(Received May 29, 1978)

THERMAL REACTION OF CHLORODEOXYCELLULOSE

By Tadashi Ishii, Atsushi Ishizu and Junzo Nakano

(Faculty of Agriculture, The University of Tokyo, Bunkyo-ku, Tokyo)

Thermogravimetric analysis showed that chlorodeoxycellulose is thermally less stable than cellulose. Hydrogen chloride, which is generated from 6-chloro-6-deoxy-D-glucose residues in chlorodeoxycellulose, catalyzed dehydration, condensation and carbonization. The well-known flame resistance of chlorodeoxycellulose was considered to come from these thermal reactions. Pyrolysis products produced by use of a curie-point pyrolyzer were identified. A route of formation of the characteristic products of chlorodeoxycellulose, 5-methyl-2-furaldehyde and 2-furyl methyl ketone, was discussed.

1. INTRODUCTION

It is well known that halodeoxycelluloses have flame resistance. Only two reports^{1,2)}, however, could be found on thermal degradation of chlorodeoxycellulose by surveying literature. Samples used by Schwenker Jr.¹⁾ had low chlorine contents. In a recent McIntyre's work²⁾, samples with varying percentages of chlorine were used in order to see the effect of chlorine on the pyrolytic reactions of cellulose. This paper deals with the thermal reaction of highly chlorinated celluloses (Cl, 11 ~ 24%) by use of a curie-point pyrolyzer as well as a usual thermal analyzer.

2. EXPERIMENTAL

2.1 Preparation of chlorodeoxycellulose and chlorodeoxysugars.

Chlorodeoxycelluloses with various chlorine contents (Cl, 11 ~ 24%; degree of substitution, 0.47 ~ 1.3) were prepared by treating cellulose in *N,N*-dimethylformamide and chloral with methanesulphonyl chloride at 75°C³⁾. Methyl 6-chloro-6-deoxy- β -D-glucopyranoside⁴⁾, 6-chloro-6-deoxy-D-glucose⁵⁾ and 3,6-anhydro-D-glucopyranose⁶⁾ were synthesized according to literature. Filter paper (Toyo Roshi Ltd, Code No. 5C) was used as a cellulose sample. Samples were ground to fine powders (80 mesh) by a ball mill made of agate prior to pyrolysis.

2.2 Thermal analysis

Thermogravimetric and differential scanning calorimetric (TG and DSC) curves were obtained

by the use of Rigaku Electric Corp. Standard Type Thermal Analyzer. All experiments were performed with 4 mg samples in covered aluminum pans and an empty pan was used as the reference. Samples were heated at a rate of 5°C/min. under nitrogen with a flow rate of 50 ml/min.

2.3 Analysis of constituent sugars in heated chlorodeoxycellulose.

Samples (10 mg) of chlorodeoxycellulose (Cl, 11%) were heated in the thermal analyzer under the same condition described above. After cooling, sugar compositions of samples were analyzed according to the method described in the previous paper³⁾.

2.4 Curie-point pyrolysis.

Curie-point pyrolysis was performed by the use of the same equipment as that which Ohnishi et al. applied to the pyrolysis of cellulose⁷⁾ and xylan⁸⁾. The curie-point temperature (heating temperature) of ferromagnetic conductors used was 423°C. The oscillation period (heating time) was 5 sec. For the analysis of volatile pyrolysis products, a curie-point pyrolyzer was directly connected with a gas-liquid chromatograph and a mass spectrograph (c.p.-g.l.c.-m.s.). Non-volatile tarry products which condensed on the quartz wall of the pyrolyzer were analyzed by g.l.c.-m.s. after trimethylsilylation³⁾. Analytical conditions of g.l.c. are summarized in Table I. Each peak in gas-liquid chromatograms (Fig. 3 and 4) was identified by comparing its retention time and mass spectrum with those of authentic samples. Mass spectra were measured by the use of a Hitachi RMU-7 at 70 eV.

