through its conversion first to the dibromide, followed by its conversion to cinnamyl tribromide.[5]

In all experiments except one, the ether solution was treated with bromine before fractionation in order to facilitate the removal of allylbenzene. The results of the various trials are summarized in Table II.

TABLE II

Products recovered	Yield in grams				
Experiment	1	2	3	4	5
CCl_3CH_2OH from solid	11	15	15	12	6
CCl_3CH_2OH from filtrate	5	..	3	..	7
$C_6H_5CH_2CH{=}CH_2$	..	12	..	..	..
$C_6H_5CH_2CHBrCH_2Br$	30	8	23	24	25
$C_6H_5CH_2CH_2CH_2CH_2CH_2CH_2C_6H_5$	7	5	3	5	3

TABLE III

Products recovered	Yield in grams		
Experiment	1	2	3
CCl_3CH_2OH from solid	13	16	12
CCl_3CH_2OH from filtrate	4	2	4
$C_6H_5CH_2CH_2CHBrCH_2Br$	33	34	29
$C_6H_5(CH_2)_8C_6H_5$	3	3	3

Action of Chloral on δ-Phenylbutylmagnesium Bromide.—In these experiments the usual procedure described above was followed except that no attempt was made to separate the 4-phenylbutene-1 formed in the reaction. In all cases this was identified as the dibromide. The results are given in Table III.

Summary

1. β - Phenylethylmagnesium bromide, γ - phenylpropylmagnesium bromide and δ-phenylbutylmagnesium bromide reacted with chloral to give trichloroethanol, unsaturated hydrocarbons and coupling products.

2. No secondary alcohols containing the trichloromethyl group were obtained under the conditions of these experiments.

BOULDER, COLORADO RECEIVED NOVEMBER 18, 1935

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[5] Ch. Prévost, *Bull. soc. chim.*, [4] 49, 1376 (1931).

[CONTRIBUTION FROM THE NEW YORK STATE COLLEGE OF FORESTRY AND DEPARTMENT OF RADIOLOGY, SYRACUSE UNIVERSITY]

x-Ray Studies of Reactions of Cellulose in Non-Aqueous Systems. I. Interaction of Cellulose and Liquid Ammonia[1]

BY A. J. BARRY, F. C. PETERSON AND A. J. KING

In the course of preliminary studies on the swelling of cellulose in non-aqueous systems, it was found that when ramie fiber is immersed in anhydrous liquid ammonia, a swelling occurs which, according to the type of subsequent treatment, results ultimately in one of two different structures as revealed by x-ray diagrams.

One of the structures seems to be analogous to the three similar products found by Trogus and Hess[2] in their treatment of cellulose with hydrazine, ethylenediamine and tetramethylenediamine.

The second structure which was obtained bears a striking similarity to that of hydrate cellulose. The sharpness of the x-ray diagram in either case indicates a crystalline structure as well defined as exists in the original cellulose used.

For the investigations, the cellulose used was ramie pretreated by digesting for one hour in 1% sodium hydroxide solution at 100°, washing with water, dilute acetic acid, and finally again with water, then drying for five to six hours at 105°. The diffraction pattern of the purified ramie agreed well with the data for normal cellulose.

Prior to treatment with liquid ammonia the fibers were wrapped into small tight bundles on small spring wire frames so that the samples were under a slight tension during treatment. In all cases, the presence of water was precluded by drying for an additional two hours just before treatment with liquid ammonia. The racked samples were placed in a reaction flask which was part of a closed system and pure, dry ammonia gas was condensed in the flask by cooling with carbon dioxide ice in acetone. Enough ammonia was condensed so that, as it evaporated under atmospheric pressure, the samples were covered with liquid ammonia for five to ten hours. The fibers during this treatment showed a perceptible swelling. Immediately after all the ammonia had vaporized, the bundles were coated with paraffin oil and subjected immediately to x-ray examination. The ammonia content of the material at this stage determined gravimetrically, indicated roughly 1 mole of ammonia to 1 mole of cellulose ($C_6H_{10}O_5$).

For a source of x-rays, a Müller tube with a

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[1] Presented before the Cellulose Division of the A. C. S. at the New York Meeting, April 25, 1935.

[2] C. Trogus and K. Hess, *Z. physik. Chem.*, B14, 387–95 (1931).

