	Ortho	Meta	Para
Vapor press. (298°K.), mm.	6.64	8.39	8.87
Entropy of vap. (298°K.) (liq. to hypoth. gas 1 atm.), cal./deg.	25.70	25.13	25.07
Entropy of the gas (298°K.), cal./deg.	84.50	85.60	84.27
Equil. comp. (323°K.), %	10	72	18

Various thermodynamic functions were calculated for mesitylene from molecular structure data, the gas entropy at 298°K. being 92.34 cal. per degree. The entropies of pseudocumene (1,2,4-trimethylbenzene) and durene (1,2,4,5-tetramethylbenzene) were estimated to be 94.2 and 98.5 cal. per degree, respectively, in the gas state at 298°K.

2. **Molecular Structure Data.**—By consideration of the lines appearing in the infrared and Raman spectra of liquid benzene (but not of gaseous benzene) in violation of the simple selection rules, it was possible to complete the assignment of fundamental vibration frequencies. Although a few values are not completely certain, all are reasonable from the point of view of the force constants of the benzene molecule. The spectra of the simpler deuterated benzenes were also considered.

The fundamental vibration frequencies were selected for toluene, all three xylenes, and mesitylene using Raman and infrared spectra from the literature. A modification of the Teller–Redlich product rule appropriate for methyl substitution was of great assistance in these assignments. The results vary from reasonably certain selections for some substances to somewhat arbitrary ones for others.

Attention is called to the striking behavior of the 1000 cm.$^{-1}$ line in benzene derivatives which are substituted in only 1,3,5-positions. Corresponding effects are observed where the trigonal positions are all similarly substituted. It is suggested that the Raman spectra might be used to determine the position of substituents in favorable cases.

Using these frequencies the vibrational entropy and heat capacity contributions can be calculated and the corresponding quantities for internal rotation of methyl groups obtained. The results indicate relatively free rotation of methyl groups in toluene, *m*- and *p*-xylene but about a 2000 cal. potential barrier for *o*-xylene. These results are shown to be reasonable in terms of steric effects.

The xylene equilibrium data show the meta compound to have lowest energy and suggest that meta orientation of identical or similar groups may be generally the most stable.

BERKELEY, CALIFORNIA RECEIVED NOVEMBER 11, 1942

[CONTRIBUTION FROM THE EASTMAN KODAK COMPANY]

Carbamates of Cellulose and Cellulose Acetate. I. Preparation[1]

BY W. M. HEARON, GORDON D. HIATT AND CHARLES R. FORDYCE

Reactions of cellulosic materials with isocyanates have been described in the patent literature. According to a U. S. patent,[2] cellulose or its derivatives containing free hydroxyl groups react with aliphatic or aromatic isocyanates in the presence of tertiary organic bases. A Swiss patent[3] describes the treatment of cellulose with phenyl isocyanate with or without the addition of a small amount of pyridine. The cellulosic structure was not changed but the material increased in weight and the product contained nitrogen. Another U. S. patent[4] covers the production of acetone-soluble organic acid esters of cellulose containing carbamyl groups. Examples in all of these patents include only phenyl isocyanate for preparing derivatives, although the claims in several cases are of a general nature.

In addition to the chemical nature of the isocyanate, several other factors must be considered in the preparation of carbamates of cellulose. Among these are the nature of the cellulosic material, the reaction solvent, concentration of reagent and the time and temperature of reaction. This paper reports a study of the reaction of both aliphatic and aromatic isocyanates on cellulosic

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(1) Presented before the Division of Cellulose Chemistry at the 104th meeting of the American Chemical Society at Buffalo, New York.

(2) P. E. C. Goissedet, U. S. Patent 1,357,450 (November 2, 1920).

(3) Gesellschaft für Chemische Industrie, Basel, Swiss Patent 142,749 (December 16, 1930).

(4) C. J. Malm and G. F. Nadeau, U. S. Patent 1,991,107 (February 12, 1935).

