About 200 ml. of a 10% KOH solution of methanol was added to a 500-ml. round-bottom three-necked flask equipped with stirrer, dropping funnel and reflux condenser. Then 36 g. of 1,1,2-trichloro-3,3,3-trifluoro-1-propene was added slowly. After the heat of reaction had subsided, the reaction mixture was refluxed for about three to four hours, and allowed to cool. It was then washed with water, the organic layer separated and dried over calcium chloride. Distillation yielded 17.4 g. of $CF_3CCl{=}CCl(OCH_3)$ which boiled at 107–108° (630 mm.). Under these conditions no $CF_3CClHCCl_2(OCH_3)$ was isolated. Similar methods were used for the ethyl, propyl and butyl derivatives. The yields were about 50% of theory.

Infrared Spectra.—The infrared absorption spectra were measured using an automatic recording Perkin–Elmer infrared spectrometer, model 12C.

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[CONTRIBUTION FROM THE CELLULOSE ACETATE DEVELOPMENT DIVISION, EASTMAN KODAK COMPANY]

Re-esterification during the Hydrolysis of Cellulose Acetate

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Acetone-soluble cellulose acetate, when treated with 99.8% acetic acid containing a catalyst, esterifies, yielding products low in primary hydroxyl. In the presence of more than 2% water hydrolysis takes place, and the products contain increasing percentages of primary hydroxyl as the percentage of water is increased. Upon hydrolysis in other solvents where re-esterification is impossible, the products contain a high percentage of primary hydroxyl regardless of the amount of water present. In 95% butyric acid, considerable butyryl is introduced into cellulose acetate upon prolonged hydrolysis. Similarly, in 95% acetic acid, considerable acetyl is introduced into cellulose butyrate. A correlation was found between the optical rotation of the products and the percentage of primary hydroxyl present.

Variation in amount of primary hydroxyl in cellulose acetate during hydrolysis in aqueous acetic acid has recently been reported.[1] Among the several variables investigated, it was found that only the percentage of water in the hydrolysis bath affected the percentage of primary hydroxyl in the product. A high percentage of water gave a high percentage of primary hydroxyl in the resulting cellulose acetate.

TABLE I

BEHAVIOR OF CELLULOSE ACETATE IN AQUEOUS ACETIC ACID

Sample	Water, %	Catalyst	Time, hours	Acetyl, %	Hydroxyl per g. u. Total	Hydroxyl per g. u. Primary	$[\alpha]^{25}D$[a]
A	(Original)			39.3	0.60	0.28	−14.6
A-1-1	0.2	0.01 *M*	72	39.9	0.54	.22	−12.5
A-1-2		HCl	168	40.7	.45	.15	−10.8
A-1-3			336	41.3	.39	.10	− 9.3
A-1-4			672	41.5	.37	.09	− 7.4
A-2-1	1.0	0.01 *M*	72	40.0	0.53	0.20	−11.0
A-2-2		HCl	168	40.0	.53	.16	− 9.3
A-2-3			336	39.7	.56	.13	− 6.0
A-2-4			672	39.9	.54	.12	− 1.7
A-3-1	2.0	0.01 *M*	48	39.8	0.55	0.24	−12.9
A-3-2		HCl	120	39.9	.54	.20	−10.3
A-3-3			384	39.7	.56	.16	− 6.0
A-3-4			624	39.6	.57	.16	− 4.0
A-3-5			960	39.0	.63	.16	− 1.7
A-4-1	5.0	0.05 *M*	48	39.3	0.60	0.24	− 9.4
A-4-2		HCl	72	38.7	.65	.23	− 4.6
A-4-3			120	37.4	.78	.24	− 1.1
A-4-4			168	36.2	.89	.25	+ 2.7
A-4-5			240	35.0	1.00	.28	+ 7.4
A-4-6			288	33.4	1.13		+ 9.7
A-4-7			336	32.9	1.19	.32	+11.2
A-5-1	20	0.10 *M*	24	38.3	0.69	0.34	−13.4
A-5-2		HCl	48	37.2	.80	.39	−11.2
A-5-3			72	36.4	.87	.42	− 9.3
A-5-4			96	35.8	.92	.44	− 7.6
A-5-5			120	34.3	1.06	.49	− 5.4
A-5-6			144	33.5	1.12	.53	− 3.7
A-6-1	45	None	1[b]	39.0	0.63	0.31	−14.6
A-6-2	50		3	37.5	.77	.39	−12.6
A-6-3			5	36.1	.90	.45	−11.6
A-6-4			6	35.3	.97	.49	−10.6
A-6-5			7	34.8	1.02	.51	−10.2
A-6-6			8	33.2	1.15	.58	− 9.4

[a] Measured in 2-dm. tubes in chloroform:ethanol (85:15 by weight), at a concentration of 5 g. per 100 ml. solution. [b] This series was run at steam-bath temperature.