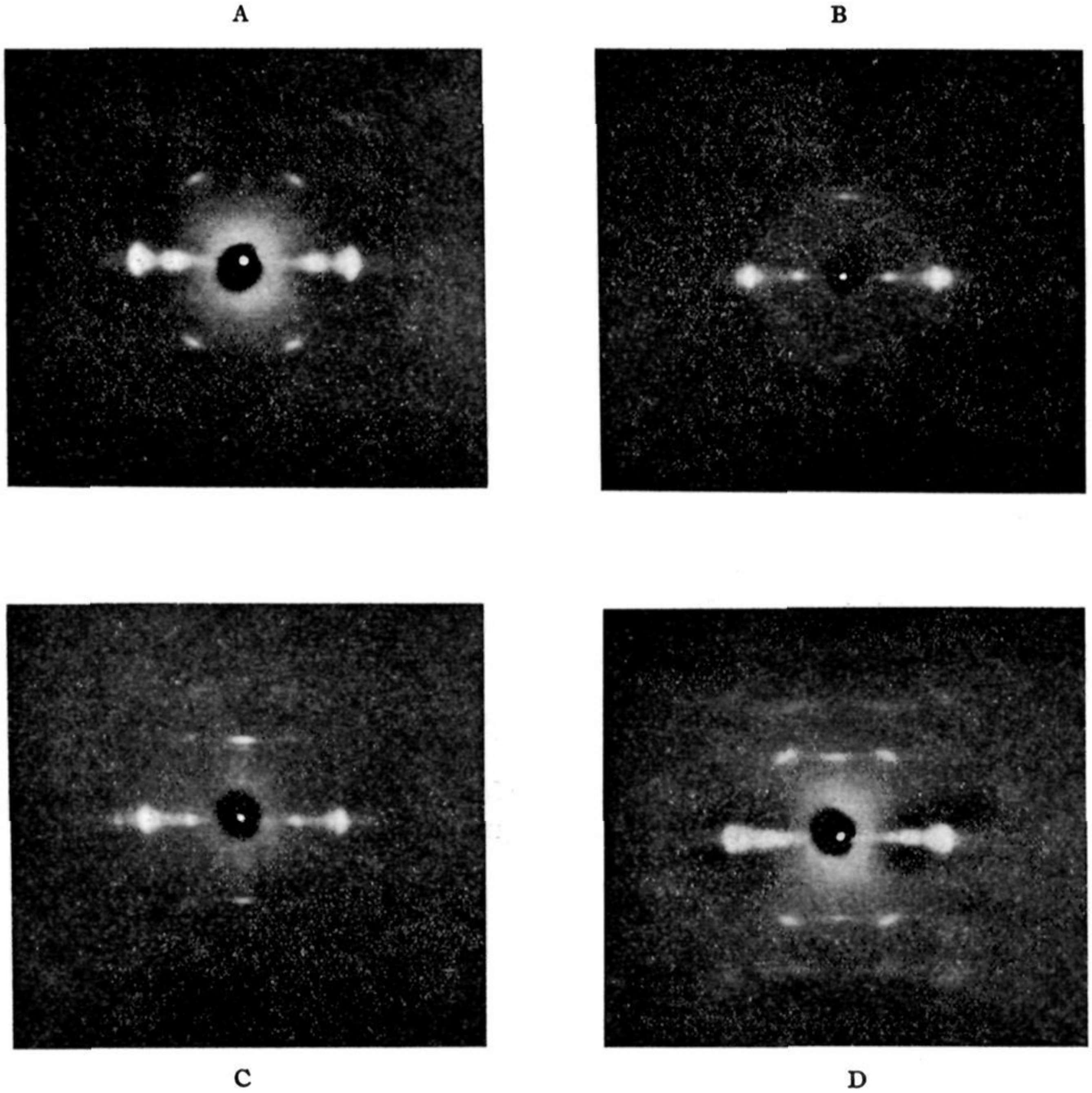

Fig. 1.—x-Ray diffraction patterns: A, ramie cellulose; B, NH_3-cellulose; C, cellulose II; D, *n*-cellulose regenerated from cellulose II.

copper target was used. The radiation was unfiltered and defined by a pin hole system. A flat photographic plate was set at a distance of 36.3 mm. from the sample which was mounted perpendicularly to the x-ray beam on a Pye x-ray goniometer. Exposures varied from five to twelve hours.

Figure 1(a) shows the x-ray pattern for normal cellulose. The equatorial spots progressing outward from the center are designated as A_1, A_2, A_3, etc., and represent, respectively, diffractions from the 101, $10\bar{1}$, 002 planes of the cellulose lattice.

