which gives a biuret test, which reacts with aniline to form phenylbiuret and with alcohols to form allophanic esters.

CAMBRIDGE, MASSACHUSETTS

[COMMUNICATION NO. 377 FROM THE KODAK RESEARCH LABORATORIES]

EFFECT OF ANILINE ON CELLULOSE TRIACETATE

BY H. LEB. GRAY, T. F. MURRAY, JR., AND C. J. STAUD

RECEIVED JANUARY 8, 1929 PUBLISHED JUNE 5, 1929

Introduction

The action of aniline and similar compounds on cellulose triacetate has been studied but little by investigators in the field of cellulose chemistry. In a paper by E. Knoevenagel,[1] published in 1914, however, mention is made that triacetylcellulose may be heated with aniline without saponification of the ester. It is pointed out that marked differences in solubility result, which the author ascribes as possibly due to a stereoisomeric change of the cellulose acetate molecule, similar to that which produces mutarotation in the sugars. No polarimetric data are given.

That an ester like cellulose acetate could be kept in contact with a base like aniline at a high temperature for a protracted period of time without saponification seemed somewhat incongruous. Therefore, a study was made of the effect of aniline at various temperatures on cellulose triacetate.

Experimental

General Procedure.—The general procedure employed in these experiments was as follows. Fifteen grams of finely-divided cellulose acetate, containing 43.9% of acetyl (theoretical cellulose triacetate, 44.8% acetyl), and 300 cc. of aniline (b. p. 88–90° at 15 mm.) were placed in a 500-cc. ring-necked Pyrex flask equipped with an air condenser.

Three series of experiments were made. The first of these at the boiling point of the aniline–cellulose acetate solution (approx. 183°) was done in an oil-bath, the solution being refluxed continuously. The second at 148–151° was carried out by placing the flask in an air-bath, the temperature of which was maintained by the vapors of boiling cyclohexanol (b. p. 157–162°) and the third series was conducted at room temperature, 20–25°.

In the series in which elevated temperatures were employed, the solutions were cooled to approximately zero degrees and the mixtures were poured into 3 liters of ethyl alcohol. The products were washed with alcohol until free from aniline; this was followed by washing with ether. They were dried at 35°, after which the samples for analyses were dried at 105° for fifteen to twenty hours. Acetyl determinations were made according to the method of Eberstadt[2] as described by Knoevenagel,[3] with slight modifications. Optical rotations were determined using a Hilger polarimeter (accuracy 0.01°) employing the 546.1 mμ line of the mercury spectrum as illuminant. Readings

[1] Knoevenagel, *Z. angew. Chem.*, **27**, 505 (1914).

[2] Eberstadt, "Dissertation," Heidelberg, **1909**.

[3] Knoevenagel, *Cellulosechemie*, **3**, 119 (1922).

were made at 25 ± 1°, in a 2-dm. tube. The concentration was 1% in chloroform–alcohol (85:15% by volume) and where possible in acetone.

Heating at 183°.—In Table I are given the results of the first series of experiments in which the aniline–cellulose acetate solutions were heated at the boiling point.

TABLE I

RESULTS AT 183°

Time, hours	Product recovered, g.	Equiv. wt. of cellulose, g.	CH_3CO— in prod., %	$(\alpha)^{25°}_{546.1}$, $CHCl_3$–EtOH	$(\alpha)^{25°}_{546.1}$, acetone
0	..	8.4	43.9	−26.0	
1	14.4	8.2	43.4	−26.0	
2	16.0	9.1	43.0	−26.0	
2	15.1	8.7	42.3	−24.5	
4	16.3	9.3	42.7	−25.0	
6	14.1	8.2	42.1	−21.5	
6	14.1	8.2	42.1	−21.5	
8	14.4	8.4	41.6	−20.0	+ 2.0
10	13.1	7.9	40.0	−15.5	+ 4.5
15	12.9	7.9	39.0	−12.5	+ 5.5
20	12.1	7.7	36.1	− 8.0	+10.0
25	10.5	7.5	28.5	Insol.	Insol.
30	10.0	7.4	26.5		
40	9.8	8.1	17.7		
50	8.7	8.0	7.9		
50	8.7	7.9	8.7		
75	8.5	8.1	4.4		
100	8.5	8.4	1.5		
100	7.9	7.7	2.3		
		Av. 8.2			

From the above table it is seen that cellulose acetate is saponified by heating with aniline at the boiling point of the aniline–cellulose acetate solutions. This is shown graphically in Curve A of Fig. 1. The decrease in acetyl content is apparent after as short a time as two hours. After one hundred hours of heating, the acetyl content had decreased to 2.0%.