Table 1 Analytical conditions of g.l.c.

Sample	Instrument	Column	Column packing	Column temperature	Carrier gas	Detector
Volatile fraction	Hitachi 063	Stainless steel 0.3 × 200 cm	Carbowax 20M 5% on Chromosorb G AW (60-80 mesh)	80-240°C 7.5°C/min	He 40 ml/min	FID
Tarry fraction (As TMS derivatives)	Shimadzu 4CMFF	Glass 0.4 × 200 cm	SE-52 3% on Chromosorb G AW	50-180°C 2.0°C/min	N ₂ 40 ml/min	FID
Water	Hitachi 063	Stainless steel 0.3 × 200 cm	Chromosorb 101 (100-120 mesh)	50-130°C 10°C/min	He 40 ml/min	TCD

Amounts of volatile pyrolysis products and water were determined by their peak areas on gas-chromatograms, while non-volatile tarry products were determined by using glucitol as an internal standard.

3. RESULTS AND DISCUSSION

TG and DSC curves of chlorodeoxycelluloses with various chlorine contents (Cl, 11~24%) are shown together with those curves of cellulose in Fig. 1 and 2. Chlorodeoxycellulose is thermally less stable than cellulose and begins to decompose in the temperature range where cellulose is still unchanged (Fig. 1). There could not be found, however, any definite relationship between the chlorine content and the initial decomposition temperature, though McIntyre²⁾ reported that this temperature decreased with the increase in chlorine content. Chlorodeoxycellulose gives char in higher yield (40~50%) than cellulose (10%) (Fig. 1) does. Chlorodeoxycelluloses containing less than 19.5% chlorine (d.s., 1.0) were substituted only at C₆-OH by chlorine atoms and a sample containing more than 19.5% chlorine was further substituted at C₃-OH in addition to C₆-OH³⁾. The phenomena that the introduction of a chlorine atom into C₆ of a glucose residue results in the increases of thermal instability and of char production, was also observed in the case of methyl 6-chloro-6-deoxy- β -D-glucopyranoside⁹⁾. DSC curves of chlorodeoxycellulose have broad endotherms within the temperature range where rapid weight-loss occurs (Fig. 2).

TG curves of chlorodeoxycelluloses are quite similar to that of cellulose treated with acid phosphate¹⁰⁾. This suggests that the mechanism of thermal degradation of chlorodeoxycellulose is

Fig. 1 TG curves of chlorodeoxycellulose and cellulose. I, chlorodeoxycellulose (Cl, 11%); II, chlorodeoxycellulose (Cl, 16%); III, chlorodeoxycellulose (Cl, 18%); IV, chlorodeoxycellulose (Cl, 24%); V, cellulose.

Fig. 2 DSC curves of chlorodeoxycellulose and cellulose. I, chlorodeoxycellulose (Cl, 11%); II, chlorodeoxycellulose (Cl, 16%); IV, chlorodeoxycellulose (Cl, 24%); V, cellulose.

similar to that of cellulose in the presence of an acid catalyst. Actually, the decomposition gas formed on heating of chlorodeoxycellulose always contained hydrogen chloride, which could catalyze

Table 2 Change of constituent sugars of chlorodeoxycellulose (Cl, 11%) on heating to different temperatures.

Temperature °C	D-Glucose %*	6-Chloro-6-deoxy- D-glucose %*	3,6-Anhydro-D- glucopyranose %*	$\frac{\text{D-Glucose} \times 100}{\text{D-Glucose} + 6\text{-Chloro-deoxy-D-glucose}}$
20	29.5	26.1	none	53.1
135	26.5	25.3	0.6	51.2
140	24.7	25.8	Trace	48.9
145	25.6	23.4	Trace	55.2
156	19.7	23.4	Trace	47.5
160	13.1	17.1	1.2	43.4
170	Trace	Trace	Trace	—

*) Based on the weight of chlorodeoxycellulose

the decomposition of chlorodeoxycellulose. The dehydrohalogenation was observed in pyrolysis of 6-chloro monosaccharides, too⁹⁾.

