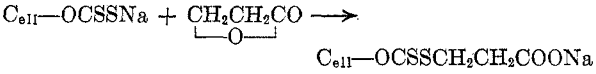
# Chemical Modification of Cellulose. Reaction of Cellulose Xanthate with β-Propiolactone[1]

MARTIN W. FARRAR

*Received November 12, 1958*

Although of primary commercial usefulness as a method for solubilizing cellulose for subsequent regeneration to form rayon, cellophane, and other cellulose products, cellulose xanthate, nevertheless possesses a high degree of chemical reactivity. In addition to the complex reactions that take place during ripening, viscose is reported to undergo a number of other chemical transformations. For example, when viscose or sodium cellulose xanthate (I), $\mathrm{C_{ell}{-}OCSSNa}$, reacts with alkyl halides (or sulfates),[2] iodine, sodium chloroacetate,[3] aniline,[4] arenediazonium chloride,[5] or acrylonitrile[6] the products, respectively, are xanthic esters $\mathrm{C_{ell}{-}OCSSR}$, a "disulfide" $\mathrm{(C_{ell}{-}OCSS{-})_2}$, an acetic derivative $\mathrm{C_{ell}{-}OCSSCH_2COONa}$, a N-substituted thiourethan $\mathrm{C_{ell}{-}OCSNHPh}$, an aryl cellulose xanthate $\mathrm{C_{ell}{-}OCSSAr}$ (with evolution of nitrogen), and a cyanoethyl ether $\mathrm{C_{ell}{-}OCH_2CH_2CN}$.

The reaction of simple xanthates with β-propiolactone has been studied recently,[7] and the present study is an extension to include (I). Reaction with the beta lactone did occur as evidenced by the rise in temperature and a change in the color of solution from deep orange to yellow when an excess of β-propiolactone had been added. In conformance with earlier results[7] the following reaction is believed to have taken place.



$$\mathrm{C_{ell}{-}OCSSNa} + \underbrace{\mathrm{CH_2CH_2CO}}_{\mathrm{O}} \longrightarrow \mathrm{C_{ell}{-}OCSSCH_2CH_2COONa}$$

Upon acidification, β-carboxyethyl cellulose xanthate (II) precipitated. The product was quite insoluble in water, alcohol, ether, and acetone but could be dissolved in dimethylformamide by warming. Evaporation of the dimethylformamide from a glass plate left a transparent, colorless, tough film of the modified cellulose. Although insoluble, the film was softened appreciably by water with concomitant increase in elasticity and decrease in strength.

Having the free carboxyl group available for further reaction, the effect of internal esterification on the properties of the polymer was next investigated. Treatment of the dimethylformamide solution at 80–90° with a small amount of sulfuric acid and removal of water by azeotropic distillation effected internal esterification. After evaporating the solvent on a glass plate a brittle film was obtained. This brittleness is probably due to a certain amount of cross linking effected by the internal esterification.

Esterification of the β-carboxyethyl group with a simple alcohol was next accomplished. Reaction with butanol in the presence of sulfuric acid was effective in bringing about the desired esterification. The dimethylformamide solution upon evaporation left a film of greater flexibility, indicating some degree of internal plasticization.

Acetylation of the viscose–β-propiolactone reaction product by two different methods was investigated. Refluxing with acetic anhydride in the presence of a trace of sulfuric acid produced a material insoluble in dimethylformamide. Some cross linking through internal esterification may be a complicating side reaction in this case. Acetylation by the pyridine–acetic anhydride method produced a different material, still insoluble in dimethylformamide, however. During this treatment it is possible that a substantial amount of the xanthic ester is decomposed with concomitant loss of carbon disulfide is indicated by the sulfur analysis on the product.

Since the aging of alkali cellulose and ripening of the viscose solution produced therefrom play a significant role in the properties of the fiber or film obtained upon regeneration, efforts to obtain optimum conditions for achieving the most desirable products are not being reported at this time.

## EXPERIMENTAL

*Preparation of viscose solution.*[8] Ten grams of absorbent cotton was treated with 250 g. of 18% sodium hydroxide solution for 1.5 hr. at 25°. At the end of this time the excess NaOH was pressed out to a final weight of 32 g. The resulting alkali cellulose was shredded by hand and allowed to stand at room temperature for 72 hr.