In the continuation of this work, the behavior of a cellulose acetate of 39.3% acetyl content has been studied in acetic acid solution over a wider range of water content (Fig. 1). In the presence of only 0.2% water (Table I, samples A-1-1 to A-1-4) and a trace of hydrochloric acid catalyst, slight esterification took place at room temperature. The products had reduced percentages of primary hydroxyl because of preferential reacetylation. It has long been known that boiling acetic acid can partially

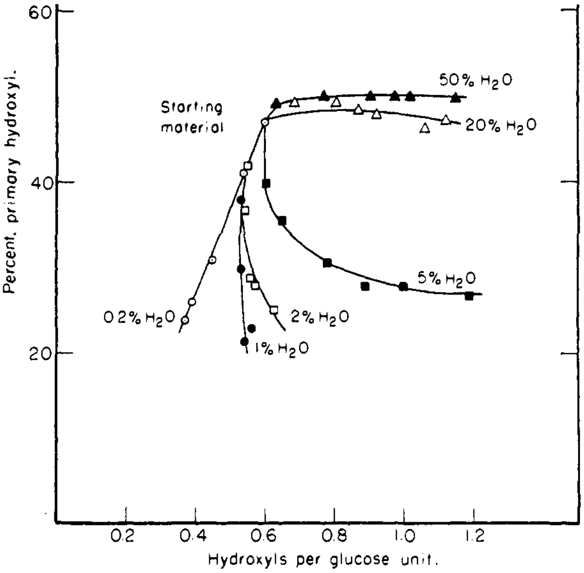

Fig. 1.—Behavior of cellulose acetate in aqueous acetic acid, effect of water concentration on primary hydroxyl.

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[1] C. J. Malm, L. J. Tanghe and B. C. Laird, THIS JOURNAL, 72, 2674 (1950).

acetylate cellulose[2] and can further acetylate hydrolyzed cellulose acetate.[3]

In the presence of 1 to 2% water (Table I, samples A-2-1 to A-3-5) there was little change in acetyl content, but a large drop in the percentage of primary hydroxyl. With higher amounts of water in acetic acid, hydrolysis took place, and the percentage of primary hydroxyl in the products increased with the amount of water. The highest percentage of water was used at steam-bath temperature, where it was found that the water content could be increased to 50% after hydrolysis of the cellulose acetate to an acetyl content of 38%.

Very few data on optical rotation of cellulose acetate have been published. However, the optical rotations of these samples were determined and were found to vary considerably with the amount of primary hydroxyl. The results are plotted in Fig. 2. The samples prepared in the presence of the largest amount of water had the lowest optical rotation. With smaller amounts of water in the hydrolysis bath, higher (*i.e.*, less negative) optical rotations were found. Since a low percentage of water in the hydrolysis bath gave a low percentage of primary hydroxyl in the product, this established, at any given acetyl content, a correlation between low primary hydroxyl content and high optical rotation.

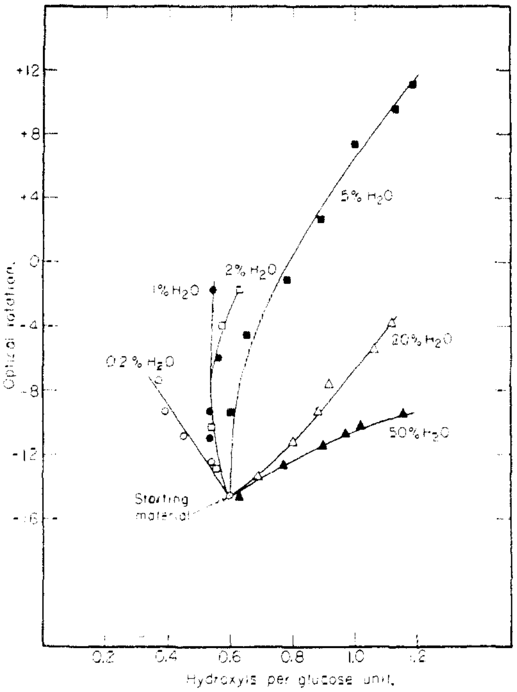

Fig. 2.—Behavior of cellulose acetate in aqueous acetic acid, effect on optical rotation.

