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Halogenodeoxy-derivatives of Cellulose

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Halogenodeoxy-derivatives of cellulose are examined for the first time in terms of a wide range of their characteristics: synthesis, methods for the determination of structure, reactions, and properties. The replacement of some of the hydroxy-groups of cellulose by halogen atoms imparts to it a number of practically important properties, for example resistance to combustion and acid or enzyme hydrolysis. The reactive halogenodeoxy-derivatives of cellulose are used for the synthesis of a wide variety of cellulose derivatives with functional groups, frequently with properties of practical interest. The bibliography includes 70 references.

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I. INTRODUCTION

Cellulose is a unique organic compound: it is available in large amounts and it is being continuously renewed. The introduction of a halogen into the glucopyranose unit of cellulose as well as the reactions of halogenodeoxycelluloses can be used to synthesise new materials with properties specified beforehand.

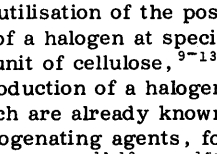
Halogenodeoxy-derivatives of cellulose have not been considered in the reviews devoted to the chemistry of halogenodeoxy-derivatives of monosaccharides.[1,2] In the monographs on cellulose chemistry, the derivatives of this class are either not considered[3,4] or their treatment is incomplete.[5,6]

Since the earlier review by the present author and Golova,[7] devoted to the synthesis and properties of various deoxycelluloses, including halogenodeoxy-derivatives, was written, methods of their synthesis known previously have been significantly developed, new methods have appeared, new procedures for the determination of their structure have been developed, and some of their properties have been investigated in greater depth.

II. METHODS OF SYNTHESIS

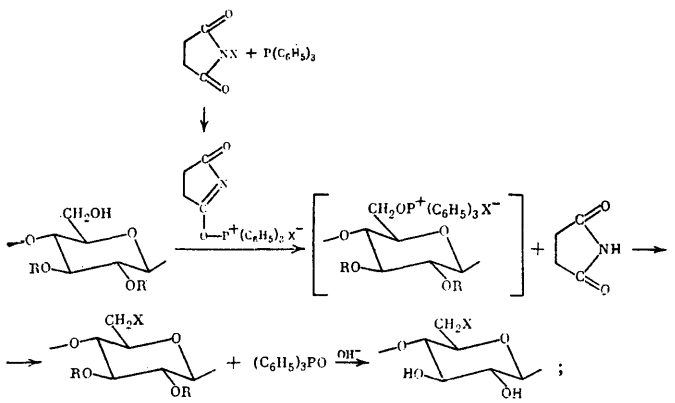
The studies in the synthesis of halogenodeoxycelluloses have developed in several directions, including procedures for the most complete substitution of all the hydroxy-groups of cellulose by halogen atoms,[8] the utilisation of the possibilities for the selective introduction of a halogen at specific carbon atoms of the glucopyranose unit of cellulose,[9-13] the development of methods for the introduction of a halogen into the cellulose macromolecule which are already known,[9,14,15] and the search for new cellulose halogenating agents, for example *N*-halogenosuccinimides,[9,10] SO_2Cl_2,[11,12] SF_4,[16-18] etc. Methods for the substitution of the relatively unreactive secondary hydroxy-groups of cellulose by a halogen are being developed[11,14,15] and a search is being prosecuted for reagents which would make it possible to introduce various halogens into the cellulose macromolecule under comparable conditions; the latter is associated with the fact that various halogenodeoxycelluloses, obtained under identical conditions, should have more similar physicochemical properties than the analogous derivatives obtained by different methods, which is extremely important for the subsequent comparative study of their properties.[9,10] The behaviour of a number of partly substituted cellulose derivatives under conditions where the free hydroxy-groups are substituted by a halogen is also being investigated;[19,20,38] in particular, the stability of various blocking groups, the removal of blocking groups in the presence of a halogen, and problems associated with the preparation (activation) of cellulose before halogenation reactions are being studied.[13,21] These and other problems have been solved to a greater or lesser extent in recent years. The principal reactions and reagents employed for the synthesis of halogenodeoxycelluloses are listed in Table 1.

Table 1. The reactions and reagents used to synthesise halogenodeoxycellulose.

Reaction, initial cellulose derivative, type of reagent	Reagent	Refs.
Nucleophilic substitution of a cellulose OH group on treatment with acid chlorides	SO_2Cl_2	[11, 12]
	$SOCl_2$	[8.14, 19—25]
	$POCl_3$	[26]
	RSO_2Cl	[13,27,28]
Nucleophilic substitution by means of metal halides of active functional groups introduced into cellulose beforehand	MX(X=Cl, Br, I, F)	[14,15,20, 29—34]
alkane- and arene-sulphonate	—	[34]
sulphate	—	[34—37]
nitrate	—	
phosphinite with alkyl halide	RCl	[38]
Nucleophilic substitution of a cellulose OH group by reaction with halogen-containing phosphorus compounds		[9,10]
	X=Cl, Br, I	
	$CH_3I \cdot P(OC_6H_5)_3$	[19,39,40]
	Cl_2 or Br_2+P	[41]
Nucleophilic substitution of cellulose OH groups by reaction with halogen-containing sulphur compounds	SF_4	[16—18]
Addition of hydrogen halide to 2,3-epoxy-derivative of cellulose	HCl	[42]
Addition of a halogen to 5,6-cellulosene	Cl_2, Br_2	[43]

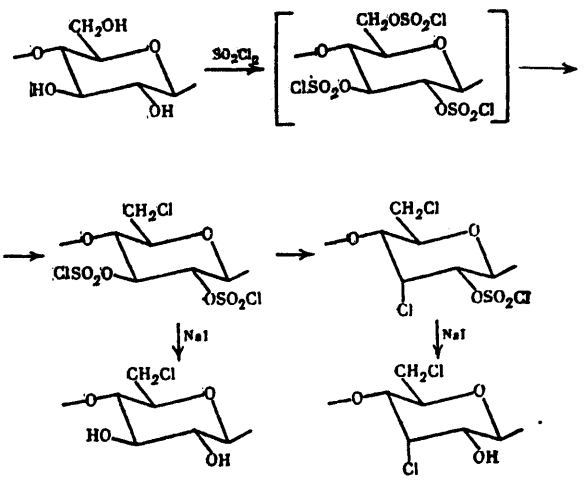
A new convenient method of synthesis of 6-chloro-, 6-bromo-, and 6-iodo-6-deoxycelluloses under comparable conditions involves the reaction of partly substituted