After this aging period the alkali cellulose was reacted with 8 ml. of carbon disulfide in a closed vessel. The mixture was agitated for 4 hr. and excess $\mathrm{CS_2}$ removed by evacuation, after which a mixture of 18 g. of 18% NaOH and 75 ml. water was added and stirring continued for 2 hr. Solution was essentially complete at this point. Filtration of the viscose was effective in producing a sparkling clear solution of 90–100 ml. volume.

*Reaction of* I *with β-propiolactone.* The above prepared viscose solution was diluted with 300 ml. of water and cooled to 20°. β-Propiolactone (15.0 g.) was added dropwise during 10 min. with cooling to maintain the temperature between 20–25°. At this point the color of the solution changed from deep orange to light yellow. Stirring at 25° was continued for 0.5 hr. longer and the mixture was poured into an excess of dilute hydrochloric acid. The light yellow solid which

---

[1] Presented at the 134th American Chemical Society Meeting, Chicago, Ill., September 7–12, 1958.

[2] L. Lilienfeld, U. S. Patent **1,680,224** (Aug. 7, 1928).

[3] T. Nakashima, *J. Soc. Chem. Ind., Japan*, **31**, Suppl. binding, 31 (1928).

[4] L. Lilienfeld, U. S. Patents **1,674,401** (June 19, 1928), **1,674,405** (June 19, 1928), **1,906,910** (May 2, 1933).

[5] J. H. Helberger, German Patent **562,180** (Oct. 1, 1931).

[6] J. P. Hollihan and S. A. Moss, Jr., *Ind. Eng. Chem.*, **39**, 929 (1947).

[7] M. W. Farrar, *J. Org. Chem.*, **23**, 1065 (1958).

[8] E. Kline, *Cellulose and Cellulose Derivatives*, Part II, Interscience Publishers, Inc., New York, 1954, p. 960.

separated was filtered and washed with water and finally with acetone in a Waring blender. The resulting product was an almost white granular solid.

*Anal.* C, 39.65; H, 5.68; S, 11.16.

A portion was dissolved in dimethylformamide by heating to 50°. Evaporation of the solvent from a glass plate left the product as a clear, tough film.

*Internal esterification of* II. Two grams of the modified cellulose was dissolved in 25 ml. of dimethylformamide by warming. A small amount of concentrated $H_2SO_4$ was added from a stirring rod and the solution was heated under vacuum at 90–95° for 4 hr. with slow distillation of the solvent. The solution remained clear upon cooling. Upon evaporation of the solvent a clear, brittle film was obtained. *Anal.* C, 40.71; H, 5.58; S, 11.01.

*Esterification of* II *with butanol.* Two grams of the modified cellulose was dissolved in 25 ml. of dimethylformamide by warming. To this solution was added 10 ml. of butanol. Some gellation of the solution occurred at this point but it remained stirrable. Once again a trace of $H_2SO_4$ was added and the mixture was heated under vacuum at 80–85° for 3 hr. with slow distillation. Evaporation of the product left a clear film of better flexibility than the original modified cellulose.

*Anal.* C, 41.47; H, 5.82; S, 10.91.

*Acetylation of* II. (a) One gram of the modified cellulose was heated to reflux for 1 hr. with 10 ml. of acetic anhydride containing a trace of sulfuric acid. During this period appreciable swelling of the polymer took place. Upon cooling, water was added to decompose excess acetic anhydride after which the granular solid was separated by filtration and was washed thoroughly with water and finally ethanol. Upon drying there was obtained 1.27 g. of the acetylated product which was found to be completely insoluble in acetone, alcohol, and dimethylformamide.

*Anal.* C, 45.33; H, 5.52; S, 8.36.

(b) One gram of the modified cellulose was heated at 90–100° for 1 hr. with 10 ml. of pyridine, 10 ml. of acetic anhydride, and 10 ml. of dimethylformamide. After quenching with water, separation of the solid, and finally washing with water and alcohol, there was obtained 1.08 g. of material.

*Anal.* C, 44.20; H, 5.28; S, 6.55.

ST. LOUIS RESEARCH DEPARTMENT
ORGANIC CHEMICALS DIVISION
MONSANTO CHEMICAL COMPANY
ST. LOUIS 77, MO.

---

## Synthesis of γ-Aminobutyryl-γ-aminobutyric Acid

R. L. EVANS[1] AND F. IRREVERRE

*Received November 17, 1958*

γ-Aminobutyric acid has been found in brain extracts by Awapara *et al.*,[2] Roberts and Frankel,[3] and Udenfriend.[4] Recently an analog, γ-guanidinobutyric acid, was isolated from brain by Irreverre *et al.*[5] Due to the demonstration of enzymatic interconversion between these two butyric acids[6,7] and their possible role as humoral agents,[8–10] we were prompted to synthesize the dipeptide of γ-aminobutyric acid for physiological testing and for comparison on paper chromatography.