Figure 1(b) shows the x-ray diagram of the ammonia swollen cellulose in which A_1 is transposed inward (increase of the 101 planar distance) and A_2, A_3, A_4 are transposed outward (decrease of planar distances). By assigning the indices ($A_1(K_\alpha) = 101$; $A_2(K_\beta) = 10\bar{1}$; $A_3(K_\alpha) = 10\bar{1}$; $A_4(K_\alpha) = 002$), the ammonia-cellulose was conceived of as indicated by the diagram in Fig. 2, which represents the projection of the 010 plane of the unit cell. That the above indices were discreetly chosen is borne out by the fact of agreement of all observed interplanar distances with those calculated on the assumed basis (see Table I). Since the A_3 spot appears with greatest intensity it seems logical that the glucose residues have their planes lined up parallel to the $10\bar{1}$ planes so that the consequent high electron density in this plane of the lattice will give a strong diffraction. The resulting unit cell closely resembles that for hydrazine cellulose. This analogy is expected when the similarity of ammonia and hydrazine are considered.

For comparison, the cell structure diagram for normal ramie is also shown in Fig. 2. A marked

TABLE I

INTERPLANAR SPACING VALUES FOR AMMONIA-CELLULOSE

Spot	I	d (obsd.), Å.	Indices	d (calcd.), Å.
A$_1$	vs	8.86	101	Assigned
A$_2$	ms	4.473	10$\bar{1}$	Assigned
A$_3$	vvs	4.467		
A$_4$	vs	4.049	002	Assigned
A$_5$	vw	3.27	103	3.19
			301	3.10
A$_6$	w	2.247	20$\bar{2}$	2.235
			30$\bar{1}$	2.16
			10$\bar{3}$	2.14
I$_1$	vw	4.12	012	3.76?
			11$\bar{1}$	4.11
I$_2$	vw	2.383	310	2.53
II$_0$	s	5.141	020	
II$_0$	ms	5.158	020	
II$_1$	vw	4.50	120	4.31
			021	4.35
			121	4.48
II$_2$	ms	3.38	12$\bar{1}$	3.37
			22$\bar{2}$	3.30
II$_3$	w	3.17	022	3.18
			220	3.14
III$_1$	ms	3.225	031	3.16
			131	3.22
III$_2$	vw	2.673	032	2.60
			230	2.61
			132	2.83
			13$\bar{1}$	2.72
			231	2.81
			232	2.69
IV$_0$	m	2.545	040	

$a:b:c = 9.83:10.30:10.05$.
$aoc = 53.5°$.

distention of the lattice size accompanies the initial swelling in ammonia. The volume of the unit cell increases from 671 cu. Å. for normal cellulose to 801 cu. Å. for the ammonia swollen cellulose. This expansion allows room for the introduction of ammonia molecules in the unit cell. It is to be noted, in this connection, that the enlargement of the unit cell to accommodate the incorporated ammonia need not be as great as the enlargement necessary to accommodate the entry of hydrazine, ethylenediamine, tetramethylenediamine. The enlargement of the lattice is found to be not as great as that for the diamine celluloses for which Trogus and Hess[2] find the increase in the 101 distance to be proportional to the length of the incorporated molecule.

We have thus arrived at a body of very definite crystalline structure which for convenience we call ammonia-cellulose. It is an example of the permutoid type of swelling described by Katz[3] though whether or not there is formed a compound as implied by Katz's theory we are not in a position to commit ourselves. Further investigation on this question is being conducted by the study of desorption isotherms.

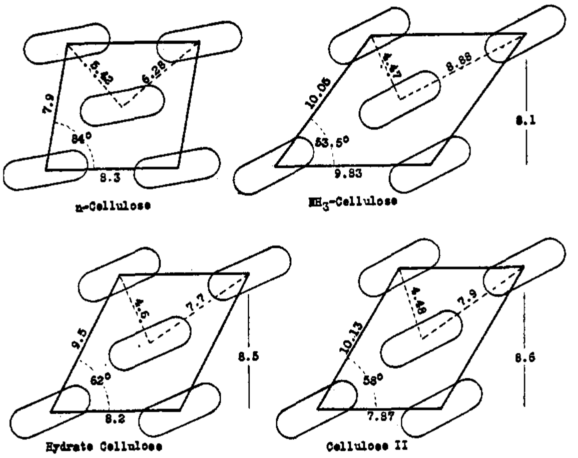

Fig. 2.—Projection of the unit cell upon the 010 plane.