2,3-di-O-acetylcellulose with the *N*-halogenosuccinimide and triphenylphosphine with subsequent deacetylation.[9,10] 2,3-Di-O-acetylcellulose is initially dissolved in dimethylformamide (DMF) and is then treated with the reagent for 5 h at 50 °C with a glucopyranose unit : *N*-halogenosuccinimide : triphenylphosphine ratio of 1 : 2 : 2 in order to obtain the chloro- and bromo-derivatives and 1 : 6 : 6 in order to obtain iododeoxycellulose. Under identical conditions, *N*-iodosuccinimide proved to be the least reactive. There are virtually no side reactions in the case of *N*-chloro- and *N*-bromo-succinimides. After the first hour, the reaction slows down sharply and the degree of substitution (D.S.) reaches a limit corresponding to the substitution by the halogen of one (or approximately one) hydroxy-group in the glucopyranose unit. Under the reaction conditions, the acetyl groups are retained but can be fully removed from halogenodeoxycelluloses by treatment with a 0.25 *N* NaOH solution for 1 h. This results in the formation of 6-chloro- and 6-iodo-6-deoxycelluloses in 83–95% yield under mild conditions with D.S. = 1.0, 0.8, and 0.7 respectively.



R = H, Ac; X = Cl, Br, I .

The mildest and most effective reagent for the substitution of the hydroxy-groups of cellulose by chlorine is sulphuryl chloride.[11,12] A suspension of cellulose in chloroform is treated with sulphuryl chloride in the presence of pyridine using the molar ratios OH : SO_2Cl_2 : Py = 1 : 1.7–5 : 1–8 during a period ranging from 20 min to 3 h. The reaction takes place at room temperature and does not require the preliminary dissolution of cellulose. A chlorosulphate derivative of cellulose is apparently formed as an intermediate. The reaction product contains, together with the chlorodeoxy-groups, also the chlorosulphate groups, which are resistant to substitution by halogen and sulphate groups. The chlorosulphate groups can be removed quantitatively by treating the polymer with sodium iodide in aqueous methanol and the sulphate groups can be eliminated by successive treatment with a base and an acid. This results in the formation of chlorodeoxycellulose containing 12.4 to 30.4% of chlorine (D.S. up to 1.7) and 1.2–0.9% of sulphur. The primary hydroxy-groups are exchanged for chlorine in the first place and then the secondary hydroxy-groups are exchanged. The substitution of a secondary hydroxy-group by chlorine atoms is accompanied by the inversion of the configuration. A distinctive feature of the reagent is its high selectivity: among the secondary hydroxy-groups, only the hydroxy-group in the C(3)-position is substituted by chlorine. The hydroxy-group at C(2) remains unsubstituted.



Highly chlorinated cellulose with D.S. = 2.8 has been obtained by treating cellulose with thionyl chloride in solution.[8] Cellulose is dissolved in 50–100 parts of DMF in the presence of 10 parts of chloral at 40 °C for 15 h and is treated with 15–30 parts of thionyl chloride at 20 °C for 15 h or at 40° and 80 °C for 1 h. The product contains 46–47.3% of chlorine and 2% of sulphur.

$$C_6H_7O_2(OH)_3 \xrightarrow{CCl_3CHO} C_6H_7O_2[OCH(OH)CCl_3]_3 \xrightarrow{SOCl_2} C_6H_7O_2(OH)_{0.2}Cl_{2.8}\ .$$

The reaction of cellulose with thionyl chloride is one of the principal reactions used for the synthesis of chlorodeoxycellulose. It has frequently attracted the attention of investigators[8,14,19–25] and its conditions have been most thoroughly investigated compared with other reactions. The principal results are compiled in Table 2.

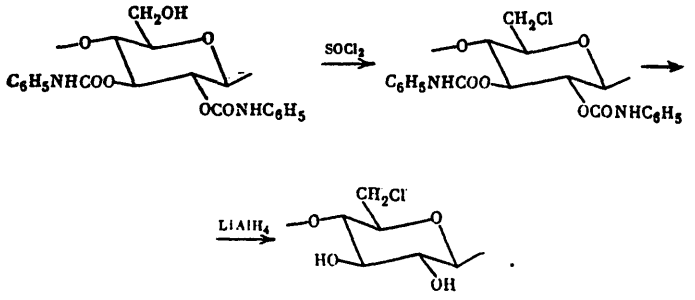
Table 2. Reactions of cellulose and its derivatives with thionyl chloride.

Reaction conditions			D.S.	Refs.
solvent	temperature, °C	time, h		
Pyridine	110	—	1	[21]
Pyridine	26–69	1.5	1	[22]
DMF	60–98	1–1.5	1.09	[23]
DMF	20	4	0.3	[24]
$CHCl_3$, CCl_4	B.p.	1–210	0.9	[25]
DMF + CCl_3CHO	20–80	1–15	2.8	[8]
DMF	70	0.4*	1	[19,20]
DMF	70	1.5–6**	0.47	[19]
HMP***	70	3**	0.75	[14,20]

*On a cellulose derivative with a free primary OH group.
**On cellulose derivatives with free secondary OH groups.
***HMP = hexamethylphosphoramide.