In orders to get information on the initial decomposition reactions of chlorodeoxycellulose, samples (Cl, 11%) heated to different temperatures were hydrolyzed. The hydrolyzates were trimethylsilylated and analyzed by g.l.c. (Table 2). 3,6-Anhydro-D-glucopyranose was detected in hydrolyzates of a heated chlorodeoxycellulose, but not in that of a heated cellulose. This result indicates that 6-chloro-6-deoxy-D-glucose residues liberate hydrogen chloride at the initial decomposition stage to give 3,6-anhydro-D-glucopyranose residues. Rogovin et al.¹¹⁾ prepared 3,6-anhydro-cellulose by treating cellulose tosylate with sodium hydroxide.

Table 2 shows that unsubstituted glucose residues in chlorodeoxycellulose decompose at much lower temperature (<170°C) than those of cellulose, owing to the presence of hydrogen chloride secondarily produced. The rate of decomposition of 6-chloro-6-deoxy-D-glucose residues is a little lower than that of unsubstituted glucose residues.

In order to get further information on the mechanism of thermal decomposition of chlorodeoxycellulose, primary pyrolysis products were investigated by the curie-point pyrolysis (c.p.p.) technique. The c.p.p.-g.l.c. chromatogram of volatile pyrolyzates obtained from the chlorinated cellulose (Cl, 11%; d.s., 0.47) is shown in Fig. 3. Each peak was identified by comparing its retention time and mass spectrum with those of authentic samples. The primary pyrolysis products in the volatile fraction consist of *N,N*-dimethyl-

Fig. 3 G.l.c. of volatile pyrolyzates obtained from chlorodeoxycellulose (Cl, 11%). 1, *N,N*-dimethylformamide; 2, 2-furaldehyde; 3, 2-furyl methyl ketone; 4, 5-methyl-2-furaldehyde; 5, 1,6-anhydro-3,4-dideoxy- β -D-glycero-hex-3-enopyranos-2-ulose; 6, 1,4:3,6-dianhydro-D-glucopyranose.

formamide, 2-furaldehyde, 2-furyl methyl ketone, 5-methyl-2-furaldehyde, 1,6-anhydro-3,4-dideoxy- β -D-glycero-hex-3-enopyranos-2-ulose (levoglucosenone)^{7,12)}, 1,4:3,6-dianhydro-D-glucopyranose¹³⁾. Among them *N,N*-dimethylformamide is not a pyrolysis product but a solvent strongly absorbed to cellulose during preparation of chlorodeoxycellulose. 2-Furaldehyde, levoglucosenone and 1,4:3,6-dianhydro-D-glucopyranose were also found in the volatile products from cellulose (Table 3). The yield of levoglucosenone was reported to attain ca. 10% in the acid-catalyzed pyrolysis of cellulose¹⁴⁾.

The tarry products contained 1,6-anhydro- β -D-glucopyranose (levoglucosan), trace amounts of 3,6-anhydro-D-glucopyranose and 1,6-anhydro- β -D-glucofuranose (Fig. 4). As described above, 3,6-anhydro-D-glucopyranose is formed as one of the

Table 3 Pyrolysis products of chlorodeoxycellulose, chlorodeoxysugars and cellulose at 423°C for 5 seconds.

