[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF DELAWARE]

Chlorophenyl Carbamates of Methyl Cellulose[1]

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Carbamates of cellulose and of a cellulose ester have been prepared by Hearon, Hiatt and Fordyce,[3] who described the action of isocyanates on cotton linters, and hydrolyzed cellulose acetates. These substances reacted readily with phenyl and α-naphthyl isocyanates, giving products of high viscosity and convenient solubilities. Because of the desirable properties of these products, it was thought of interest to prepare carbamates of another commercially available cellulosic material, a partially substituted methyl ether. In order to introduce chlorine into the molecule, the isocyanates chosen were *o*- and *p*-chlorophenyl isocyanates.

The progress of the reaction of the methyl cellulose with the respective isocyanates was followed by removing samples from the reaction mixture at various times, purifying and analyzing the products. Evidence of complete reaction of the free hydroxyl groups was obtained (see Tables I and II) after about six hours at 65° in the case of both the *o*- and the *p*-isomers. This is comparable to the ease of reaction of hydrolyzed cellulose acetates with phenyl isocyanate itself.[3]

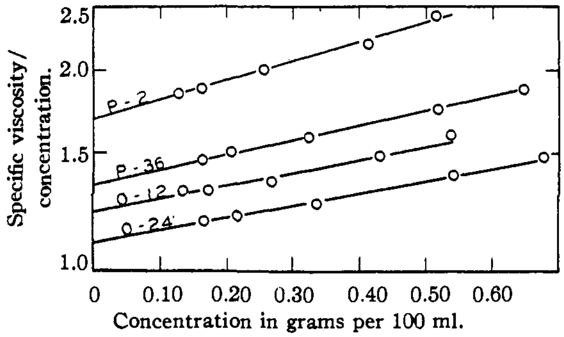

Fig. 1.—Viscosities of methyl cellulose chlorophenyl carbamates; *p*, para isomers; *o*, ortho isomers; the numbers refer to reaction time in hours.

TABLE I

METHYL CELLULOSE *p*-CHLOROPHENYL CARBAMATES

Hours of reaction	% N	% Cl	% OCH_3	Substituent groups per glucose unit ClC_6H_4NHCOO[a]	OCH_3	OH
2	4.08	10.50	15.89	1.00	1.82	0.18
4	3.95	10.63	16.27	0.98	1.78	.24
6	4.86	12.18	14.06	1.38	1.81	− .19
12	4.85	11.84	14.54	1.34	1.85	− .19
36	4.76	12.06	13.82	1.32	1.73	− .05

[a] The per cent. of carbamate used to calculate this figure was the average of that calculated from the per cent. of N and of Cl.

TABLE II

METHYL CELLULOSE *o*-CHLOROPHENYL CARBAMATES

Hours of reaction	% N	% Cl	% OCH_3	Substituent groups per glucose unit ClC_6H_4NHCOO[a]	OCH_3	OH
4	4.10	11.08	15.51	1.12	1.80	0.08
6	3.98	11.34	15.47	1.18	1.84	− .02
12	3.99	11.12	15.84	1.13	1.86	.01
24	4.08	11.35	15.25	1.17	1.81	.02
30	3.92	10.90	15.49	1.08	1.76	.16

[a] In the ortho carbamates the per cent. of N was low by any variation of the Kjeldahl method, and therefore the number of carbamate groups present was calculated from the per cent. of Cl only.

The intrinsic viscosities of acetone solutions of certain of the products were determined in order to have some estimate of the amount of degradation that had occurred during the reaction. Figure 1 shows that the extension of the time of heating from twelve to twenty-four hours in the case of the ortho carbamates or from two to thirty-six hours with the para carbamates brought about relatively little degradation. The cause of the consistently lower values of the ortho carbamates is not known. The intrinsic viscosities of these samples of methyl cellulose chlorophenyl carbamates are comparable to those of the middle fractions of cellulose acetates obtained by Sookne and Harris[4] from a carefully prepared laboratory specimen of the acetates.

Since the interaction of the chlorophenyl isocyanates with water and methyl alcohol during the preparation or purification process gave by-product ureas and methyl carbamates, these were synthesized. Three of these products are not recorded in the literature: methyl *p*-chlorophenyl carbamate, methyl *o*-chlorophenyl carbamate, and di-*o*-chlorophenyl urea.

Experimental

Methyl Cellulose *o*-Chlorophenyl Carbamates and Methyl Cellulose *p*-Chlorophenyl Carbamates.—In all experiments Hercules Powder Co. methyl cellulose having 1.86 methoxyl groups per glucose unit was used. The following description of the preparation of the ortho carbamates is applicable with practically no changes to the para isomers.

To the methyl cellulose obtained by drying 31.9 g. of the commercial product with benzene[5] was added 250 ml. of pyridine (dried by refluxing over barium oxide) and a solution of 47 g. of *o*-chlorophenyl isocyanate in 50 ml. of dry pyridine. The mixture was heated in a constant temperature bath at 65° with occasional shaking. After four hours the mass was a nearly homogeneous brown sirup. About one-fifth of the material was removed in each of five samples taken after four, six, twelve, twenty-four and thirty hours of heating.

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[1] From the Master's Thesis of Katheryne Levis, University of Delaware, 1945.