In order to introduce chlorine in a specific position in the glucopyranose cellulose unit, thionyl chloride in DMF is allowed to react with partly substituted cellulose derivatives: 2,3-di-O-phenylcarbamoylcellulose, 6-O-trityl-2(3)-tosylcellulose, 2(3),6-di-O-tosylcellulose, and 6-O-phenylcarbamoyl-2(3)-tosylcellulose.[19,20] It has been shown that the primary hydroxy-group in 2,3-di-O-phenylcarbamoylcellulose is fully substituted by chlorine already in the course of the first

15 min of the reaction (70 °C, tenfold excess of the reagent).[19] The phenylcarbamate groups can be removed by treatment with lithium tetrahydroaluminate in tetrahydrofuran (THF) for 1 h at 70 °C with the preferential retention of chlorine.[20]



The free secondary hydroxy-groups in the partly substituted 6(2,3)-*O*-phenylcarbamoyl-2(3)-*O*-tosylcellulose are much less reactive. Under the same conditions, they are substituted to the extent of only 20% after 1.5 h of the reaction and, when the reaction time is raised from 1.5 to 6 h, the degree of substitution is 50%. The nitrogen and sulphur contents in the products indicate the retention of the blocking phenylcarbamate and tosylate groups under the reaction conditions. On increasing the reaction time to 12 h, partial removal of the phenylcarbamate groups is observed.[19]

The free hydroxy-groups in the tosylated cellulose 6(2,3)-phenylcarbamate can be fully substituted by chlorine on treatment with thionyl chloride using hexamethylphosphoramide (HMP) as the solvent.[14,20] After 1.5 h of the reaction in HMP, the hydroxy-groups are replaced by chlorine to the extent of 70% and after 3 h their substitution is complete. The contents of sulphur and nitrogen in the final product indicate the retention of the tosylate and phenylcarbamate groups under the reaction conditions: the degree of substitution is 1.55 for the $OCONHC_6H_5$ groups, 0.7 for the OTs groups, and 0.75 for Cl atoms. The use of HMP as the solvent increases the rate of reaction of the hydroxy-groups of cellulose with thionyl chloride and also the degree of their substitution by chlorine.[14]

The reaction involving the substitution of active functional groups (alkane- and arene-sulphonate groups, nitro-groups, etc.), introduced into cellulose beforehand, by a halogen atom by treatment with alkali metal halides constitutes a widely used method for the halogenation of cellulose:[14,15,20,29-37]

$$C_6H_7O_2(OH)_{3-n}(OR)_n \xrightarrow{MX} C_6H_7O_2(OH)_{3-n}(OR)_{n-m}X_m$$

$R = SO_2R'$, SO_2OH, NO_2;

$R' = CH_3$, C_2H_5, C_6H_5, C_7H_7, $C_6H_4NO_2$, C_6H_4Br;

X = Cl, Br, I, F .

The principal results of the use of this reaction for the halogenation of cellulose and its derivatives are presented in Table 3.

The possibility of substituting the secondary hydroxy-groups in cellulose by halogen atoms via the reactions of cellulose alkane- and arene-sulphonates with alkali metal halides has been investigated. The trityl ether of cellulose is esterified by the chlorides of methane-, ethane-, benzene-, toluene-, *p*-bromobenzene-, and *p*-nitrobenzene-sulphonic acids and is then treated with NaI at 100 °C for 10–100 h.[15] Tritylcellulose *p*-nitrobenzenesulphonate is the most reactive. When this ester, having D.S. = 0.91 with respect to the $OSO_2C_6H_4NO_2$ groups, is iodinated for 100 h at 120 °C, a product with D.S. = 0.52 with respect to I is obtained, while the remaining esters give rise to products with D.S. = 0.25 with respect to I.

The use of HMP as the solvent makes it possible to substitute 60–80% of the secondary tosyloxy-groups in tritylcellulose tosylate on treatment with LiCl. The chlorine content in the final product corresonds to D.S. = 0.65–0.72.[14,20]

Table 3. The reactions of cellulose alkane- and arene-sulphonates, sulphates, and nitrates with alkali metal halides.

Reaction conditions			D.S.	Refs.
solvent	temperature, °C	time, h		
Acetone	100	2	0.2	[29]
Cyclohexanone	120	2	0.2	[30]
Acetylacetone	120	0.5—6	0.95—1.2	[31]
H_2O	—	—	—	[32]
DMF	97	24	0.9—1.22	[33]
H_2O	108—130	1—35	0.2—0.4	[34]
DMF	100—140	16—50	0.3—0.5*	[15]
HMP	97	10	0.65—0.72*	[14,20]

*Substitution of secondary arene- and alkane-sulphonyloxy-groups in 6-*O*-tritylcellulose esters.

The reaction with methanesulphonyl chloride has been proposed recently for the preparation of chlorodeoxycelluloses.[13,27] Chlorodeoxycellulose with D.S. = 0.58 is obtained by treating cotton cellulose activated with alkali or acetylcellulose in DMF with methanesulphonyl chloride.[27] The reaction mechanism involving the formation of an intermediate iminium derivative has been proposed[27] on the basis of the data of Edwards et al.:[44]

$$CH_3SO_2Cl + (CH_3)_2NC(=O)H \rightarrow \left[(CH_3)_2N^+=C(OSO_2CH_3)H\right]Cl^- ;$$

$$C_6H_7O_2(OH)_3 + \left[(CH_3)_2N^+=C(OSO_2CH_3)H\right]Cl^- \rightleftarrows (CH_3)_2NC(OSO_2CH_3)(OC_6H_7O_2(OH)_2)H + H^+ + Cl^- \rightleftarrows$$

$$\rightleftarrows (CH_3)_2NC(OC_6H_7O_2(OH)_2)H + Cl^- + CH_3SO_2H \rightarrow C_6H_7O_2(OH)_2Cl + (CH_3)_2NC(=O)H .$$

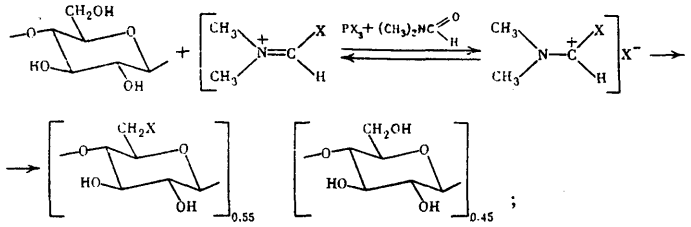
The higher D.S. = 0.83 in the reaction with methanesulphonyl chloride is attained when cellulose regenerated from its solution in cupriethylenediamine by precipitation in DMF is employed.[13] It has been noted that the effectiveness of the reaction is higher when it is carried out at 90 °C for a shorter time than at 60 °C for a longer time. A side reaction involving the introduction of formyl groups into cellulose is observed. They are removed by keeping the reaction product in an aqueous solution of sodium carbonate at room temperature.