Table I

Cellulose Acetate Methyl Carbamates Obtained from Cellulose Acetate of 30.8% Acetyl

Hours of reaction	Temp., °C.	% Acetyl	% CH_3NHCO	Substituent groups per glucose unit			Solubilities				
				CH_3CO	CH_3NHCO	OH	Acetone	Pyridine	1,4-Dioxane	Chloroform	Ethyl acetate
0	...	30.8	0	1.66	0	1.34	−	+	+	−	−
1	40	30.3	1.7	1.66	0.07	1.27	−	+	+	−	−
3	40	29.7	3.6	1.66	.15	1.19	−	+	±	−	−
5	40	29.3	5.0	1.66	.21	1.13	−	+	±	−	−
7	40	28.8	6.8	1.66	.29	1.05	−	+	±	−	−
1	100	26.1	15.5	1.66	.73	0.61	−	+	−	−	−
5	100	24.6	20.4	1.66	1.02	.32	−	+	−	−	−

Table II

Cellulose Acetate Ethyl Carbamates Obtained from Cellulose Acetate of 30.8% Acetyl

Hours of reaction	Temp., °C.	% Acetyl	% C_2H_5NHCO	Substituent groups per glucose unit			Solubilities				
				CH_3CO	C_2H_5NHCO	OH	Acetone	Pyridine	1,4-Dioxane	Chloroform	Ethyl acetate
0	...	30.8	0	1.66	0	1.34	−	+	+	−	−
2	40	30.15	2.1	1.66	0.07	1.27	−	+	+	−	−
4	40	29.4	4.6	1.66	.16	1.18	−	+	+	−	−
6	40	28.9	6.3	1.66	.21	1.13	−	+	+	−	−
1	100	29.3	4.7	1.66	.16	1.18	−	+	+	−	−
5	100	Reaction mixture gelled									

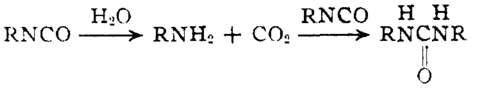
Table III

Cellulose Acetate Phenyl Carbamates Obtained from Hydrolyzed Cellulose Acetates

% Acetyl original acetate	Hours of reaction	Temp., °C.	% Acetyl calcd. for complete reaction	% Acetyl found	% RNHCO found	Substituent groups per glucose unit		Solubilities				
						CH_3CO	RNHCO	Acetone	Pyridine	1,4-Dioxane	Chloroform	Ethyl acetate
16.7	18	100	7.0	6.4	57.3	0.75	2.25	+	+	+	−	+
23.7	10	50	11.6	11.5	53.6	1.16	1.84	+	+	+	+	+
30.8	10	50	18.25	18.3	41.1	1.66	1.34	+	+	+	+	+
38.6	10	50	29.5	29.3	23.6	2.33	0.67	+	+	+	+	+

materials, including an evaluation of the several variables involved.

Any organic isocyanate reacts readily with water to give the primary amine which in turn reacts with more isocyanate to yield a symmetrical urea as the final product, according to the equations



$$RNCO \xrightarrow{H_2O} RNH_2 + CO_2 \xrightarrow{RNCO} R\overset{H}{N}\underset{\underset{O}{\|}}{C}\overset{H}{N}R$$

Since two moles of isocyanate are used for every mole of water, all components of reaction mixtures were kept as nearly anhydrous as possible.

The simplest urethan would be that of carbamic acid itself. Several attempts were made to prepare this by reaction of cyanic acid in a pyridine solution of cellulose acetate, but only products of low nitrogen content were obtained.

As examples of alkyl carbamates, reactions with methyl and ethyl isocyanates were studied. Partial esterification of the free hydroxyl groups of partially hydrolyzed cellulose acetate was readily obtained. Attempts to completely esterify the free hydroxyl groups were unsuccessful, and in some cases gelatinous reaction solutions were formed. Solubilities and analytical characteristics of the cellulose acetate methyl and ethyl carbamates prepared are given in Tables I and II.

In contrast with the aliphatic reagents, aromatic isocyanates reacted very readily and completely with cellulosic materials. Cellulose acetate with excess phenyl isocyanate in pyridine at 60° reacted to the extent of 81% in the first hour and completely in seven hours. Analytical data and solubilities of the products obtained from four cellulose acetates are given in Table III.