Samples Products	Chlorodeoxy- cellulose (Cl 11%)	Chlorodeoxy- cellulose (Cl 16%)	Chlorodeoxy- cellulose (Cl 24.3%)	Methyl 6-chloro- 6-deoxy- β -D- glucoside	6-Chloro-6- deoxy-D- glucose	Cellulose
Volatile products						
2-Furaldehyde	1.1%	0.6%	0.5%	Trace	0.1%	0.3%
5-Methyl-2-furaldehyde	1.5	1.3	0.8	0.2%	0.4	none
2-Furyl methyl ketone	Trace	Trace	Trace	Trace	Trace	none
Levoglucosenone	2.3	1.7	0.6	Trace	0.2	0.4
1,4:3,6-Dianhydro-D- glucopyranose	0.4	Trace	Trace	0.3	0.1	Trace
5-Hydroxymethyl-2- furaldehyde	none	none	none	none	none	Trace
Levulinic acid	none	none	none	none	none	Trace
Water	13.9	11.9	5.3	4.9	—	6.4
Char	24.8	32.3	22.7	14.9	15.3	17.6
Tar	4.7	4.4	6.4	15.1	7.4	39.4
Levoglucosan	2.7	Trace	Trace	none	none	14.8
3,6-Anhydro-D-gluco- pyranose	Trace	Trace	1.4	none	—	none

Fig. 4 G.L.C. of trimethylsilyl derivatives of the tarry pyrolyzates obtained from chlorodeoxycellulose (Cl, 11%). 7 and 7', 3,6-anhydro- α - and - β -D-glucopyranose; 8, 1,6-anhydro- β -D-glucopyranose; 9, 1,6-anhydro- β -D-glucofuranose; 10, D-glucitol (internal standard).

constituent sugar residues in the polymer chain (Table 2). The presence of this sugar in the non-volatile tarry products, therefore, shows that the formation of 3,6-anhydro-D-glucopyranose residue from 6-chloro-6-deoxy-D-glucose residues is partly accompanied by the cleavage of glycosidic bonds.

Pyrolysis products from chlorodeoxycellulose,

chlorodeoxysugars and cellulose are summarized in Table 3. Introduction of chlorine atoms resulted in the increase of water and char, and the decrease of tar. Yields of levoglucosan and levoglucosenone decreased significantly by the substitution of C_6-OH by chlorine atoms, as expected. Introduction of chlorine atoms, furthermore, caused the production of 2-furyl methyl ketone and 5-methyl-2-furaldehyde. They had been detected in the pyrolyzate of 6-chloro-6-deoxy sugars by Shafizadeh et al.⁹⁾ but were not produced from cellulose by the curie-point pyrolysis. The c.p.p. of 3,6-anhydro-D-glucopyranose gave these furan derivatives as minor products together with 2-furaldehyde and 1,4:3,6-dianhydro-D-glucopyranose as major products (Fig. 5). As 3,6-anhydro-D-glucopyranose residue can be formed from 6-chloro-6-deoxy-D-glucose residue by elimination of hydrogen chloride, it may be conceivable that the former two furan derivatives are produced via 3,6-anhydro-D-glucopyranose residues from 6-chloro-6-deoxy-D-glucose residues in chlorodeoxycellulose. However, the main route of the formation of these furan derivatives might be another one, because the yields of 2-furaldehyde and 1,4:3,6-dianhydro-D-glucopyranose, which are major products from 3,6-anhydro-D-glucopyranose, are lower than that of 5-methyl-2-furaldehyde in the case of chlorodeoxycellulose (Table 3).

Shafizadeh et al.⁹⁾ investigated the thermal

Fig. 5 G.L.C. of volatile pyrolyzates obtained from 3,6-anhydro-D-glucopyranose. 2, 2-furaldehyde; 3, 2-furyl methyl ketone; 4, 5-methyl-2-furaldehyde; 5, 1,6-anhydro-3,4-dideoxy- β -D-glycero-hex-3-enopyranos-2-ulose; 6, 1,4:3,6-dianhydro-D-glucopyranose.

degradation of 6-chloro-6-deoxy sugars by the use of a furnace type pyrolyzer and proposed the following decomposition scheme; 6-chloro-6-deoxy-D-glucose $\rightarrow$ 3,6-anhydro-D-glucopyranose $\rightarrow$ 5-hydroxymethyl-2-furaldehyde $\rightarrow$ levulinic acid $\rightarrow$ 4-hydroxy-3-pentenoic and 4-hydroxy-2-pentenoic acid lactones (α - and β -angelica lactones). Among these compounds, however, only 3,6-anhydro-D-glucopyranose could be detected in the volatile fractions of the curie-point pyrolyzates of 6-chloro-6-deoxy-D-glucose. This discrepancy must be due to the difference in the type of pyrolyzers used. Further reactions of primary products are known to occur more remarkably in the furnace type pyrolyzer than in the curie-point pyrolyzer.