Chlorodeoxycellulose with D.S. = 1.3 has been obtained by this reaction by dissolving cellulose in the DMF–chloral system (in the course of a week at room temperature) and subsequent treatment with methanesulphonyl chloride at 75 °C.[28] The chlorine content in cellulose reaches 16% after 1 h of the reaction and 24% after 48 h.

$$C_6H_7O_2(OH)_3 \xrightarrow{CCl_3CHO} C_6H_7O_2[OCH(OH)CCl_3]_3 \xrightarrow{CH_3SO_2Cl} C_6H_7O_2(OH)_{1,7}Cl_{1,3} .$$

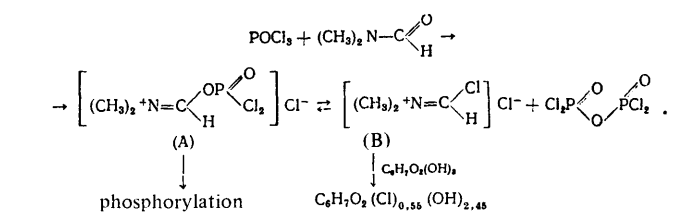
Extensive substitution of the secondary hydroxy-groups of cellulose by chlorine on interaction of tritylcellulose with alkane- and arene-sulphonyl chlorides, especially ethanesulphonyl chloride, has been reported.[15] With increase of reaction time from 24 to 72 h, the D.S. increases from 0.5 to 0.7.

Among other methods, mention should be made of the reaction of cellulose with halogen-containing phosphorus derivatives. Thus the hydroxy-groups of cellulose have been substituted by halogen on treatment with bromine or chlorine in the presence of phosphorus.[41] The reaction is carried out in DMF. The synthesis of bromodeoxycellulose by this reaction has been studied in greatest detail. A temperature of 50–70 °C and glucopyranose unit : phosphorous : bromine molar ratios of 1 : 1 : 30 are optimum for the maximum introduction of bromine. The bromodeoxycellulose obtained under these conditions contains 16% of bromine. The formation of cellulose phosphates in side reactions (phosphorus content 1.5%) and the appearance of carbonyl groups (an absorption band occurs in the IR spectrum at 1693 cm^{-1}) have been noted. When chlorine was passed through the reaction mixture under the same conditions at 60 °C for 6 h, chlorodeoxycellulose containing 10.2% of chlorine and 1.4% of phosphorus was obtained.



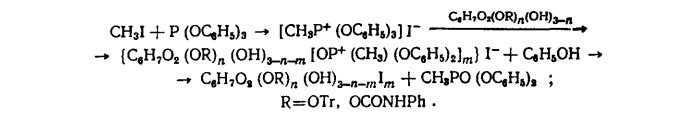
X = Cl, Br .

When cellulose is treated with phosphoryl chloride in DMF, chlorodeoxycellulose or phosphorylated cellulose is obtained depending on the reaction conditions.[26] The mode of reaction depends to a large extent on the reagent concentration and this dependence is maintained over a wide temperature range. It has been found that the following conditions are optimal for the synthesis of chlorodeoxycellulose: concentration of phosphoryl chloride in DMF 12%, temperature 75 °C, time 1 h. D.S. = 0.55 is attainable. On the basis of literature data,[45,46] the intermediate formation of active compounds (A) and (B)has been postulated:[26]



At a high phosphoryl chloride concentration, the interaction of cellulose with compound (B) leads to the formation of chlorodeoxycellulose. It had been shown earlier[47] that compound (B) plays an important role in the formation of chlorodeoxycellulose.

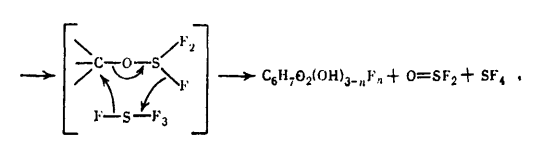
The reaction involving the substitution of the hydroxy-groups of cellulose by iodine on treatment of the following cellulose derivatives with triphenoxymethylphosphonium iodide has been investigated: tritylcellulose,[19,39,40] 2,3-di-*O*-phenylcarbamoylcellulose, and 2(3),6-di-*O*-tosylcellulose.[19,39] A possible reaction mechanism has been proposed.[48]



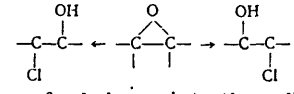
R=OTr, OCONHPh .

The products of the reaction with tritylcellulose were found to contain 15.2% of iodine after 3 h, 16.1% after 5 h, and 12.25% after 10 h.[19,39] It has been shown[40] that, when tritylcellulose is acted upon by the complex of triphenyl phosphite with an alkyl halide at a temperature below 60 °C, the substitution of hydroxy-groups by iodine is not observed. An increase of temperature from 60° to 120 °C leads to an appreciable increase of D.S. with respect to iodine (from 0.25 to 0.98). When the reaction of 2,3-di-*O*-phenylcarbamoylcellulose with triphenoxymethylphosphonium iodide is carried out in chloroform with a glucopyranose unit: halogenating complex molar ratio of 1 : 15 and a reaction time of 10–40 h at 60–120 °C, the maximum iodine content in the product is 11.6% (D.S. = 0.4).[19,39] Despite the fact that the reaction of 2(3),6-di-*O*-tosylcellulose with triphenoxymethylphosphonium iodide in chloroform takes place under homogeneous conditions, the D.S. with respect to iodine remains low (0.42). The reduced sulphur content indicates a decrease in the number of blocking tosylate groups under these conditions.[19,39]