α-Naphthyl isocyanate reacted readily and completely to give cellulose acetate α-naphthyl carbamates. It is essential, in this case, to have practically no water present in the cellulosic material or solvent (pyridine), otherwise a voluminous precipitate of di-α-naphthyl urea forms which must be removed by filtration before precipitation of the ester.[5]

(5) A convenient and sensitive qualitative test for traces of water consists in adding to the solvent a few drops of dry pyridine (as a catalyst) followed by addition of α-naphthyl isocyanate. The water is converted to di-α-naphthyl urea which, being insoluble (or very nearly so) in all organic solvents tested, precipitates out in a short time. The volume of this precipitate is a measure of the water present.

TABLE IV

CELLULOSE ACETATE α-NAPHTHYL CARBAMATES OBTAINED FROM HYDROLYZED CELLULOSE ACETATES

				Substituent groups per glucose unit			Solubilities				
Hours of reaction	Temp., °C.	% Acetyl	% RNHCO	CH_3CO	RNHCO	OH	Acetone	Pyridine	1,4-Dioxane	Chloroform	Ethyl Acetate
2	60	25.8	16.0	1.66	0.26	1.08	−	+	+	−	−
5	20	19.9	35.6	1.66	.75	0.59	+	+	+	Swells	−
1	60	17.6	43.2	1.66	1.03	.31	+	+	+	Swells	−
5	60	15.2	49.7	1.66	1.34	.00	+	+	+	+	+
60	25	9.6	60.0	1.16	1.84	.00	+	+	+	+	+

Variation in reaction time showed that with aromatic isocyanates ten hours is sufficient for complete reaction at 40–50°, while with the aliphatic reagents esterification remained incomplete after one hundred and thirty-seven hours.

Excess isocyanate increased the tendency for reaction. With both the aliphatic isocyanates the amount of entering carbamate group was increased, and with the aromatic types, all free hydroxyls were esterified. With excess cellulose ester the aromatic isocyanates could be made to react quantitatively under suitable conditions of time and temperature.

Effect of temperature is shown in Fig. 1. Similar results were obtained with α-naphthyl isocyanate. Within experimental error, its rate of reaction at each temperature is about that of phenyl isocyanate. Properties of cellulose acetate α-naphthyl carbamates are given in Table IV.

Considerably different conditions were encountered when the cellulose acetate was replaced by cellulose. Cotton linters and regenerated cellulose exhibited little or no reaction with cyanic acid or with methyl and ethyl isocyanates. Both phenyl and α-naphthyl isocyanates, however, reacted readily with low viscosity cotton linters to produce trisubstituted derivatives. No appreciable reaction occurred at 50°, but at 100° complete esterification was accomplished within forty-eight hours Solution of the cellulose was evidence of complete reaction; samples taken as soon as the cellulose had dissolved showed upon analysis that the derivative already contained three carbamate groups for each glucose unit.

With less than the theoretical amount of phenyl isocyanate the cellulose did not dissolve, but increased in weight. Nitrogen was found present corresponding closely to the calculated amount. The final products still retained the original fibrous structure.

Although the aromatic isocyanates reacted readily with low viscosity linters, regenerated celluloses from viscose, cuprammonium rayon, or from deacetylation of cellulose acetate remained unreacted after three-day treatments in pyridine on a steam-bath. Negligible results were also obtained in one experiment using quinoline at 150°.

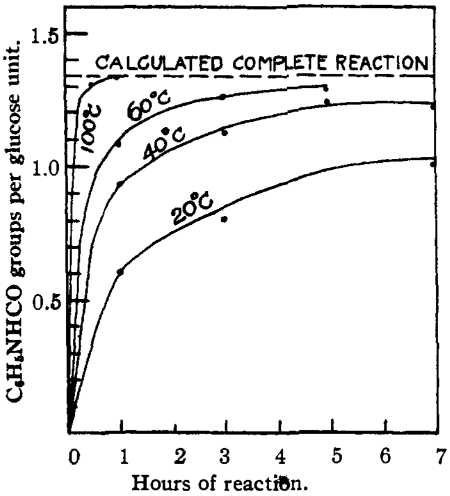


Fig. 1.—Effect of temperature on the rate of reaction of phenyl isocyanate with hydrolyzed cellulose acetate.