When the ammonia-cellulose is heated at 105° for several hours, it loses all its ammonia and undergoes a decided change in structure. The samples studied were baked for fourteen hours immediately following the previously described ammonia treatment. Analysis by the Kjeldahl method showed the presence of no ammonia. Eighteen hours of additional heating at 105° did not further affect the material as shown by the diffraction pattern. In Fig. 1(c) is shown the diffraction pattern for the baked out ammonia-treated ramie which we will hereafter designate as Cellulose II. The pattern is definitely not that of the original cellulose. Compared to the pattern for ammonia-cellulose, the new pattern shows a migration outward of the A$_1$(101) spot and A$_3$-(10$\bar{1}$) spot showing a decrease in these lattice constants. The spot A$_4$(002) seems to have coalesced with A$_3$ (see Fig. 3). Therefore, assigning the indices (A$_1$(K) = 10$\bar{1}$ and 002; A$_3$(K) = 10$\bar{1}$ and 002) a model for Cellulose II is obtained, the projection of the 010 plane for which is shown in Fig. 2. The calculation of the interplanar spacings on the basis of the above assignment of indices checks very well with the observed data and confirms the correctness of choice of indices (see Table II).

The volume of the unit-cell of cellulose II (702 cu. Å.) is much smaller than that of the

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(3) Discussion by The Faraday Society on the Colloid Aspects of Textile Materials and Related Topics, Sept., 1932, pp. 279–300.

ammonia-cellulose (801 cu. Å.) as is to be expected since the ammonia, whose entry caused the extention of the lattice size, has been driven off. However, the volume does not approach that of normal cellulose (671 cu. Å.). Herein is found the analogy to hydrate cellulose which is formed by regeneration from compounds of cellulose or from drastically swollen cellulose and whose lattice has not yet been shown to revert to that of normal cellulose but which remains in a distended form.

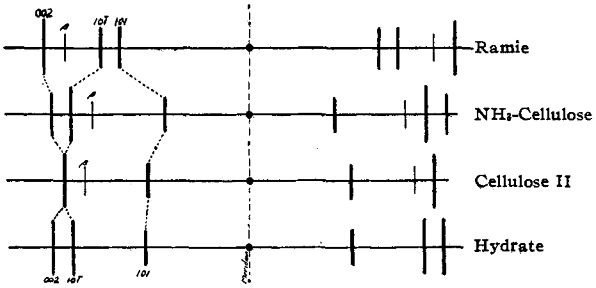

Fig. 3.—Comparison of equatorial spots (*h*0*l*) diffractions).

Between the ammonia-cellulose, cellulose II, and the original cellulose, there exists a relationship the study of which has been enlarged upon by the following experiments.

First, the attempt to prepare the ammonia-cellulose by soaking the purified ramie in saturated aqueous ammonia solution for several hours resulted in failure. Further, the ammonia-cellulose could not be obtained by suspending the cellulose for fifty hours in ammonia gas at atmospheric pressure. The x-ray diagram did not change from that of ramie in either case. This perhaps explains the absence from the literature of any previous x-ray studies of the ammonia-cellulose system.

Regeneration of the normal cellulose from the ammonia compound can be brought about easily by immersing the ammonia-cellulose in weak acetic acid, water, or aqueous ammonia, either dilute or concentrated. The pattern of the regenerated material is the same as the pattern of the untreated ramie. These results are in conformity with the similar observations of Trogus and Hess[2] in their studies of the effect of the diamines on cellulose and subsequent washing out of the reagent used.

If the ammonia-cellulose is allowed to stand in paraffin oil for forty-eight or more hours at room temperature, it loses ammonia and undergoes the same transformation that takes place on baking at 105° for a few hours, *i. e.*, reverts to cellulose II as indicated by the fact that the patterns for the material after either treatment are superimposable.