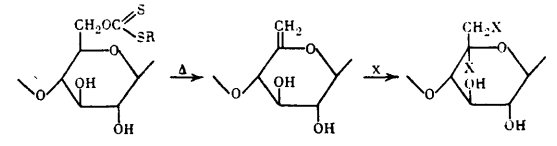
Fluorodeoxycellulose with a high degree of substitution has been obtained by the reaction of cellulose with SF_4.[16,17,18] The degree of fluorination depends on the ratio of the initial components and the reaction time. With increase of the sulphur tetrafluoride: glucopyranose unit molar ratio, the rate of reaction and the content of the fluorine introduced into cellulose increase. The maximum amount of fluorine was introduced on treatment of the glucopyranose unit with a 30-fold molar excess of SF_4 for 6 h. The fluorodeoxycellulose with D.S. = 1.5 obtained was characterised by elemental analysis and IR spectra.[16–18] The substitution of hydroxy-groups by fluorine can take place without the inversion of configuration via the mechanism[49]



When the trityl group was split off from the 6-*O*-trityl-2,3-anhydro-derivative of cellulose with a solution of hydrochloric acid in methanol or chloroform for 24 h at room temperature, products with D.S. = 0.2–0.4 with respect to chlorine were obtained.[42] The authors suggested the formation of 2-chloro-2-deoxyglucose and 3-chloro-3-deoxyaltrose units:



The introduction of a halogen into the cellulose macromolecule can be achieved via a reaction involving the addition of the halogen to the double bonds in 5,6-cellulosene.[43] 5,6-Cellulosene is obtained by the pyrolysis of cellulose 6-(alkylxanthate) at 170 °C in a stream of argon. Cellulose derivatives containing 17.5% of bromine or 8.5% of chlorine have been obtained by treating a solution of 5,6-cellulosene in carbon tetrachloride with Br_2 and Cl_2 at room temperature for 3 h. The reaction products were characterised by elemental analysis and IR spectra:



X = Cl_2, Br_2 .

III. METHODS FOR THE DETERMINATION OF STRUCTURE

The determination of the structure of halogeneodeoxycelluloses is essential for the solution of two interrelated problems: on the one hand, for the identification of a newly synthesised derivative and, on the other, for the elucidation of the transformations which cellulose undergoes under the conditions of a particular reaction. The question of the determination of the structure is the most complex: (1) on partial substitution of hydroxy-groups; (2) on non-selective substitution of three different hydroxy-groups of the glucopyranose unit of cellulose; (3) on inversion of the configuration in the reaction centre whereupon the secondary hydroxy-groups enter into the reaction; (4) when secondary reactions occur. The macromolecule of the cellulose derivative can contain in the general case, together with the unchanged glucopyranose units, also a series of glucopyranose units differing in the degree of substitution, the position of the substituent, and the stereochemistry of their reaction centres, as well as monosaccharide units formed as a result of side reactions. The determination of the structure of cellulose derivatives therefore involves the solution of two problems: (1) the determination of the monosaccharide composition, which entails the elucidation, in its turn, of problems such as that of the degree of substitution, the position of the substituent in the glucopyranose unit, and the configuration of the substituent; (2) the determination of the squence in which the monosaccharide residues are linked up in the macromolecule.

Until recently, there were no reliable methods for the investigation of the structure of halogenodeoxycelluloses. Due to the general development of the methods for the determination of the structure of carbohydrates and their derivatives and also in connection with the advances in the research into the reactions of halogenodeoxycelluloses, such methods have now been developed.

In order to establish the structure of halogenodeoxycelluloses, methods which both cause and do not cause the degradation of the polysaccharide chain are used. The former include acid hydrolysis in combination with paper–thin-layer–(TLC) or gas–liquid (GLC) chromatography together with chromatomass-spectrometric, and spectrophotometric methods for the investigation of the hydrolysates. Among the non-degradative methods, chemical methods based on selective reactions with the primary hydroxy-group (tosylation with subsequent iodination), and the glycol group (periodate oxidation), as well as spectroscopic methods (^{13}C NMR) are used for the determination of the structure of halogenodeoxycelluloses.

Quantitative analysis of the monosaccharide composition of 6-bromo- and 6-iodo-6-deoxy-celluloses has become possible since a procedure has been found for their quantitative reduction to 6-deoxycellulose.[9,10] In contrast to halogenodeoxycelluloses, the latter does not undergo side reactions during the hydrolysis of the polysaccharide, the tetrahydroborate reduction, and acetylation and can be investigated by the usual methods for the structural analysis of polysaccharides. The position of the halogen in the bromo- and iodo-deoxycelluloses obtained by reaction with *N*-halogenosuccinimide and triphenylphosphine has been rigorously demonstrated by this method.[9,10] The amount of 6-deoxyglucose found by GLC and spectrophotometric methods in the reduced specimens of bromo- and iodo-deoxycelluloses corresponds to the halogen content in the halogenodeoxycelluloses investigated. This demonstrates unambiguously that the entire bromine and iodine introduced into cellulose is located at the six carbon atom of the glucopyranose unit of cellulose.[9,10]

Chlorodeoxycellulose is only partly reduced by $NaBH_4$. Apart from 6-deoxyglucose and glucose, 6-chloro-6-deoxyglucose and 3,6-anhydroglucose were detected in the hydrolysis products after the reduction of chlorodeoxycellulose. Owing to the instability of these compounds under the hydrolysis conditions, it is impossible to carry out a complete quantitative analysis of the monosaccharide composition of the polymer using the hydrolytic and chromatographic methods.

A convenient procedure for the determination of the structure of chlorodeoxycelluloses is ^{13}C NMR.[12,50] The characteristics of the changes in the chemical shifts of the signals due to the carbon atoms on substitution of the hydroxy-groups by chlorine atoms in both the given and neighbouring monosaccharide units in the disaccharides investigated have been established for the model compounds β-methyl cellobioside, methyl 6,6'-dichloro-6,6'dideoxycellobioside, methyl (3',6'-dichloro-3',6'-dideoxyallopyranosyl)-6-chloro-6-deoxyglucopyranoside, and methyl (3',6'dichloro-3',6'-dideoxyallopyranosyl)-3,6-dichloro-3,6-dideoxyallopyranoside.[50] The chemical shifts of the C(1) signals have been calculated on the basis of the spectra of the test compounds for all the possible sequences in which the monosaccharide derivatives comprising unsubstituted D-glucose, 6-chloro-6-deoxy-D-glucopyranose, and 3,6-di-chloro-3,6-dideoxy-D-allopyranose are joined together. The spectra of model compounds and the chlorodeoxycelluloses investigated, obtained by the reaction of cellulose with sulphuryl chloride, are recorded in solution in deuterated dimethyl sulphoxide (DMSO-d_6). The agreement of the chemical shifts of the most intense signals both in the region of the anomeric carbon atoms and in the region of the C(2)–C(6) atoms with the signals of the carbon atoms of the corresponding model compounds showed that 6-chloro-6-deoxy-D-glucose units linked to one another predominate in chlorodeoxycellulose with D.S. = 0.7 and that unsubstituted D-glucose units and a certain number of 3,6-dichloro-3,6-dideoxy-D-allose residues are present. The 3,6-dichloro-3,6-dideoxy-D-allose residues linked to one another predominate in chlorodeoxycellulose with D.S. = 1.5 and there is a small amount of 6-chloro-6-deoxy-D-glucose and unsubstituted D-glucose units. Thus the method makes it possible to establish not only the monosaccharide composition of chlorodeoxycellulose but also the main sequence in which the sugar units forming part of the composition of the polysaccharide are linked together.[12,50]