Experimental

In all experiments, the starting cellulosic material was dried by distilling benzene from it. Without changing flasks the solvent and reagent were then added. Residual benzene did not affect the subsequent reaction. The weights of starting materials were corrected for moisture present to produce the desired dry weight.

In working up products, the standard procedure was to precipitate the reaction mixture in a suitable nonsolvent which would allow any impurities or by-products to remain in solution. The ester on recovery by filtration was redissolved in a solvent, generally acetone or pyridine and reprecipitated. This process was repeated until the ester was free from impurity.

Cellulose Acetate and Urea.—A solution of 50 g. of cellulose acetate (30.8% acetyl) in 300 g. of pyridine (water less than 0.01%) was heated on a steam-bath with 52.0 g. (3 times theoretical) of urea for eighty hours. The mixture, still containing undissolved urea, had become somewhat darker. Precipitation into warm water and purification gave a fibrous and nearly colorless product.

Anal. Acetyl, 29.3; N, 0.4, corresponding to 0.07 carbamate group for each glucose unit.

The above experiment was repeated using 400 cc. of quinoline at 150° for twenty hours. Ammonia was liberated throughout the heating and the gray colored product showed evidence of degradation.

Anal. N, 1.40, corresponding to 0.26 carbamate group, or 19.4% of the original free hydroxyls.

Cellulose Acetate and Nitrourea.—To a solution of 50 g. of cellulose acetate (30.8% acetyl) in 300 g. of pyridine was added 45.5 g. (1.5 times calcd.) of nitrourea. After ten minutes on a steam-bath considerable gas was liberated and the reaction mixture boiled. Gas evolution subsided in a few minutes, but heating was continued for sixteen hours, and the white, fibrous product was then isolated.

Anal. Acetyl, 30.2; N, 0.65, corresponding to 0.11 carbamate group for each glucose unit.

Cellulose Acetate and Dry Cyanic Acid.—Cyanic acid gas, generated from 12.6 g. of cyanuric acid, was bubbled for one hour through a solution of 30 g. of cellulose acetate (32.9% acetyl) in 300 g. of dry pyridine on a steam-bath. Heating and stirring were then continued for four hours. The product after isolation contained 31.5% acetyl, which corresponds to 0.24 carbamate group for each glucose unit.

Cellulose Acetate and Methyl Isocyanate.—Fifty grams of cellulose acetate (30.8% acetyl) in 300 g. of dry pyridine was treated with 24.7 g. (1.5 times theoretical) of methyl isocyanate[6] for seven hours at 40°. Samples taken at intervals (Table I) were all fibrous and colorless.

Reaction of 20 g. of cellulose acetate (32.9% acetyl) in 150 g. of pyridine and 11.2 g. (2 times theoretical) of methyl isocyanate gave, after one hundred and thirty-seven hours at 40° a soft, thin gel which dissolved on dilution with pyridine. The isolated product contained 26.25% acetyl, corresponding to 1.05 methyl carbamate groups for each glucose unit, or 90% complete reaction.

Duplicate 10-g. samples of cellulose acetate (30.8% acetyl) were dissolved in 60 g. of pyridine and treated with 4.1 g. (1.25 times theoretical) of methyl isocyanate in sealed bottles on a steam-bath for one and five hours, respectively.

The one-hour sample on cooling was thick and grainy. Dilution with pyridine gave a poor solution which was precipitated into water. The purified product (acetyl, 26.1%) was white and fibrous, but insoluble in acetone or acetone–water mixtures.

The five-hour sample had formed a stiff gel which was found to be insoluble in all the usual solvents. The material was ground up and extracted thoroughly with methanol, then water: acetyl, 24.6.

Cellulose Acetate and Ethyl Isocyanate.—Reaction of 50 g. of cellulose acetate (30.8% acetyl) in 300 g. of pyridine with 51.3 g. (2.5 times theoretical) of ethyl isocyanate[6] at 40° yielded white, fibrous products showing good solubilities (Table II).

After one hundred and thirty-seven hours at 40° 20 g. of cellulose acetate (32.9% acetyl) in 150 g. of pyridine and 14.3 g. of ethyl isocyanate (2 times theoretical) gave a yellow, viscous solution which yielded a white, fibrous product of 26.8% acetyl, indicating reaction of 66% of the free hydroxyl groups.