Table II

Interplanar Spacing Values, Cellulose II

Spot	I	*d* (obsd.), Å.	Indices	*d* (calcd.), Å.
A_1	s	7.55	101	Assigned
A_2	ms	4.31 } 4.30	$10\bar{1}$	Assigned
A_3	vvs	4.29	002	Assigned
A_4	vw	3.78	202	3.76
A_5	m	3.40	103	3.36
A_6	w	2.89	$10\bar{2}$?	2.99
A_7	vw	2.48	301	2.51
			303	2.55
A_8	vw	2.24	$20\bar{2}$	2.16
			$10\bar{3}$	2.25
I_1	vw	3.99	$11\bar{1}$	3.99
			012	3.97
I_2	vw	3.23	210	3.28
			113	3.21
I_3	vw	2.73	013	2.76
			$21\bar{1}$	2.62
I_4	m	2.45	312	2.53
			311	2.45
			313	2.46
II_0	vs	5.14	020	
II_0	m	5.17	020	
II_1	s	4.43	021	4.43
II_2	s	4.28	121	4.26
			120	4.13?
II_3	vw	3.33	$12\bar{1}$	3.31
			022	3.29
II_4	vw	3.03	221	3.07
			222	3.05
II_5	vvw	2.84	220	2.87
			123	2.82
III_1	ms	3.17	031	3.20
			131	3.12
			130	3.08
III_2	mw	2.68	$13\bar{1}$	2.67
			032	2.68
III_3	vw	2.55	231	2.55
			232	2.53
III_4	vw	2.06	331	2.05
			$23\bar{1}$	2.11
IV_1	vw	2.43	041	2.48
			141	2.43
			140	2.44
IV_2	vw	2.21	141	2.22
			042	2.21

$a:b:c = 7.87:10.31:10.13.$
$aoc = 58°.$

Cellulose II seems, in these instances, to be in itself a stable end-product. This view can be supported since samples of the cellulose II treated either with saturated aqueous ammonia or 1% acetic acid for several hours at room temperature, or on prolonged baking at 105°, produces no further change in the pattern.

However, if the cellulose II is retreated with liquid ammonia it is reconverted to ammonia-cellulose. The diffraction pattern is identical to that obtained from the directly ammonia treated ramie. From this reformed ammonia-cellulose, the normal cellulose may be regenerated by washing the ammonia out with water or dilute acetic acid. The x-ray pattern of the regenerated material is shown in Fig. 1(d). Very little evidence of cellulose II remains. If the reformed ammonia-cellulose is heated as before, cellulose II again is produced.

The most important facts to be noted in connection with the experiment lie in the process by which the ammonia-cellulose and cellulose II may be obtained and in the reversibility of the reactions to allow for the regeneration of the normal cellulose as summarized by the equations

$$n\text{-Cellulose} \underset{H_2O}{\overset{NH_3\ (1)}{\rightleftarrows}} NH_3\text{-cellulose} \underset{NH_3\ (1)}{\overset{\text{Heating}}{\rightleftarrows}} \text{Cellulose II}$$

That the cellulose II bears a striking resemblance to hydrate cellulose has been pointed out already. This similarity applies not only in structural configuration but also in the enhanced chemical reactivity as indicated by an increased Schwalbe Copper Number.[4] However, cellulose II, in that it may be reconverted to normal cellulose, differs markedly from hydrate cellulose for the latter has never been shown to revert back to normal cellulose by any treatment.

Hydrate cellulose prepared by alkali mercerization was also studied in a manner similar to that applied to normal ramie. Ammonia swollen hydrate cellulose gives the same diffraction pattern as ammonia-cellulose from unmercerized ramie. This on baking out also yields the same cellulose II pattern. However, the ammonia swollen hydrate cellulose, on treating with water, yields a body which does not give an x-ray pattern sharp enough to measure.

Further work is being conducted in the study of the action of a series of monoamines on cellulose. Metallic derivatives of cellulose, resulting from the action of liquid ammonia solutions of the alkali metals on liquid ammonia suspensions of cellulose, also are being studied both by x-ray and chemical methods.

Summary

1. x-Ray diffraction data are given for a body, ammonia-cellulose, resulting from the interaction of ramie-cellulose and liquid ammonia and for the body, which we call cellulose II, obtained when the ammonia is driven out in the absence of water.

2. A space lattice has been developed for ammonia-cellulose. Compared to the lattice for normal cellulose, the *b* axis remains unchanged while the *a* axis is increased in length from 8.3 to 9.83 Å. and the *c* axis is increased from 7.9 to 10.05 Å. The angle between *a* and *c* is decreased from 84 to 53.5°.

The space lattice developed for cellulose II gives the following measurements: $a:b:c = 7.87:10.31:10.13$ with the $\angle aoc = 58°$.

3. Cellulose II seems to be analogous to hydrate cellulose in structure and in enhanced chemical reactivity.

4. Normal cellulose can be regenerated by proper treatment from both ammonia-cellulose and cellulose II.

SYRACUSE, NEW YORK RECEIVED DECEMBER 2, 1935

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(4) C. A. Schwalbe, *Z. Angew. Chem.*, **21**, 1321 (1908); **22**, 197 (1909).