Some information about the structure of chlorodeoxycellulose can be obtained by the periodate oxidation method.[12] Chlorodeoxycellulose with D.S. = 0.7, obtained by the reaction with sulphuryl chloride, absorbed ~1 mole of the oxidant per mole of the glucopyranose unit of cellulose, which indicates the retention of all the glycol groups of cellulose at the given stage of substitution. Chlorodeoxycellulose with D.S. = 1.5 absorbs 0.5 mole of IO_4 per monosaccharide residue, which means that, when cellulose is treated with sulphuryl chloride, initially the primary hydroxy-groups and then one of the secondary hydroxy-groups are substituted by chlorine atoms.

The method for the determination of unsubstituted primary hydroxy-groups, based on the successive application of reactions involving the tosylation of the hydroxyl-groups and the subsequent substitution of the primary tosyl groups by iodine on treatment with NaI, has been used[41] to determine the position of the halogen in the monosaccharide residues of halogenodeoxycelluloses obtained by the action of Br_2 or Cl_2 in the presence of phosphorus. The number of free primary hydroxy-groups in the halogenodeoxycellulose investigated and hence the amount of halogen attached to the primary carbon atoms are inferred from the amount of iodine

introduced. However, such proof of the position of the halogen is not rigorous, since under the conditions governing the substitution of the tosyl group by iodine there is a possibility that the bromine atoms at a primary carbon atom are also substituted by iodine.

A number of workers have used hydrolysis and the study of the composition of the hydrolysate by chromatographic methods (paper and TLC, GLC, and chromatomass-spectrometry) for the determination of the structure of chlorodeoxycelluloses.[13,22,28] However, the incomplete hydrolysis of chlorodeoxycellulose[12,22,28,51] and also the occurrence of side reactions of the sugars with increase of the time during which chlorodeoxycellulose is kept in 72% sulphuric acid from 2 h in the standard method to 16 h [13] or 36 h [28] preclude the derivation of complete information.

IV. THE PROPERTIES OF HALOGENODEOXY-DERIVATIVES OF CELLULOSE

The data accumulated at the present time on various properties of halogenodeoxycelluloses, including those of practical importance such as the resistance to acid hydrolysis, combustion, and enzyme hydrolysis, are widely scattered. Only some workers[22] have published data obtained in a comparative study of the chemical properties as a function of the degree of substitution of halogenodeoxycellulose or the type of halogen introduced.

1. Physical, Physicochemical, and Mechanical Properties

There have been no systematic studies on the physical, physicochemical, and mechanical properties of halogenodeoxycelluloses.

Chlorodeoxycellulose obtained by reaction with $SOCl_2$ in pyridine from mercerised cotton linters is coloured;[21] according to Boechm,[22] the colour deepens with increase of reaction temperature. The replacement of pyridine by the more polar DMF as the solvent leads to the formation of less coloured products.[23] Colourless products are obtained in chloroform and carbon tetrachloride. Chlorodeoxycellulose obtained using methanesulphonyl chloride from soluble sulphide cellulose is slightly coloured after chlorination for more than 2 h.[28] According to Boechm,[22] chlorodeoxycellulose with D.S. = 0.29, 0.67, and 1.04 gives rise to low-viscosity solutions in copper–ammonia solution and only a small proportion of such cellulose can be precipitated from the solution. It has been reported[28] that chlorodeoxycellulose containing 16% of chlorine is soluble in water, while that containing 20% of chlorine is insoluble. Data on the molecular weight distribution of these two chlorodeoxycellulose specimens indicate the absence of the degradation of the polymer during chlorination with methanesulphonyl chloride up to a chlorine content of 16%; when a chlorine content of 20% is attained, the degree of degradation is slight. The molecular weight distribution has been established by gel chromatography using chlorodeoxycellulose nitrate. On chlorination with thionyl chloride, the loss of the fibrous structure of cellulose has been noted.[21] The tensile strength does not decrease on chlorination of methanesulphonylcellulose by alkali metal halides.[32]

2. Chemical Properties

The substitution of some of the hydroxy-groups of cellulose by chlorine hinders the acid hydrolysis of the glycoside linkages between the monosaccharide units in chlorodeoxycellulose.[12,22,28,51] According to Boechm's data,[22] an increase of the D.S. with respect to chlorine from 0.33 to 1.04 entails an increase of the fraction of unhydrolysable residue from 0 to 8.3% under the conditions of the standard two-stage hydrolysis of cellulose; incomplete hydrolysis products are present in the soluble part. 3,6-Dichloro-3,6-dideoxy-derivatives of cellulose with D.S. = 1.6 are almost stable under the conditions corresponding to the hydrolysis of cellulose: under standard hydrolsyis conditions, only 13–20% of the total sugars pass into solution (via the reaction with the phenol–H_2SO_4 reagent).[12] Chlorodeoxycellulose with D.S. = 2.8 is fully resistant to acid hydrolysis.[51] There are data indicating the resistance of the C–Cl bond in chlorodeoxycellulose to acid hydrolysis: when $AgNO_3$ is added to the chlorodeoxycellulose hydrolysate, only traces of AgCl are formed.[22]