The weight of the recovered material affords evidence that no appreciable hydrolysis to alcohol- or ether-soluble products, such as acetylated sugars, has taken place. The theoretical yield of cellulose obtainable from the saponification of 15 g. of cellulose acetate containing 43.9% acetyl is 8.4 g. If the weights of recovered cellulose acetate, after various times of heating, be calculated back to their cellulose contents, by multiplying the weight of recovered acetate by the percentage of cellulose which they contain (100 − % acetyl),[4] values between 7.4 and 9.1 grams are obtained.

[4] The value given does not rigorously represent the cellulose content since the CH_3CO removed would be replaced by an equivalent weight of hydrogen. Such calculation, however, is quite outside the accuracy of these experiments. It does not affect the results by more than 0.2 g. of cellulose.

The average recovered material, calculated to cellulose, is 8.2 g., which shows very acceptable agreement with this theoretical value, as does the material which has been almost completely saponified (2.0% acetyl) by heating with aniline for one hundred hours, the latter value being 8.2 g.

To test further the action of aniline on the product obtained after one hundred hours' heating, a 5-g. sample of this material was heated for an additional one hundred hours in 300 cc. of aniline at its boiling point. The material did not dissolve and at the end of the second one hundred hours of heating, 4.6 g. of material was recovered. On analysis this showed an acetyl content of 1.3%.

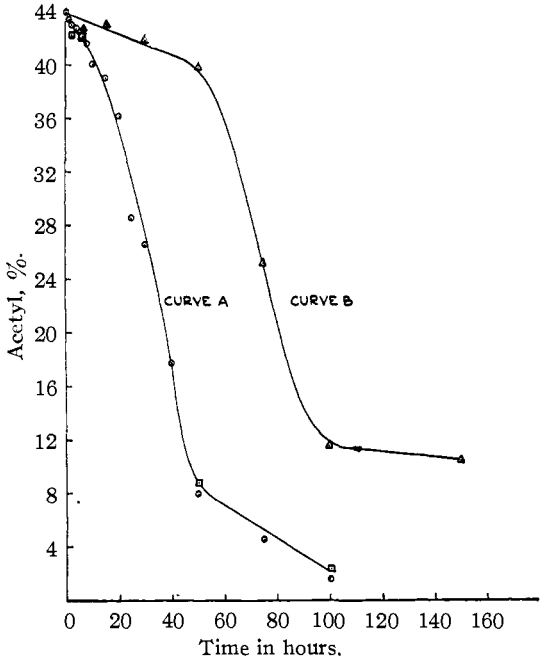

Fig. 1.—Acetyl content of cellulose acetate heated with aniline *vs.* time of heating.

According to Knoevenagel profound changes in the solubility of cellulose acetate are induced by the action of aniline, which he ascribes to stereoisomerism. It has been found that changes in solubility do take place, but they appear to follow the normal course observed in the saponification of cellulose acetate. In the experiments described it was observed that the cellulose acetate obtained, after heating with aniline for eight hours, was soluble in acetone and in a solution consisting of 85% chloroform and 15% ethyl alcohol by volume. After twenty-five hours' heating, the material obtained was practically insoluble in acetone and not entirely soluble in the chloroform–alcohol mixture mentioned above, but soluble in hot 75% ethyl alcohol. At the end of thirty hours' heating the product was soluble in aniline but not in the other solvents mentioned, and at the close of forty hours' heating it became insoluble, even in boiling aniline.

For the purpose of determining whether the final product of aniline saponification

was cellulose or one or more of its decomposition products, 5 g. of the material obtained after one hundred hours' heating with aniline was reacetylated and 7.8 g. of a compound was obtained (theoretical for cellulose triacetate 8.9 g.) which contained 44.2% of CH_3CO (theoretical for cellulose triacetate, 44.8%) and had a specific rotation of −26.0°, which is the same value as that of the starting material.

Heating at 148–151°.—To determine the difference in rate of saponification of cellulose acetate by aniline resulting from a change in temperature, a series of experiments was made at 148–151°, for a maximum time of 150 hours. At the close of this period the rate of hydrolysis had become very low. The data obtained are given in Table II.