The evidence pointed strongly to the explanation that the low primary hydroxyl content, upon hydrolysis in the presence of a low concentration of water, was due to partial preferential re-esterification of primary hydroxyl groups. Hence, the hydrolysis of cellulose acetate in other solvents in the absence of acetic acid was more thoroughly investigated. Previous experiments[1] hydrolyzing cellulose acetate in dioxane in the presence of 6% and of 25% water were repeated. High primary hydroxyl and low optical rotation were found in both cases throughout hydrolysis (Table II, samples B-1-1 to B-2-3). Similar hydrolysis series were carried out, starting with another sample of cellulose acetate and hydrolyzing in dioxane, acetone and methyl cellosolve in the presence of various amounts of water. In every series about 50% of the hydroxyl was primary, and the optical rotation remained at about −15°. Contrary to preliminary indications,[1] the percentage of primary hydroxyl is high regardless of the water content when the hydrolysis is carried out in solvents where there can be no re-esterification.

Table II

Hydrolysis of Cellulose Acetate in Other Aqueous Solvents

Sample	Solvent	Catalyst	Time, hours	Acetyl, %	Hydroxyl per g. u. Total	Hydroxyl per g. u. Primary	$[\alpha]^{25}D$
A	(Original)			39.3	0.60	0.28	−14.6
A-7-1	98% dioxane	0.01 *M*	96	38.4	.68	.37	−15.5
A-7-2		HCl	192	37.2	.80	.43	−15.0
A-7-3			384	35.6	.94	.49	−15.0
A-7-4			572	34.5	1.04	.52	−14.7
A-8-1	80% dioxane	0.06 *M*	24	38.5	0.67	0.33	−15.4
A-8-2		H_2SO_4	48	37.8	.74	.36	−15.2
A-8-3			72	36.8	.83	.40	−14.8
A-8-4			96	36.2	.89	.43	−15.1
A-8-5			120	35.4	.96	.47	−14.5
A-8-6			144	34.3	1.06	.52	−14.3
A-9-1	98% acetone	0.01 *M*	48	38.8	0.65	0.31	−15.2
A-9-2		HCl	120	38.0	.72	.36	−15.2
A-9-3			192	37.2	.80	.42	−15.3
A-9-4			384	34.4	1.05	.53	−14.9
A-10-1	80% acetone	0.10 *M*	24	38.0	0.72	0.35	−15.6
A-10-2		HCl	48	37.5	.77	.37	−16.4
A-10-3			72	36.6	.85	.42	−16.2
A-10-4			144	33.8	1.10	.53	−16.4
A-10-5			192	31.9	1.25	.60	Insol.
A-11-1	98% methyl cellosolve	0.01 *M*	192	38.5	0.67	0.33	−15.5
A-11-2		HCl	384	37.5	.77	.38	−15.7
A-11-3			792	35.5	.95	.47	−15.7
A-12-1	80% methyl cellosolve	0.025 *M*	1[a]	37.7	0.75	0.36	−15.6
A-12-2		HCl	2	36.0	0.90	.39	−14.8
A-12-3			3	33.8	1.10	.50	−14.7
A-12-4			4	32.5	1.21	.55	Insol.
A-12-5			5	31.4	1.37	.60	Insol.
B	(Original)			40.4	0.49	0.20	−14.4
B-1-1	94% dioxane	0.06 *M*	24	38.0	.72	.30	−14.7
B-1-2		H_2SO_4	48	36.6	.85	.38	−15.1
B-1-3			72	34.8	1.02	.45	−14.3
B-2-1	75% dioxane	0.06 *M*	96	38.1	0.71	.30	−14.2
B-2-2		H_2SO_4	168	35.4	0.96	.44	−15.1
B-2-3			288	31.6	1.35	.69	Insol.

[a] This series was run at steam-bath temperature.

Further evidence for the partial re-esterification during hydrolysis of cellulose acetate was obtained by hydrolyzing cellulose acetate in aqueous butyric acid. On prolonged hydrolysis in 95% butyric acid, considerable amounts of butyryl were introduced (Table III, Samples A-13-1 to A-13-3), giving products low in primary hydroxyl and high in optical rotation. Upon hydrolysis in 60% butyric acid, only a small amount of butyryl was introduced, and the products remained high in primary hydroxyl and low in optical rotation.

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(2) H. T. Clarke and C. J. Malm, *ibid.*, **51**, 274 (1929).

(3) H. T. Clarke and C. J. Malm, U. S. Patent 1,668,946 (1928); *C. A.*, **22**, 2272 (1928).

