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CHLORINATION AND PHOSPHORYLATION OF COTTON CELLULOSE BY REACTION WITH PHOSPHORYL CHLORIDE IN *N,N*-DIMETHYLFORMAMIDE

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ABSTRACT

Native cotton yarn reacts rapidly with phosphoryl chloride in *N,N*-dimethylformamide to produce highly chlorinated cellulose (degree of substitution of 0.5 or greater), phosphorylated cellulose, and cellulose formate. The ratio of chlorination to phosphorylation was readily controlled by varying the concentration of phosphoryl chloride in *N,N*-dimethylformamide.

Reaction variables studied were the reagent concentration, reaction temperature, and reaction time. The effect that each of these variables has on the tensile and flammability properties of the resultant yarns was investigated. Yarns containing large proportions of chlorine have high tensile-strength and are unusually extensible, whereas yarns containing phosphorus have high flame-resistance. A mechanism for the selective chlorination or phosphorylation of the cotton cellulose is advanced.

INTRODUCTION

Previous studies utilized various reagents for halogenation and phosphorylation of cellulose, but, in many instances, either the reaction had to be performed under stringent and cumbersome conditions, or the reagents were not selective in their chemical behavior towards cellulose. Rath and co-workers[1] achieved bromination or chlorination of cotton fibers by adding bromine or chlorine to cotton cellulose suspended in a mixture of red phosphorus and *N,N*-dimethylformamide (DMF), but the overall retention of strength of the fibers was 40% or less, and the reaction time required ranged from 2 to 6 h. Reid and Mazzeno[2] treated cotton with phosphoryl chloride in pyridine, and a high degree of phosphorylation was achieved at 120°. Large proportions of chlorine were incorporated into the cellulose, regardless of the concentration of the reagent used.

Experimental procedures giving only chlorination are usually cumbersome (the thionyl chloride–pyridine method[3]) or require extensive pretreatment prior to

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reaction, *viz.*, mercerization and solvent-exchange[4,5]. Although we recently chlorinated cotton rapidly *via* an iminium salt[6], namely, chlorodimethylformiminium chloride ($HCClNMe_2Cl$), the proportion of chlorine incorporated was limited to ~6% by the low solubility of the iminium salt in DMF and by the accelerated degradation occurring at the high reaction-temperatures needed to increase chlorination.

However, we have found that, depending on the concentrations used, the reaction of phosphoryl chloride in DMF with cotton cellulose at 70–80° can selectively yield either chlorodeoxycellulose or phosphorylated cellulose.

Chlorination produces highly extensible fibers having useful tensile properties, whereas phosphorylation imparts flame resistance. The present report describes the effect of reaction conditions on the chemical and physical properties of these cellulosic derivatives. In addition, a mechanism for the selective chemical behavior of the reaction system with cotton cellulose is proposed.

EXPERIMENTAL

General. — The cellulose employed was loose-twist, 12/3 (tex-151), Deltapine, cotton yarn purified by kier-boiling. Phosphoryl chloride ($POCl_3$), DMF, sodium hydroxide, and glacial acetic acid were reagent-grade, commercial materials.

In the usual treatment, untreated, kiered yarn was immersed in an excess of DMF for 30 min at 25°, and then treated with $POCl_3$–DMF at the ratio of 40 g of this solution per g of cotton. The yarn was then successively washed three times with DMF, ice water (until the pH of the washings was 4 or higher), and tap water (for 30 min), and air-dried. In some instances, the yarns were also successively washed with 5% aqueous sodium hydroxide (after the ice-water wash), water, 5% aqueous acetic acid, and tap water (10 min each), and air-dried.

Elemental analyses for chlorine and phosphorus were performed by a commercial laboratory; analyses for calcium were obtained by X-ray fluorescence, and for nitrogen by the Kjeldahl method at our laboratories. Infrared (i.r.) spectra were recorded on a Perkin–Elmer Model 137B Infracord spectrophotometer* for pellets of the cellulose derivatives in potassium bromide.

The breaking strength, elongation-at-break, and tenacity of the yarns were determined by ASTM method D-2256-64T. The match or "clock" test to determine flame resistance is that described by Reeves *et al.*[7].