The elimination of the halogen from chloro- and bromodeoxycelluloses on treatment with 1 *N* NaOH solution has been investigated as a function of temperature (20–100 °C) and reaction time (30–120 min).[41]

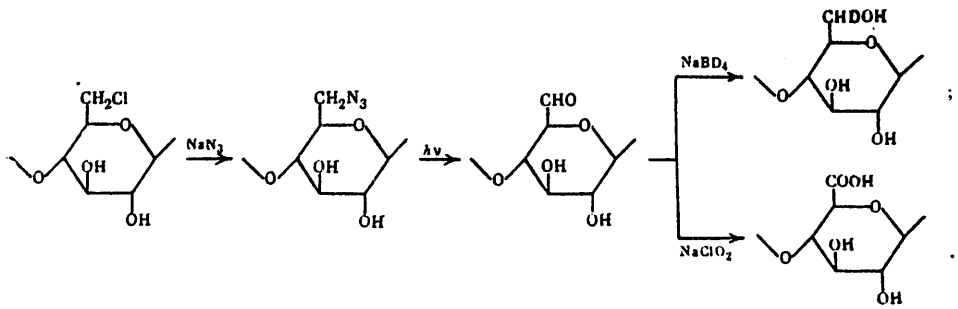
According to the data of a number of workers, the introduction of a halogen into cellulose increases its resistance to combustion. In terms of their resistance to inflammation, methanesulphonyliodo- and methanesulphonylbromo-deoxycelluloses are superior to the initial methanesulphonylcellulose and methanesulphonylchlorodeoxycellulose.[32] Judging from the length of the charred region, the area of charring, and the residence time of the ash in the hot state, chlorodeoxycellulose is much more resistant to burning than cellophane and is little inferior in this respect to poly(vinyl chloride).[8]

According to thermogravimetric data, chlorodeoxycellulose produces more water and carbon and less tar on decomposition than does cellulose.[52] The difference in the behaviour of cellulose and chlorodeoxycellulose has been explained by reactions involving the elimination of HCl from chlorodeoxycellulose. Chlorodeoxycellulose has been investigated by special methods and also by IR spectroscopy, X-ray diffraction, and thermogravimetric measurements. It has been established that the Cl atom bound chemically in chlorodeoxycellulose or added to cellulose in the form of chlorine-containing paraffins has little influence on the combustibility of the materials.[53] The combination of Cl atoms and added Sb_2O_3 effectively retards combustion (the introduction of Sb_2O_3 alone is ineffective). It has been suggested that the synergism in the action of the above agents is associated with the catalytic acceleration of the dehydration of chlorodeoxycellulose, which is accompanied by the formation of a thermostable polyene structure.[53]

The study of the morphology of the charring of chlorodeoxycellulose fibres by scanning electron microscopy has shown that their thickness appreciably diminishes under these conditions, in contrast to the fibres of cotton treated with fireproofing agents.[54]

Chlorodeoxycellulose obtained by the reaction with thionyl chloride, methanesulphonyl chloride, or phosphoryl chloride has been frequently used as the starting compound for the preparation of new deoxy-derivatives of cellulose by the nucleophilic substitution reactions with KSCN,[33] NH_3, NH_2NH_2, KCN,[23,55,56] $HSCH_2COOH$, RNH_2,[24] diethylenetriamine,[57] ethylenediamine, thiourea, thiosemicarbazide, thioacetamide,[58] and 1,6-diaminohexane.[59] Cellulose phosphonimidate has been synthesised by the reactions of chloro- and bromodeoxycelluloses with phosphoramidites.[60] Mercaptodeoxycellulose has been obtained from chlorodeoxycellulose.[61,62]

The nucleophilic substitution reaction between chlorodeoxycellulose and sodium azide has been studied in greatest detail.[13] Chlorodeoxycellulose with different D.S. (0.12, 0.37, and 0.67) was treated with sodium azide in DMF, water, and DMSO:



It was established that, when the reaction is carried out in DMF, the degree of polymerisation falls from 506 to 153, whereas in water the fall is to 448 and in DMSO to 463. Furthermore, in the presence of DMSO the greatest degree of conversion of the halogenodeoxy-groups into azidodeoxy-groups was noted. Further reactions of azidodeoxycellulose take place quantitatively and serve as proof of the structures of both azido deoxycellulose and the initial chlorodeoxycellulose.

Another reaction of halogenodeoxycelluloses which has been studied in detail is their reduction. The reduction of 6-halogeno-6-deoxycellulose by various reducing agents in order to obtain 6-deoxycellulose has been investigated by a number of workers.[9,10,20,63]

When 6-iodo-6-deoxy-2,3-di-*O*-tosylcellulose is reduced with zinc in methanol, the iodine content falls only from 28 to 22%, while on reduction with sodium in dioxan it diminishes from 34 to 6%.[63] The formation of C=C bonds in the reaction product was noted in the latter case, which indicates the simultaneous occurrence of the HI elimination reaction.

The reductive elimination of phenylcarbamate groups from 6-chloro-6-deoxy-2,3-di-*O*-phenylcarbamoylcellulose on treatment with $LiAlH_4$ in THF is accompanied by the elimination of chlorine: 25% of chlorine is eliminated after 1 h and the chlorine is lost entirely after 5 h. 6-Deoxyglucose and glucose were detected by paper chromatography in the reaction product after its hydrolysis.[20]

The reaction conditions and the structure of the products were investigated most completely in the reduction of 6-chloro-, 6-bromo-, and 6-iodo-6-deoxycelluloses with $NaBH_4$ in DMSO.[9,10] 6-Deoxycellulose with the highest content of 6-deoxyglucopyranose units (~80%) compared with the products obtained previously in other reactions was produced by the reduction of 6-bromo-6-deoxycellulose. The bromodeoxy- and iododeoxyglucopyranose units are then quantitatively converted into 6-deoxyglucopyranose units; apart from the 6-deoxyglucopyranose residues, the final product contains only the unchanged glucopyranose units.

