loss increases as glycosidic bonds at intermediate positions in the chain molecules become progressively more accessible. Similarly, as water is added to the system, the curves (3, 4, and 5–except for the initial part of 3) are shifted progressively towards that for aqueous hydrochloric acid, again indicating a progressive increase in the proportion of intermediate glycosidic linkages that are attacked.

The initial part of Curve 3 appears to be anomalous. A plausible explanation is that whatever water is present in the nominally, completely dry cellulose is trapped in the regions of greatest disorder, where the proportion of chain ends is greatest[10], whilst the adsorption of a very small quantity of water by the "dry" material may
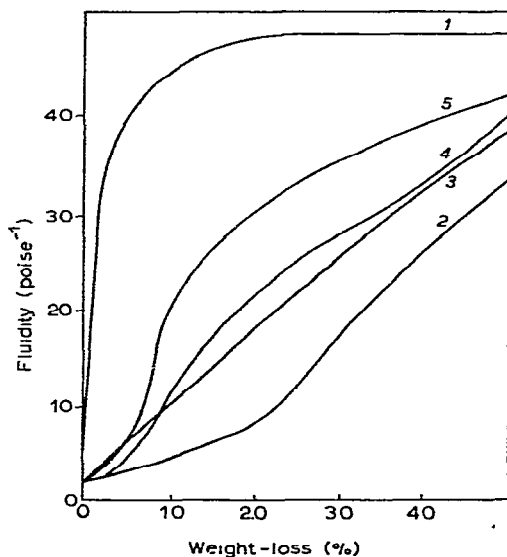
Fig. 6. Relation between fluidity and weight-loss of cotton treated with hydrogen chloride in benzene at 25° and washed with ethanol and water: (*1*) 0.4M (aqueous acid), ~6% moisture regain; (*2*) 0.38M (benzene-HCl), "0.0%"; (*3*) 0.38M, 0.5%; (*4*) 0.42M, 1.7%; (*5*) 0.39M, 2.7%.
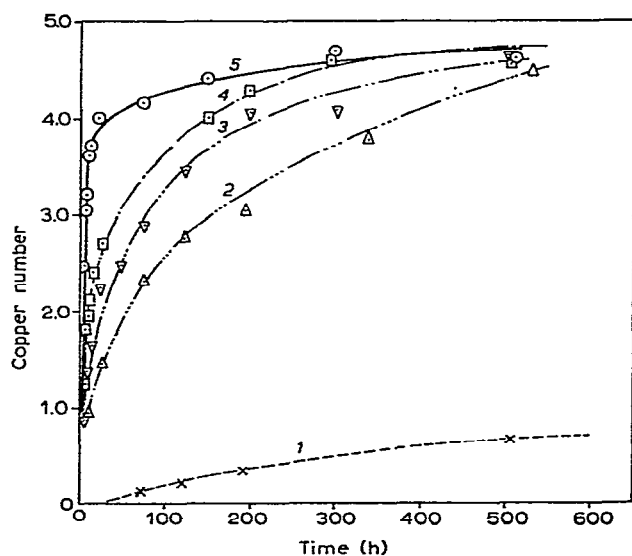

Fig. 7. Rate of increase of copper number of cotton treated with hydrogen chloride in benzene at 25° and washed with ethanol and water: (*1*) 0.45M (aqueous acid), moisture regain ~6%; (*2*) 0.38M (benzene-HCl), "0.0%"; (3) 0.38M, 0.5%; (4) 0.42M, 1.7%; (5) 0.39M, 2.7%.

take place only on fibrillar surfaces, where all glycosidic linkages are accessible to attack. Thus, when water is added to "dry" material, a first portion is adsorbed on fibrillar surfaces already exposed, a second portion in regions of disorder rich in chain ends, and the remainder on new fibrillar surfaces formed by opening up the original structure. The initial part of Curve 3 represents the only conditions among those studied where the effect of the adsorption of the first portion of the water was discernible. In the later part of Curve 3 and in Curves 4 and 5, the effects of the second and residual portions of adsorbed water predominate.