TABLE II

RESULTS AT 148–151°

Time, hours	Product recovered, g.	Equiv. wt. of cellulose, g.	CH_3CO in prod., %	$(\alpha)^{25°}_{546.1}$, $CHCl_3$ – EtOH	$(\alpha)^{25°}_{546.1}$, acetone
0	..	8.4	43.9	−26.0	
6	14.9	8.4	42.6	−23.5	
15	13.6	7.8	43.0	−24.5	Insol.
30	13.6	7.9	41.9	−20.0	(0.0)
50	12.7	7.7	39.8	−16.0	+2.0
75	9.7	7.3	25.2	Insol.	Insol.
100	9.2	8.2	11.5		
150	9.0	8.1	10.4		
		Av. 8.0			

The decrease in acetyl content with time of heating is shown in Curve B of Fig. 1. It is seen to be of the same form as that obtained at the higher temperature. It appears of interest to note that both curves exhibit an S-form, in which the saponification is slow at the start, increasing during the intermediate stages with a marked decrease in the rate toward the close.

A calculation of the cellulose equivalent of the various cellulose acetates obtained in this series varied from 7.3 to 8.4 g., with an average of 8.0 g., which shows good agreement with the theoretical value of 8.4 g. previously mentioned, as well as with the yields obtained in the first series.

Effect of Standing at 20–30°.—Since in each experiment of the above two series the contents of the reaction flask were allowed to cool to room temperature and permitted to stand at that temperature for irregular periods of time before being poured into alcohol, a check on the action of aniline on cellulose acetate at room temperature seemed necessary to establish the validity of the results obtained at higher temperatures.

A 15-g. sample of the same cellulose acetate that was used in the previous experiments, therefore, was placed in 300 cc. of aniline and the containing flask was heated in a 148–151° bath for one hour. At the end of this time all of the cellulose acetate had dissolved. The solution was then allowed to stand at room temperature, and twenty-five hours after removal from the bath, a portion was precipitated in ethyl alcohol, washed with alcohol, dried and analyzed. The acetyl content was found to be 43.5%, and the specific rotation in chloroform–alcohol (85:15) was −26.5°. The

remainder of the solution was permitted to stand at room temperature for an additional 125 hours. It was then precipitated, washed and dried in a similar manner, and upon analysis gave the following values: acetyl content 43.2%; specific rotation, chloroform–alcohol (85:15) −25.5°. The difference between these values and those of the original cellulose acetate of 43.9% acetyl, and specific rotation of −26.0°, is so slight that it appears that no appreciable changes have taken place during the 150 hours' standing at room temperature. Since this time is far in excess of that during which any of the samples was permitted to stand before precipitation, it is concluded that the validity of this procedure is established and also that the deësterifying action of aniline on cellulose acetate at room temperature is exceedingly slow.

Discussion of the Polarimetric Data.—From the data given in the tabulations, it is obvious that there is a continuous decrease in specific rotation in chloroform–alcohol, within its solubility range, of the products obtained after various periods of heating in aniline, and conversely a progressive increase in specific rotation in acetone of the products which are soluble in this reagent.

If the phenomenon of change of solubility were one of stereoisomerism, comparable with the mutarotation of the sugars, from the definition of mutarotation,[5] a "steady state" should be found. The polarimetric data fail to indicate any such "steady state" and, in fact, since the acetyl values change continuously during the heating, a simultaneous change in optical rotation might be expected.

Summary

1. The effect of aniline on cellulose acetate has been investigated at room temperature and two higher temperatures.

2. The acetyl contents and specific rotations, where possible, have been determined on the products.

3. It has been found that the cellulose equivalent of all the products agrees approximately with the theoretical value.

4. Contrary to Knoevenagel, it has been observed that there is a continuous decrease in acetyl content with time of heating.

5. The specific rotations, so far as present interpretation permits, do not seem to indicate the possibility of a stereoisomeric change comparable with the mutarotation of the sugars, as suggested by Knoevenagel.

6. The product obtained by prolonged saponification with aniline at 183° is shown to contain approximately 2% of acetyl, and upon reacetylation to revert to a product having the analytical constants of cellulose triacetate.

7. It has been shown that in the saponification of cellulose acetate with aniline, at the boiling point of the aniline–cellulose acetate solution (*ca.* 183°) and at 148–151°, the acetyl–time curves present similar contours.

ROCHESTER, NEW YORK

[5] "Polarimetry," Bureau of Standards Circular 44, 2d ed., **1918**, p. 81.