RESULTS AND DISCUSSION

Effect of reagent concentration and reaction temperature on the P:Cl ratio. — The mode of reaction of cotton cellulose with $POCl_3$–DMF was extremely dependent on the concentration of the reagent. This was true over a wide range of temperature

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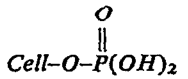
*Use of the name of a company or product does not imply approval or recommendation of the product by the Department to the exclusion of others that may also be suitable.

(50–100°), although the most noticeable differences were observed at 75°. At 75°, cotton yarns pretreated with DMF, centrifuged, and treated for 1 h with 2–12% $POCl_3$ showed wide variation in phosphorus and chlorine contents (see Table I). The yarn treated with 2% $POCl_3$ contained 3.3% of P and only 0.8% of Cl, corresponding to a degree of substitution (d.s.) of 0.19 by phosphate and of 0.04 by chlorine. With 4% $POCl_3$, equal percentages of chlorine and phosphorus were incorporated into the cellulose (d.s., by each, of 0.08). With 8% $POCl_3$, however, chlorination predominated, and the resultant yarns contained 9.7% of Cl (d.s., by chlorine, of 0.47) as well as 1.2% of P (d.s., by phosphate, of 0.06). Increasing the concentration to 10–12% $POCl_3$–DMF produced moderate additional increases in the chlorination, but the degree of phosphorylation remained low (1.3–1.4% of P). The phosphorus content reached a maximum with 2% $POCl_3$, and levelled off sharply at higher concentrations, whereas the chlorine content was negligible for 2% $POCl_3$, but showed a marked increase when the concentration was raised to 8% (see Fig. 1).

TABLE I

EFFECT OF REACTION TEMPERATURE AND REAGENT CONCENTRATION ON THE MODE OF REACTION OF $POCl_3$–DMF WITH CELLULOSE

Reaction temp. (°C)	*$POCl_3$ (%)*[a]	*Gain in wt. (%)*	*P (%)*[b]	*Cl (%)*[b]	*D.s.*[b]  $\mathrm{Cell{-}O{-}\overset{\overset{O}{\Vert}}{P}(OH)_2}$	*D.s.*[b] *Cell–Cl*
50	2	9.8	1.6	0.4	0.09	0.02
	4	11.3	1.5	0.6	0.08	0.03
	8	10.9	0.6	0.6	0.03	0.03
75	2	17.7	3.3	0.8	0.19	0.04
	4	13.2	1.5	1.8	0.08	0.08
	8	29.2	1.2	9.7	0.06	0.47
	10	32.3	1.4	10.8	0.08	0.52
	12	34.8	1.3	11.4	0.07	0.55
100	2	19.7	3.8	0.8	0.22	0.04
	4	22.9	3.2	2.5	0.18	0.12
	8	36.7	3.5	7.7	0.20	0.37

[a] After immersion in DMF for 30 min, all yarns were centrifuged for 1 min, and then allowed to react for 1 h at the above-listed temperatures and reagent concentrations (bath ratio of 40 g of solution/g of cotton), cooled, washed with DMF, ice water, and tap water (for 30 min), and air-dried. [b] Uncorrected for moisture, ash, and gain in weight due to production of cellulose formate; Cell–OH = cellulose.

At 50°, similar trends were observed when the concentration of $POCl_3$ was varied, but the degrees of chlorination and phosphorylation obtained were much lower than at 75° (see Table I), and, therefore, use of the lower temperature was infeasible for achieving useful levels of chemical substitution. More phosphorus was incorporated into the cellulose at 100° than at 75°, and the phosphorus content remained constant, even on increasing the concentration of the $POCl_3$ to 8%. At 100°,