Measurements of copper number. Rate plots of copper number (Fig. 7) show a pattern similar to that already described for fluidity. However, the significance of the copper-number measurements is best revealed by correcting them for the amount of reducing material dissolved during the washing of the samples, and then considering them in relation to fluidity, as has been done with the loss-of-weight results. The diminution of the copper number due to dissolution of short-chain material would be $63.5Nw/162n$, where w is the percentage loss of weight, N the number of atoms of copper reduced per end-group during the measurement, and n the average d.p. of the soluble oligomers. The value of N has been reported[11] as 22. A value of 8 has been chosen for n, as this represents the limit of solubility of the oligosaccharides[12] and would therefore give the minimum, reasonable correction.
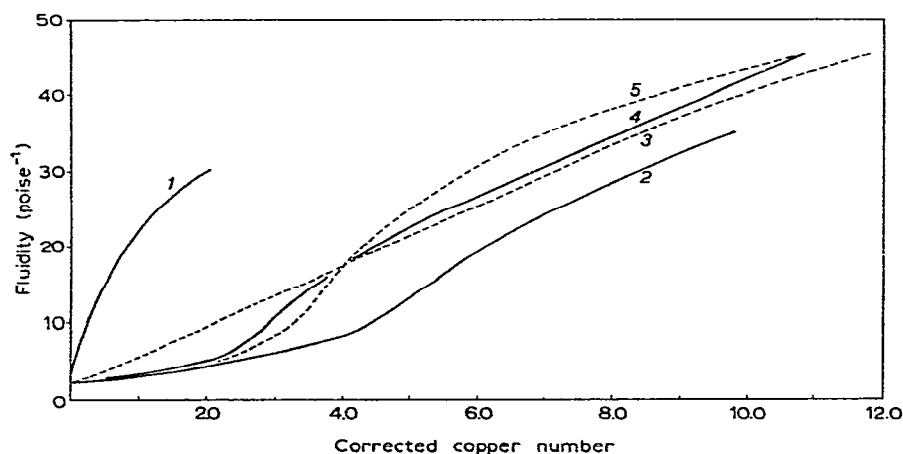

Fig. 8. Relation between fluidity and corrected copper number of cotton treated with hydrogen chloride in benzene at 25° and washed with ethanol and water: (*1*) 0.45M (aqueous acid), moisture regain ~6%; (*2*) 0.38M (benzene–HCl), "0.0%"; (*3*) 0.38M, 0.5%; (*4*) 0.42M, 1.7%; (*5*) 0.39M, 2.7%.

A plot of fluidity against corrected copper number (Fig. 8) is very similar to that for loss of weight (Fig. 6). The main difference is that Curve 4, as well as Curve 3, falls above Curve 5 in the early stages of the reaction. This is probably because the loss of weight and copper number are both indicative of the relative proportion of scissions at the ends and middle of chains, but are not related to it in exactly the same

way, and so lead to slightly different conclusions as to the point up to which the effect of the first portion of adsorbed water will predominate. In general, the results confirm the previous conclusions.