Table III

Hydrolysis of Cellulose Acetate in Aqueous Butyric Acid

Sample	Water, %	Catalyst	Time, hours	Weight % acyl Acetyl	Weight % acyl Butyryl	Acyl per g. u. Acetyl	Acyl per g. u. Butyryl	Hydroxyl per g. u. Total	Hydroxyl per g. u. Primary	$[\alpha]^{25}\mathrm{D}$
A	(Original)			39.3	..	2.40	..	0.60	0.28	−14.6
A-13-1	5	0.01 *M*	24[a]	29.6	5.2	1.69	0.18	1.13	.38	− 5.2
A-13-2		HCl	48	21.6	10.8	1.19	.36	1.45	.46	+ 3.4
A-13-3			72	12.7	16.1	0.67	.51	1.82	.58	Insol.
A-14-1	40	None	1.5[b]	36.9	0.3	2.18	0.01	0.81	0.36	−13.8
A-14-2			3.0	35.2	.2	2.03	.01	0.96	.43	−12.6
A-14-3			4.5	32.7	.7	1.83	.02	1.15	.51	−11.8
A-14-4			6.0	30.7	.6	1.67	.02	1.31	.59	Insol.

[a] This series was run at 50°. [b] This series was run at steam-bath temperature.

Also, a sample of high-butyryl cellulose acetate butyrate was hydrolyzed in aqueous acetic acid. In the presence of 5% water, a large amount of acetyl was introduced; whereas, in the presence of the maximum amounts of water which the solution would tolerate at steam-bath temperature, the amount of acetyl remained almost unchanged (Table IV). The optical rotations were higher when the hydrolysis was carried out in the presence of the smaller amount of water. Primary hydroxyl determinations could not be made on these samples because of their wide solubility in organic solvents. No suitable solvent could be found for precipitating and purifying the tritylated derivatives.

Table IV

Hydrolysis of High-butyryl Cellulose Acetate Butyrate in Aqueous Acetic Acid

Sample	Water, %	Catalyst	Time, hours	Weight % acyl Acetyl	Weight % acyl Butyryl	Acyl per g. u. Acetyl	Acyl per g. u. Butyryl	$[\alpha]^{25}\mathrm{D}$
C	(Original)			5.2	49.4	0.42	2.42	−12.4
C-1-1	5	0.3 *M*	48	6.9	45.3	.53	2.12	− 6.9
C-1-2		HCl	96	8.2	42.1	.61	1.90	− 4.0
C-1-3			168	11.3	35.9	.79	1.53	+ 2.4
C-1-4			216	13.4	31.5	.90	1.28	+ 4.5
C-1-5			264	15.4	27.3	1.00	1.07	+ 9.7
C-1-6			334	18.7	19.8	1.13	0.72	+15.0
C-2-1	18	None	24[a]	5.5	44.6	0.41	2.01	−10.3
C-2-2	25		48	6.0	39.4	.41	1.62	− 3.2
C-2-3	30		72	7.4	32.1	.46	1.20	+ 2.1

[a] This series was run at steam-bath temperature.

Experimental

The starting material for most of the hydrolysis series described herein was a commercial cellulose acetate (Sample A, Tables I, II and III) containing 39.3% acetyl. Forty-seven per cent. of the hydroxyl groups in this material was primary. Sample B (Table II) was the same cellulose acetate used in the previous work. It contained 40.4% acetyl, and 40% of its hydroxyl groups was primary. Sample C (Table IV) contained 5.2% acetyl and 49.4% butyryl, corresponding to 0.42 acetyl and 2.42 butyryl groups per glucose unit.

The cellulose ester was dissolved in seven to nine parts of solvent. The catalyst, in one additional part of solvent, was then added. Except where otherwise indicated in the tables, the reactions were carried out at room temperature. Samples were removed from time to time, and the products were precipitated and washed in distilled water.

Primary hydroxyl was determined by tritylation as previously described.[1] Some of the trityl determinations were made by the method of Hearon[4] and others by ultraviolet absorption at 259 mμ. For this purpose a 0.1% solution of the tritylated cellulose acetate was prepared in methylene chloride:methanol (90:10 by weight) and the absorbance determined in a 1.00-cm. cell in a Beckman model DU instrument. Samples of known high and low trityl contents and a blank on the solvent were run with each group of unknowns.

Acknowledgments.—The method for the determination of trityl content by ultraviolet absorption was developed by Dr. Don H. Anderson of the Color Control Division. The optical rotations were measured by Mr. J. R. Olson of the Physical Chemistry Department, Kodak Research Laboratories.

ROCHESTER, NEW YORK

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(4) W. M. Hearon, G. D. Hiatt and C. R. Fordyce, THIS JOURNAL, **65**, 2449 (1943).