Duplicate 10-g. samples of cellulose acetate (30.8% acetyl) in 60 g. of pyridine were heated at 100° in sealed bottles with 6.2 g. (1.5 times theoretical) of ethyl isocyanate for one and five hours, respectively.

The one-hour sample gave a slightly yellow viscous solution, which yielded a white, fibrous product of 29.3% acetyl, indicating reaction of 12.2% of the free hydroxyl groups.

The five-hour reaction gave a gelatinous product soluble only in pyridine.

Cellulose Acetate and Phenyl Isocyanate.—Ten grams of cellulose acetate (16.7% acetyl) was dissolved in a mixture of 100 g. of formamide (0.63% water) and 100 g. of pyridine, then diluted with 100 g. of pyridine and 29.1 g. of phenyl isocyanate (1.5 times theoretical plus sufficient isocyanate to react with all water present), added slowly because of carbon dioxide evolution. After eighteen hours on a steam-bath the clear, tan, viscous solution yielded a white, fibrous product.

Anal. Acetyl, 6.4. Calcd. for complete esterification, 7.0.

Ten-gram portions of cellulose acetates of 23.7, 30.8 and 38.6% acetyl content were dissolved in 100-g. portions of pyridine and treated, respectively, with 15.6 g. (1.5 times theoretical), 8.6 g. (1.25 times theoretical) and 4.6 g. (1.5 times theoretical) of phenyl isocyanate for ten hours at 50°. The white, fibrous products were precipitated and purified as usual. Esterification in all cases was essentially complete (Table III).

When treated with sufficient phenyl isocyanate (26.0 g.) to esterify only part of the free hydroxyl groups, 50 g. of cellulose acetate (30.8% acetyl) in 300 g. of pyridine after six hours at 60° gave a product of 20.6% acetyl, indicating complete reaction of available isocyanate (calculated acetyl, 20.4).

Reactions at varying temperatures were made using 50-g. samples of cellulose acetate (30.8% acetyl) in 300 g. of pyridine and 34.8 g. of phenyl isocyanate (theoretical for all free hydroxyls). Samples were withdrawn at various times, worked up, and analyzed (Fig. 1). All products were white, fibrous, and soluble in many of the usual cellulose ester solvents.

Cellulose Acetate and α-Naphthyl Isocyanate.—Fifty grams of cellulose acetate (30.8% acetyl) in 300 g. of pyridine was treated with 73.3 g. (1.5 times theoretical) of α-naphthyl isocyanate at 60°. A fine haze of di-α-naphthyl urea gradually appeared. Samples after one, three and five hours were isolated, reprecipitated from acetone solutions into large volumes of methanol and finally precipitated into water. All samples were white and fibrous.

Anal. Acetyls of 16.6, 16.0 and 15.6% corresponded, respectively, to 87, 94 and 100% reaction of free hydroxyl groups.

Cotton Linters and Excess Isocyanate.—Phenyl isocyanate (99 g., 1.5 times theoretical) reacting with 30 g. of cotton linters (of low viscosity) in 400 g. of pyridine show no visible change after eighty hours at 50° so the mixture was placed under reflux on a steam-bath. After four hours the linters were well swollen and broken up. The condenser was replaced by a mechanical stirrer and

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[6] Prepared by the method of Slotta and Lorenz, *Ber.*, **58**, 1332 (1925).

heating continued, producing a clear solution after thirty-six hours. The white, fibrous product showed good solubilities, giving solutions of high viscosity; yield, 95.2 g. (99%); N, 8.16; calcd., 8.09.

Treated with 47 g. (1.5 times theoretical) of α-naphthyl isocyanate, 10 g. of low viscosity cotton linters in 300 g. of pyridine after forty hours, yielded a clear, highly viscous solution. After dilution with methanol and pyridine, purification was carried out as usual. The white, fibrous product was soluble in many common cellulose ester solvents: yield, 35.5 g. (86%); N, 6.25; calcd. 6.28.