Halogenodeoxycellulose has been frequently used to obtain 5,6-cellulosene by the reaction involving the elimination of a hydrogen halide molecule with alkali. When 6-iodo-6-deoxycellulose is treated with 9–10% alcoholic alkali for 1–2 days at 20–70 °C, a mixed cellulose derivative containing 5,6-glucosene, 3,6-anhydroglucopyranose, and glucopyranose residues is formed.[37,64,65] The use of potassium t-butoxide in DMSO makes it possible to achieve the quantitative conversion of chlorodeoxycellulose into 5,6-cellulosene.[27]

The photoinitiated grafting of methyl methacrylate on chlorodeoxycellulose has been achieved.[66]

3. Biochemical Properties

The enzyme hydrolysis of 6-chloro-, 6-bromo-, and 6-iodo-6-deoxycelluloses by the cellulases from *T. viride* and *A. niger* has been investigated and compared with that of 6-deoxycellulose and cellulose hydrate which are the starting materials in their synthesis.[67] From the accumulation of non-reducing and reducing sugars in the hydrolysates, it was established that, under conditions optimal for the enzyme hydrolysis of cellulose hydrate, the specimens of the modified celluloses are also cleaved by the *T. viride* cellulase. However, the hydrolysis is not complete. The obstacles to enzyme hydrolysis increase with increasing bulk of the substituent: H < Cl < Br < I. The reactions involving the formation of non-reducing sugars are hindered to a greater extent than the reactions resulting in the formation of reducing sugars. Among the soluble products of the enzyme hydrolysis of 6-chloro-, 6-bromo-, and 6-iodo-6-deoxycelluloses, there is no modified monosaccharide. The joint action of the *T. viride* and *A. niger* cellulases leads to the formation (according to paper chromatographic data) of a certain amount of modified monosaccharide from 6-chloro-6-deoxycellulose with D.S. = 0.3 and 0.9.

V. PRACTICAL APPLICATIONS

Although halogenodeoxycelluloses have properties important from the practical point of view such as resistance to inflammation and acid and enzyme hydrolysis, they have not themselves found applications as yet. It is noteworthy that their resistnace to acid and enzyme hydrolysis has been discovered comparatively recently, the possibility of using for their synthesis sulphuryl chloride—the most readily available, cheapest, and most effective halogenating agent. However, there exist many recommendations for the employment of halogenodeoxycelluloses in the synthesis of deoxy-derivatives of cellulose of practical importance.

In order to render cotton fabric creaseless, the latter is treated with phosphoryl chloride in DMF at 65–78 °C for 0.5–1 h.[68] The chlorodeoxycellulose formed is treated with a 1–10% solution of ethylenediamine hydrogen sulphite in ethylenediamine. The resulting cellulose, cross-linked by polysulphide linkages, has effective creaseless properties: the opening angle is 210–300°, while more than 65% of the strength is retained. However, owing to the appearance of a yellow colour in the fabric, this method has not found a practical application.

In order to obtain a cationic polyelectrolyte capable of adsorbing transition metal ions, particularly mercury and copper ions, microcrystalline cellulose is activated with a 20% NaOH solution and is treated with thionyl or methanesulphonyl chloride in DMF at 90–100 °C for 1.5–16 h.[69] The resulting deoxycellulose is acted upon by hydrazine hydrate at 70–110 °C for 1–60 h. It has been suggested that the resulting hydrazinodeoxycellulose be used for analytical (detection of traces of polyvalent metals) and technological (purification of sewage) purposes.[69]

Compounds useful as adsorbents have been obtained by the reaction of chlorodeoxycellulose with diethylenetriamine,[57] ethylenediamine, thiourea, thiosemicarbazide,[58] 1,6-diaminohexane,[59] and other compounds. 2,2'-Diaminodiethylaminodeoxycellulose, obtained by the method of Smits and van Grieken,[57] is characterised by an ion-exchange capacity of 2.4 μequiv.cm^{-2} in relation to variable-valence metals. The limiting concentrations of iron, zinc, and copper ions detectable in one litre of water with the aid of membranes prepared from the given derivative are 1.5×10^{-7}, 0.5×10^{-7}, and 0.2×10^{-7}% respectively. The cellulose derivatives obtained by the method of Tashiro and Shimura[58] remove mercury ions from aqueous $HgCl_2$ solutions (concentration 1×10^{-3}%) to an extent greater than 99%. The mercaptodeoxycellulose obtained from chlorodeoxycellulose is used to immobilise enzymes and also as carriers for chromatography.[62,70]

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Analysis of the available data shows that the chemistry of halogenodeoxycelluloses has developed significantly in recent years.

A series of halogenating agents, new as regards cellulose, have found applications in the synthesis of halogenodeoxycelluloses. The possibility of using a readily available, cheap, and effective halogenating agent, namely sulphuryl chloride, for the synthesis of chlorodeoxycellulose with different D.S. has been demonstrated. A method has been developed for the introduction of any halogen (Cl, Br, or I) in the C(6)-position in the glucopyranose unit of cellulose under comparable conditions. Fluorodeoxycellulose with a high D.S. has been synthesised. Approaches have been outlined towards the selective substitution of the secondary hydroxy-groups in cellulose by halogen. The behaviour of a series of blocking functional groups in the reactions involving the substitution of the hydroxy-groups by a halogen and methods for their successive elimination in the presence of a halogen have been investigated.

New methods for the determination of the position of the halogen in the glucopyranose unit of halogenodeoxycellulose have appeared. A quantitative chemical procedure for the determination of the structures of 6-bromo- and 6-iodo-6-deoxycelluloses has been developed. A method has been devised for the establishment of the structure of chlorodeoxycellulose by ^{13}C NMR. Apart from the position of the halogen atom, the latter makes it possible to determine the stereochemistry of the process involving the substitution of the secondary hydroxy-groups by chlorine and the sequence in which the sugar residues, differing in the number, positions, and stereochemistry of halogen atoms, are linked to one another.

The physicochemical and other properties of halogenodeoxycelluloses have been little studied. The investigation of the biochemical properties, in particular the enzyme hydrolysis reactions, has only just begun.

A series of derivatives, which are difficult or are altogether impossible to obtain by other methods, have been synthesised from chlorodeoxycellulose. Some of them have found novel applications (for the immobilisation of enzymes and as adsorbents).

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