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[3] Hearon, Hiatt and Fordyce, THIS JOURNAL, 65, 829 (1943).

[4] Sookne and Harris, *Ind. Eng. Chem.*, 37, 476 (1945).

[5] Ref. 3, p. 831.

The portion of the sirup removed was treated with about 70 ml. of absolute methanol to destroy unreacted isocyanate as the soluble methyl *o*-chlorophenyl carbamate. The cellulosic product was precipitated by the slow addition of this diluted sirup to about two liters of rapidly stirred absolute methanol. A total of 51 g. of crude product was obtained from all the samples.

An 8-g. portion of the dried product from a particular sample was then dissolved in about 300 ml. of dry dioxane by standing at least twelve hours with frequent shaking. Unreacted gelatinized methyl cellulose and the crystalline di-*o*-chlorophenyl urea which was formed in small amounts in spite of efforts to exclude moisture were removed by filtration, using Hyflo Super-cel. The dioxane solution was evaporated *in vacuo* at 40–45° to a volume of about 250 ml., and then added dropwise to three liters of rapidly stirred distilled water. The precipitated product was washed by decantation at least eight times, filtered, dried in a vacuum desiccator and the dioxane purification process repeated. It was then twice dissolved in acetone, with filtration from a trace of insoluble matter and reprecipitated with water. The product was a white material with a fibrous appearance. Analyses are given in Tables I and II.

The completely substituted carbamates, both ortho and para, are soluble in acetone, dioxane, chloroform, cyclohexanone and pyridine, insoluble in methanol and in water, whereas the original methyl cellulose is insoluble in the first four solvents, gelatinized in pyridine, and soluble in water. When heated in a melting-point tube, the twelve and thirty-six hour samples of the para compound started to shrink above 180° and were melted by 210°. Samples of the ortho carbamates (four hour and twenty-four hour specimens) shrank above 160° and were melted by 200°.

Viscosity Determinations.—The original methyl cellulose was material of "medium viscosity" reported as 50 centipoises in a 2% aqueous solution at 20°. The viscosities of the carbamate esters were determined in acetone solution by means of an Ostwald viscosimeter in a constant temperature bath kept at 25 ± 0.05°. Extrapolation of the curves obtained by plotting specific viscosity over concentration against concentration (Fig. 1) gave 1.70 and 1.35 as the intrinsic viscosities of the two-hour and the thirty-six-hour *p*-chlorophenylcarbamates, respectively. The corresponding values for the twelve-hour and twenty-four-hour *o*-chloro derivatives were $[\eta]$, 1.24 and $[\eta]$, 1.10.

Methyl *p*-Chlorophenyl Carbamate.—A mixture of 5 g. (0.03 mole) of *p*-chlorophenyl isocyanate and 6.2 ml. (0.15 mole) of absolute methanol reacted immediately with evolution of heat to form methyl *p*-chlorophenyl carbamate in quantitative yield. After two recrystallizations from 2:1 methanol–water solution, the melting point was 117–117.5° (cor.). The substance is soluble in acetone, dioxane and methanol, insoluble in water.

Anal. Calcd. for $C_8H_8O_2NCl$: N, 7.55; Cl, 19.10. Found: N,[6] 7.93; Cl, 18.93.

Methyl *o*-Chlorophenyl Carabamate.—When 15 g. (0.10 mole) of *o*-chlorophenyl isocyanate was added to 25 ml. (0.78 mole) of absolute methanol an immediate exothermic reaction occurred. The pure product, isolated by distillation under reduced pressure, boiled at 138–138.5° (uncor.) at 18 mm. Distillation under atmospheric pressure resulted in decomposition, giving di-*o*-chlorophenyl urea. The carbamate ester is very soluble in acetone, dioxane, benzene, and methanol and insoluble in water.

Anal. Calcd. for $C_8H_8O_2NCl$: N, 7.55. Found: N, 7.23.

Di-*o*-chlorophenyl urea was prepared by the interaction of *o*-chlorophenyl isocyanate with excess water at room temperature. The product melted at 240.5–241.5° (cor.) after recrystallization from glacial acetic acid. It is slightly soluble in acetone, dioxane and pyridine.

Anal. Calcd. for $C_{13}H_{10}ON_2Cl_2$: N, 9.97; Cl, 25.23. Found: N, 9.42; Cl, 25.01.

The di-*p*-chlorophenyl urea, prepared according to Vittenet,[7] is insoluble in dioxane and slightly soluble in acetone and pyridine.

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Summary

1. Methyl cellulose *o*- and *p*-chlorophenyl carbamates have been prepared by the action of *o*- and *p*-chlorophenyl isocyanates in the presence of pyridine on a methyl cellulose containing free hydroxyl groups.

2. Complete substitution was attained within six hours at 65°. The products had convenient solubilities and were relatively undegraded as shown by viscosity measurements.

3. Methyl *o*- and *p*-chlorophenyl carbamates and di-*o*-chlorophenyl urea are described.

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[6] The nitrogen analysis was a micro Dumas done by Arlington Laboratories, Fairfax, Virginia. Kjeldahl determinations were unsatisfactory on this substance.

[7] Vittenet, *Bull. soc. chim.*, (3) **21**, 302 (1899).