Cotton Linters and Restricted Amounts of Phenyl Isocyanate.—Duplicate 10-g. portions of dried cotton linters (low viscosity) in 200 g. of pyridine and (a) 16.5 g. (0.75 theory) and (b) 11.0 g. (0.5 theoretical) of phenyl isocyanate after sixty-five hours of stirring on a steam-bath did not dissolve. They were diluted with pyridine and isolated by water washing. Both still resembled cotton linters. Purification by washing with water, then methanol, gave products insoluble in all usual solvents: yield, (a) 18.0 g., (b) 19.5 g.; N, (a) 6.24, (b) 7.14; calcd. for complete reaction, (a) 6.17, (b) 7.32.

Summary

1. Cellulose acetate containing free hydroxyl groups reacts incompletely with cyanic acid, and methyl and ethyl isocyanates. The latter two have a pronounced tendency to produce materials insoluble in the usual cellulose ester solvents.
2. With excess quantities of phenyl or α-naphthyl isocyanates in the presence of pyridine products of good solubility are obtained.
3. The factors of time, temperature, amount of reagent, nature of cellulose material, and catalyst, for the reaction of phenyl isocyanate with free hydroxyls of cellulose acetate were studied.
4. Low viscosity cotton linters react readily with phenyl or α-naphthyl isocyanates in the presence of pyridine to give products of high viscosity and good solubilities. When less than enough isocyanate to esterify all hydroxyl groups is used, the reagent reacts completely, giving a product unchanged in appearance from the original cellulose and insoluble in the usual cellulose ester solvents.

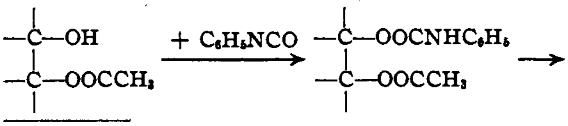
ROCHESTER, N. Y. RECEIVED NOVEMBER 27, 1942

[CONTRIBUTION FROM THE EASTMAN KODAK COMPANY]

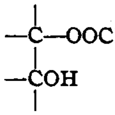
Carbamates of Cellulose and Cellulose Acetate. II. Stability toward Hydrolysis[1]

BY W. M. HEARON, GORDON D. HIATT AND CHARLES R. FORDYCE

In the preceding paper were given conditions for preparation of carbamates of cellulose and of cellulose acetates containing free hydroxyl groups. It was found that phenyl and α-naphthyl isocyanates could be made to react quantitatively with free hydroxyl groups of cellulose acetate without disturbing acetyl groups which were present, and that the former reagent was particularly suitable for this purpose. Furthermore, the phenyl carbamate group was noted to be very stable toward hydrolysis. These facts presented the possibility of covering free hydroxyls of cellulose acetate with a group which would permit quantitative removal of acetyl groups while it itself remained essentially unaffected. Products thus formed would contain free hydroxyls exactly representing the original acetyl groups as shown by the formulas



$$\begin{matrix}|\\-C-OH\\|\\-C-OOCCH_3\\|\end{matrix} \xrightarrow{+\ C_6H_5NCO} \begin{matrix}|\\-C-OOCNHC_6H_5\\|\\-C-OOCCH_3\\|\end{matrix} \longrightarrow$$



$$\begin{matrix}|\\-C-OOCNHC_6H_5\\|\\-COH\\|\end{matrix}$$

Cellulose acetate in solution with an acid catalyst undergoes a uniform, gradual reduction in acetyl content. If higher aliphatic acyl groups are present, they are usually somewhat more resistant to hydrolysis, but are simultaneously removed in sufficient quantity to make selective hydrolysis impractical.

Cellulose acetate phenyl carbamates were subjected to such a hydrolytic treatment to measure the relative rates of removal of these two substituent groups. No removal of phenyl carbamyl groups resulted, while the acetyl values showed a continual decrease (Fig. 1) at a constant rate.

As an extreme test a cellulose acetate phenyl carbamate was heated in acid solution for eighteen hours on a steam-bath. The product was badly degraded but was isolated and found to contain nitrogen equivalent to that for complete removal of acetyl groups and entire retention of carbamate.

Stability toward alkaline reagents was tested by

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(1) Presented before the Division of Cellulose Chemistry at the 104th meeting of the American Chemical Society, Buffalo, New York.