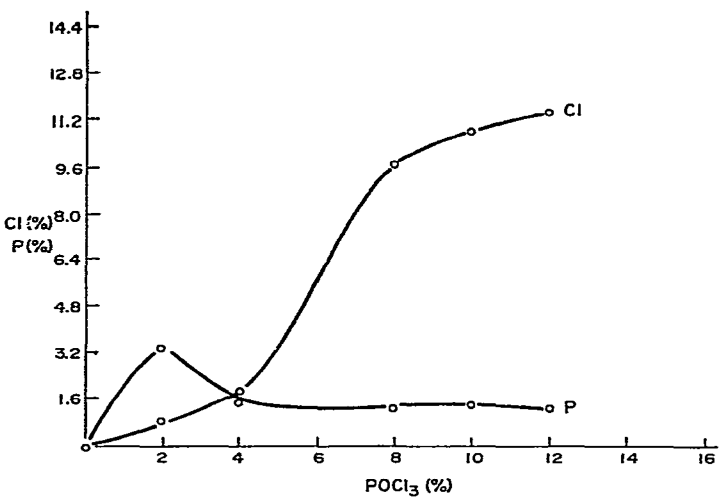


Fig. 1. Plot of P (%) and of Cl (%) content *versus* concentration of $POCl_3$ in DMF (reaction time 1 h, temperature 75°, conventional washing with tap water).

chlorination markedly increased as the concentration of the reagent was increased from 2 to 8%, but the product composition was not nearly so selective as that achieved at 75°.

The d.s. by phosphate and chlorine cannot account for all of the gain in weight of the resultant yarns (see Table I). As shown in our earlier work[6], chlorination of cellulose with the iminium salt derived from thionyl chloride and DMF afforded substantial amounts of cellulose formate also. The production of cellulose formate was also observed in the reaction of cotton with $POCl_3$–DMF. Although a quantitative assessment has not been made, the d.s. of the cellulose formate probably varies from 0.2 to 1.0, depending on the reaction temperature and the concentration of the $POCl_3$–DMF; this was shown qualitatively by the differences in weight loss of resultant yarns that were washed briefly with 5% aqueous sodium hydroxide. This alkaline treatment caused the strong carbonyl absorption present in the i.r. spectra of the treated yarns to disappear, without accompanying hydrolysis of the phosphate or chloro groups in the cellulose, as ascertained by elemental analyses. The presence of cellulose formate, the ratio of chlorinated to phosphorylated products, and the role of temperature in the distribution of the cellulosic products, will be discussed later in terms of a mechanism proposed for the reaction of $POCl_3$–DMF with cellulose.

Effect of reaction time on chlorination of cellulose. — As chlorination predominated over phosphorylation at 75° when an excess of $POCl_3$–DMF reacted with cotton cellulose, we studied the effect of reaction time at 75° on the rate of chlorination when the reagent concentration was varied.

At reagent concentrations as low as 4%, both the phosphorus and the chlorine contents increased with reaction time, reaching values of 2.4–3.1% after 180 min (see Table II). At these concentrations, the reaction with cotton was not particularly selective; however, as previously observed, concentrations of phosphoryl chloride as high as 12% mainly caused chlorination, and 1% or less of phosphorus was incorporated. Yarn treated with this concentration for 15 min had a substantial degree of chlorination, namely, a d.s. of 0.38, corresponding to 7.9% of Cl. After 5 min, little or no reaction was observed. When the reaction time was increased to 1 h, the d.s. of the chlorodeoxycellulose increased to 0.55, corresponding to 11.4% of Cl.

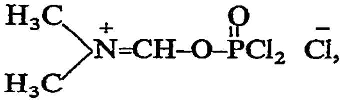
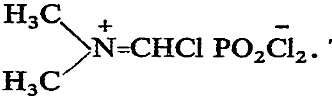
TABLE II

EFFECT OF REACTION TIME AND REAGENT CONCENTRATION ON THE MODE OF REACTION OF $POCl_3$–DMF WITH CELLULOSE AT 75°

Reaction time (min)	*$POCl_3$ (%)*[a]	*Gain in wt. (%)*	*P (%)*[b]	*Cl (%)*[b]	*D.s.*[b] *$Cell\text{–}O\text{–}\overset{\overset{O}{\|}}{P}(OH)_2$*	*D.s.*[b] *Cell–Cl*
15	4	8.7	1.1	0.9	0.06	0.04
60		13.2	1.5	1.8	0.08	0.08
180		18.7	2.4	3.1	0.13	0.14
5	12	6.3	0.3	0.1	0.02	0.005
15		27.5	0.9	7.9	0.05	0.38
60		34.8	1.3	11.4	0.07	0.55
5	14	7.8	0.4	0.3	0.02	0.01
15		30.7	0.8	9.7	0.04	0.47