4. CONCLUSION

- 1) Chlorodeoxycellulose decomposes at much lower temperature than cellulose.
- 2) Chlorodeoxycellulose yields water and char in higher yields, and tar in lower yield than cellulose on pyrolysis. These results can be ascribed to the reactions catalyzed by hydrogen chloride, which is liberated from 6-chloro-6-deoxy-D-glucose residue.
- 3) Curie-point pyrolysis of chlorodeoxycellulose produces the following (possibly primary) pyrolysis products: 2-furaldehyde, 2-furyl methyl ketone, 5-methyl-2-furaldehyde, levoglucosenone and

1,4:3,6-dianhydro-D-glucopyranose as the volatile products, and levoglucosan, 3,6-anhydro-D-glucopyranose and 1,6-anhydro-D-glucofuranose as the non-volatile tarry products.

4) Elimination of hydrogen chloride from 6-chloro-6-deoxy-D-glucose residue produces 3,6-anhydro-D-glucopyranose residue. This product may be the precursors of 5-methyl-2-furaldehyde and 2-furyl methyl ketone, both of which are the characteristic products in the pyrolysis of chlorodeoxycellulose.

Acknowledgement

The authors wish to thank Drs. Kunio Kato and Akio Ohnishi of the Central Research Institute, The Japan Tobacco Salt Public Corporation, for generously allowing them to use the curie-point analyzer and other instruments and for giving them much kind advice.

REFERENCE

- 1) R. I. Schwenker, Jr. and E. Pacsu, *Ind. Eng. Chem.*, **50**, 91 (1958).
- 2) C. McIntyre, Univ. Montana, Ph. D. Thesis, 1975, p. 107, from ABIPC, **46**, 922 (1976).
- 3) T. Ishii, A. Ishizu and J. Nakano, *Carbohydr. Res.*, **59**, 155 (1977).
- 4) M. F. Evans, L. Long, Jr. and F. W. Parrish, *J. Org. Chem.*, **33**, 1074 (1968).
- 5) B. Helferich and H. Bredereck, *Ber.*, **60**, 1965 (1927).
- 6) F. A. Lewis, F. Smith and A. M. Stephen, "Methods Carbohydr. Chem.," Academic Press, N.Y., **2**, p. 172 (1963).
- 7) A. Ohnishi, K. Kato and E. Takagi, *Polymer J.*, **7**, 431 (1975).
- 8) A. Ohnishi, K. Kato and E. Takagi, *Carbohydr. Res.*, **50**, 275 (1976).
- 9) F. Shafizadeh, Y. Z. Lai and C. R. Nelson, *J. Appl. Polym. Sci.*, **20**, 139 (1976).
- 10) K. Inagaki and K. Katsuura, *Kogyo Kagaku Zasshi*, **73**, 1433 (1970).
- 11) Yu M. Makhsudov, L. S. Gal'braikh, A. I. Polyakov and Z. A. Rogovin, *Vysokomol. Soed.*, **8**, 1289 (1966).
- 12) Y. Halpern, R. Riffer and A. Broido, *J. Org. Chem.*, **38**, 204 (1973).
- 13) D. Gardiner, *J. Chem. Soc. (C)*, 1473 (1966).
- 14) F. Shafizadeh and P. P. S. Chin, *Carbohydr. Res.*, **58**, 79 (1977).