The synthesized γ-aminobutyryl-γ-aminobutyric acid in a concentration of 5.3 μm/ml. is not effective in blocking the neutromuscular transmission of crustaceans while γ-aminobutyric acid was effective at the threshold concentration of 9.7 × $10^{-3}$ μm/ml.[11] The dipeptide as well as the benzyl ester of γ-aminobutyric acid give negative reactions in the specific enzymatic method for the determination of γ-aminobutyric acid developed by Jakoby and Scott.[12]

### EXPERIMENTAL

*N-Carbobenzoxy-γ-aminobutyric acid.* This compound was prepared by a procedure similar to that used for the preparation of *N*-carbobenzoxyglycine,[13] using 0.05 mole of γ-aminobutyric acid and 0.05 mole of carbobenzoxy chloride. The yield was 7.8 g. (66%). Recrystallized from ethylacetate-petroleum ether the compound melted at 66–67°.

*Anal.* Calcd. for $C_{12}H_{15}O_4N$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.89; H, 6.23; N, 5.90.

*γ-Aminobutyric acid benzyl ester hydrochloride.* This derivative was prepared using the procedure employed by Erlanger and Hall[14] for the synthesis of D,L-phenylalanine benzyl ester hydrochloride. Using 0.033 mole of γ-aminobutyric acid and 70 ml. of benzyl alcohol there was obtained 5.2 g. of material (69%). Recrystallized three times from ethyl acetate it melted at 109–110°.

*Anal.* Calcd. for $C_{11}H_{16}O_2NCl$: C, 57.66; H, 7.02; N, 6.10. Found: C, 57.38; H, 7.05; N, 5.81.

*N-Carbobenzoxy-γ-aminobutyryl-γ-aminobutyric acid benzyl ester.* To a mixture of 2.6 g. of *N*-carbobenzoxy-γ-aminobutyric acid and 1.51 ml. of triethylamine in 20 ml. of methylene chloride pre-cooled to −5° was added 1.0 ml. of ethylchloroformate and stored at −5° for 5 min. A second flask containing a solution of 2.6 g. of γ-aminobutyric acid benzyl ester hydrochloride and 4.68 ml. of triethylamine in 20 ml. of methylene chloride pre-cooled to −5° was added to above mixture. An additional 10 ml. of methylene chloride was used for washing out the flask. The reaction mixture was kept at −5° for 20 min. and allowed to come to room temperature with continuous stirring (magnetic) for 4 hr. The solution was extracted with 50 ml. of dilute hydrochloric acid, then with a cold, saturated solution of $NaHCO_3$ and finally with water. The methylene chloride layer was

---

(1) Present address: Mead Johnson and Co., Evansville, Ind.

(2) J. Awapara, A. J. Landua, R. Fuerst, and B. Seale, *J. Biol. Chem.*, **187**, 35 (1950).

(3) E. Roberts and S. Frankel, *J. Biol. Chem.*, **187**, 55 (1950).

(4) S. Udenfriend, *J. Biol. Chem.*, **187**, 65 (1950).

(5) F. Irreverre, R. L. Evans, A. R. Hayden, and R. Silber, *Nature*, **180**, 704 (1957).

(6) G. Kobayashi, *J. Jap. Biochem. Soc.*, 19, 85 (1947).

(7) J. J. Pisano, C. Mitoma, and S. Udenfriend, *Nature*, **180**, 1125 (1957).

(8) A. Bazemore, K. A. Elliott, and E. Florey, *Nature*, **178**, 1052 (1956).

(9) C. Edwards and S. W. Kuffler, *Federation Proc.*, **16**, 34 (1957).

(10) D. P. Purpura, M. Girado, and H. Grundfest, *Science*, **127**, 1179 (1958).

(11) J. Dudel and S. W. Kuffler, personal communication.

(12) W. B. Jakoby and E. Scott, *J. Biol. Chem.*, **234**, 937 (1959).

(13) H. E. Carter, R. L. Frank, and H. W. Johnston, *Org. Syntheses*, **Coll. Vol. III**, 167 (1955).

(14) B. F. Erlanger and R. M. Hall, *J. Am. Chem. Soc.*, **76**, 5781 (1954).