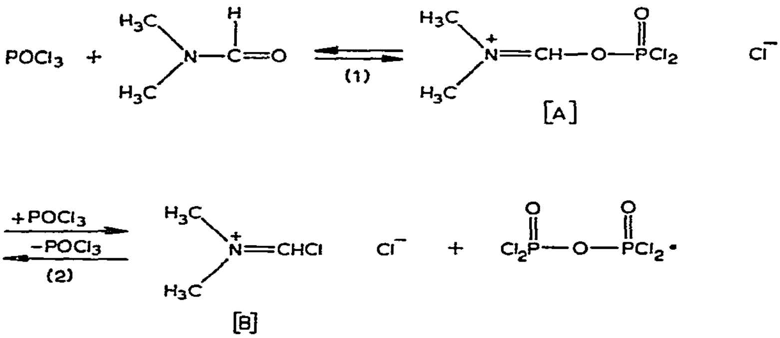
[a] Experimental conditions as listed in Table I, footnote a. [b] Uncorrected for moisture, ash, and gain in weight due to the production of cellulose formate.

With 14% $POCl_3$, no reaction occurred within 5 min, but the d.s. was 0.47 for the chlorodeoxycellulose after 15 min. This chlorine content, 9.7%, is the same as that obtained by using 8% $POCl_3$ for 1 h at 75°; this means that, at 75°, by approximately doubling the reagent concentration, the rate of chlorination is increased by a factor of four. Preliminary experiments indicated, however, that concentrations of $POCl_3$ greater than 14–17% did not greatly enhance the rate of chlorination.

Proposed mechanism for reaction of phosphoryl chloride–DMF with cellulose. — The mode of reaction of phosphoryl chloride with DMF has been a controversial subject, with sufficient evidence presented by various workers for the formation of (*a*) the phosphorus-containing iminium salt[8]  $(H_3C)_2\overset{+}{N}{=}CH\text{–}O\text{–}\overset{O}{\overset{\|}{P}}Cl_2\ \overset{-}{Cl}$, and (*b*) the chloroiminium[9] salt  $(H_3C)_2\overset{+}{N}{=}CHCl\ PO_2\overset{-}{Cl_2}$. These appear to be the reactive intermediates in the phosphorylation and chlorination of cellulose, respectively. A study of the kinetics of the reactions of phosphoryl chloride, thionyl chloride, and phosgene with DMF by n.m.r. spectroscopy[9] showed that, under comparable reaction-conditions, the rate of reaction of phosphoryl chloride with DMF is higher than that of thionyl chloride with DMF in producing an iminium salt structure. In both cases, thionyl chloride or phosphoryl chloride is an effective chlorinating agent for cellulose *via* a chloroiminium salt structure.

Because of the equilibrium kinetics, however, there was more chloroiminium salt present in phosphoryl chloride–DMF than in thionyl chloride–DMF; consequently, there is less free acid halide available in the former system to degrade the cellulose. Although this may explain why it is more practical to use phosphoryl chloride to chlorinate cotton cellulose, it does not explain why chlorination predominates when a high concentration of reagent is used.

The following mechanism seems consistent with the ratios of chlorination: phosphorylation observed.



Thus, when low concentrations of $POCl_3$ were used, phosphorylated cellulose was the major product, and this could be formed from [A]. At intermediate concentrations, both [A] and [B] probably exist in equal amounts, because, as observed, the extents of phosphorylation and chlorination of cellulose were equal. However, at high concentrations of $POCl_3$, equilibrium (2) was shifted far to the right, and chlorination occurred almost exclusively by reaction of cellulose with structure [B]. That [B] is highly effective in producing chlorodeoxycellulose and cellulose formate has been previously shown[6].