   Mechanism and site of hydrolysis. The acid-catalysed hydrolysis of glycosides[13] is generally believed to proceed *via* protonation of the glycosidic oxygen followed by the formation of a cyclic carbonium ion by scission of the glycosidic linkage. The hydrolysis of cellulose is represented in Scheme 1; usually, only steps *1* and *4* are regarded as reversible, but in principle all four steps may be reversible. Under the usual conditions, the rate-controlling step is *2*, but it is probable that step *3* would also become quite slow under nearly water-free conditions. Under special conditions, such as when the two new chain-ends resulting from hydrolysis are prevented from separating by being in the solid state, the reverse of step *2* (*i.e.*, recombination) might occur to a significant extent.
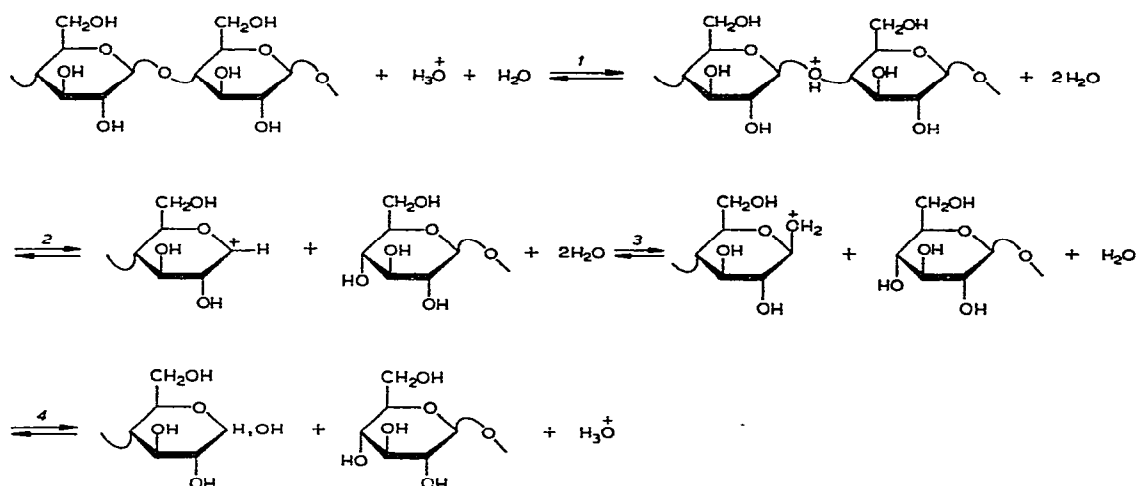
Scheme 1. Hydrolysis of cellulose.

   The most-stable conformation of the carbonium ion formed in step *2* is probably the half-chair, in which C-1, C-2, C-5, and O have been brought into one plane by a small amount of rotation about the C-2–C-3 and C-4–C-5 bonds[14]. These rotations are more difficult in cellulose than in simple glycosides because of the long chain of D-glucose residues attached to C-4 and because of hydrogen bonding between adjacent chain molecules. Both these factors will impede rotation about the C-4–C-5 bond to an extent that depends on the relative disposition of the chain molecules in the solid cellulose.

   Cotton cellulose is highly crystalline; its fibres consist of macro-, micro-, and ultimate fibrils, the last-named being of indeterminate length and $\sim$40 $\times$ 60 Å (*i.e.*, 8 $\times$ 12 chain molecules) in cross section[15]. The ultimate fibrils are likely to contain

randomly distributed regions of disorder associated with chain ends[10]. Chemical reactions, such as hydrolysis, that do not involve intrafibrillar swelling can take place only in these disordered regions or in fibrillar surfaces. They are, however, affected by the presence of substances that can cause an increase in "accessibility" by, for example, interfibrillar swelling. This picture of the supermolecular structure of cotton cellulose is consistent with Sharples's work[9] (in which he sited hydrolysis first in randomly distributed "amorphous regions" and then at crystallite ends). It also explains the present results. Under conditions where very little water is present, hydrolysis is largely confined to the regions of disorder where chain ends are preponderant. Any reaction that may occur at intermediate bonds in fibrillar surfaces will be retarded by the retardation of steps 2 and 3 already referred to. As water is added to the system, interfibrillar swelling will take place, thus exposing more intermediate glycosidic bonds in fibrillar surfaces. The retardation of step 3 due to lack of water will be diminished, although the reverse step 2 will continue to exert an influence. The overall effect will be an increase in the proportion of intermediate glycosidic linkages hydrolysed as the amount of water present is increased.

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