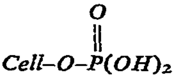
Textile properties of cotton yarns treated with phosphoryl chloride–DMF. — The textile properties (breaking strength, elongation-at-break, and flame resistance) of the yarns treated with phosphoryl chloride in DMF varied greatly with the reaction temperature and the composition of the cellulosic products.

Tensile properties were generally superior for yarns treated at 75° with an excess of phosphoryl chloride in DMF, as compared to yarns treated with equimolar amounts of $POCl_3$ (see Table III).

For example, yarn treated with 2% $POCl_3$ to a d.s. of 0.19 by phosphate and of 0.04 by chlorine retained only 38% of its breaking strength relative to that of untreated yarn, whereas yarn treated with 8% $POCl_3$ (under comparable conditions) to a d.s. of 0.06 by phosphate and of 0.47 by chlorine had a breaking-strength retention

TABLE III

TEXTILE PROPERTIES OF YARNS DERIVED FROM THE REACTION OF $POCl_3$–DMF WITH UNTREATED CELLULOSE

D.s.[a]  $\text{Cell–O–}\overset{\text{O}}{\overset{\|}{\text{P}}}\text{(OH)}_2$	*D.s.*[a] *Cell–Cl*	*B.s.*[b] *(lb)*	*Strength*[c] *retained (%)*	*Elong. at break (%)*	*Tenacity (g/tex)*	*Match test*[d] *angle (°)*
0.19	0.04	2.0	38	7.5	5.2	90
0.13	0.14	2.3	44	9.4	5.8	60
0.06	0.47	3.3	63	40.9	5.3	75
0.07	0.55	3.5	67	41.3	4.9	75
0.04	0.47	3.8	73	45.2	6.0	75
0.22	0.04	1.4	27	7.5	3.6	120
0.18	0.12	1.6	31	7.6	4.0	105
0.20	0.37	2.2	42	15.3	4.7	105
—[e]	—	5.2	100	11.7	17.0	0

[a]The first five rows of values correspond to data for treatment at 75° (see Tables I and II); the last three rows of values correspond to data for treatment at 100° (see Table I). [b]B.s. = breaking strength. [c]Based on untreated, kiered yarn. [d]Test conducted as in ref. 7. [e]Untreated, kiered yarn.

of 63%, and a very high elongation-at-break (40.9%). The high elongation is probably due to the great shrinkage undergone by the yarn at this level of chlorination. The shrinkage is evidently caused by solvent-induced swelling resulting from loss of hydrogen-bonding hydroxyl groups. Improved tensile properties at the same d.s. by chlorine (0.47) can be achieved by reaction with 14% $POCl_3$ for 15 min at 75°; the resultant yarn retained 73% of its breaking strength and had an elongation-at-break of 45%. In all cases, however, the tenacity of the yarns was lowered as the result of these treatments; this may be partly due to the increase in weight of the yarns.

Reactions conducted at 100° produced yarns having tensile properties inferior to those of the products from treatment at 75° (see Table III). With 2% $POCl_3$, the yarn retained only 27% of its tensile strength when treated to a d.s. of 0.22 by phosphate and 0.04 by chlorine. Increasing the reagent concentration at 100° afforded little improvement in strength properties of the yarns. Treatment with 8% $POCl_3$ produced a yarn retaining 42% of its breaking strength; this may be due to the less-selective nature of the reaction at 100°, as the resultant yarn had a d.s. of 0.37 by chlorine and 0.20 by phosphate.

As expected, the flame resistance (as evaluated by the match test angle[7]) of the resultant yarns was somewhat superior for the phosphorus-containing cottons to that for the chlorodeoxycellulose, although the differences were not great. For yarns treated at 75° to a d.s. of 0.19 by phosphate (3.3% of P), the match test angle was 90°; for yarns having a d.s. of 0.47 (9.7% of Cl), or greater, by chlorine, the test angle was only 75°. With yarns treated at 100°, the trend was the same. For yarns having a d.s. of 0.22 by phosphate (3.8% of P), the test angle was 120°, whereas, for yarn having a d.s. of 0.20 by phosphate and 0.37 by chlorine, the angle was 105°.

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