(200 ml. per mole of acid), distilling off the ether until the temperature reached 83° and then refluxing for two hours. For example, when this method was used, the yield of 2-methyl-3-ethyl-3-pentanol was 70% instead of 53%.

The addition of the second molecule of alkylmagnesium halide to the salt and subsequent elimination of oxymagnesium halide was relatively slow. Less than fifteen per cent. of ketone was formed from butyric acid and *s*-butylmagnesium bromide, and less than two per cent. from the same acid and *t*-butylmagnesium bromide.

The addition of the final molecule of primary Grignard is more rapid but there was always a considerable amount (10–20%) of ketone in the reaction product. Attempts to prepare ketones by adding two moles of primary Grignard reagent to one of the acid gave, as the main product, the tertiary alcohol. This final step gave less than one per cent. of tertiary alcohol in the cases of secondary butyl and tertiary butyl Grignard reagents.

In all cases where primary Grignard reagents were used, the same colorless crystalline salt separated from the reaction mixture after most of the acid had been added. (It did not separate when acids were added to secondary or tertiary butylmagnesium bromide.) The ether was decanted off. The crystals were washed with anhydrous ether and dried in a vacuum desiccator over sulfuric acid. Analysis and reactivity shows a complex made up of one molecule and BrMg-OMgBr, two molecules of $MgBr_2$ and four molecules of ether.

Anal. Calcd. for $C_{16}H_{40}O_5Mg_4Br_6$: Mg, 10.93; Br, 54.0; equiv. wt., 444.5. Found: Mg, 10.90; Br, 53.93; equiv. wt., 447.

When treated with water, the double salt decomposed rapidly and gave off ether. A sample was hydrolyzed. Concentration of the filtered solution gave $MgBr_2 \cdot 6H_2O$.

KEDZIE CHEMICAL LABORATORY
MICHIGAN STATE COLLEGE
EAST LANSING, MICHIGAN
RECEIVED MARCH 11, 1946

The Alcoholysis of Cellulose[1]

BY RICHARD E. REEVES, WILHELMINA M. SCHWARTZ, AND JOEL E. GIDDENS[2]

Although acid-catalyzed hydrolysis of cellulose has been the subject of numerous investigations, the alcoholysis of cellulose seems to have received less attention. Hibbert and co-workers,[3] Brown, Heddle and Gardner,[4] and unpublished investigations by Ambler[5] have been concerned chiefly with the non-cellulosic substances which pass into solution upon alcoholysis of wood or other cellulosic materials. Pulping with alcohols has been studied,[6] but the conditions were unfavorable for acid-catalyzed alcoholysis and the products did not resemble those described below. Mark and Siggia[7] encountered the alcoholysis of modified "carboxy cellulose," but their interest was principally concerned with the esterification of carboxyl groups, not in the cleavage of the glucosidic linkages.

In hydrolysis of cellulose certain glucose-glucose linkages are ruptured with addition of a molecule of water. It was anticipated that alcoholysis would result in rupture of glucose-glucose bonds with the addition of a molecule of alcohol. This conception of the reaction seems to receive confirmation in the experiments described below.

Alcoholyzed cellulose differs from hydrocellulose in a number of ways: It is stable toward hot aqueous alkali, is non-reducing by the copper number determination, and it contains measurable amounts of alkoxyl groups attached by glycosidic (acid labile) linkages. Although degradation of cellulose appears to be more rapid by alcoholysis than by hydrolysis, it is found that approximately the same upper limit of fluidity is reached in each instance.

Experimental

Rate of Alcoholysis.—Parallel experiments were set up employing 0.5 *N* hydrochloric acid in methanol, ethanol, methanol-water (9:1 by volume), and water. Commercial grades of absolute methanol and ethanol were used without further purification. Samples of cotton fiber[8] were placed in glass-stoppered flasks containing 30 volumes of one of the acid solutions. After having been allowed to stand various lengths of time in a thermostat at 20°, the samples were removed, filtered on sintered glass filters, rinsed with water until free from acid, and allowed to dry in air. The recovery of fiber was greater than 95% in all instances. The results of fluidity measurements[9] on the products from the experiments with absolute methanol, 90% methanol, and water are shown in Fig. 1. Inspection of this figure shows that the rate of degradation is greatest for absolute methanol, intermediate for the

---

[1] From Southern Regional Research Laboratory, New Orleans, Louisiana. One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. **Not copyrighted.**

[2] **Resigned January 3, 1945.**

[3] L. Brickman, W. L. Hawkins and H. Hibbert, THIS JOURNAL, **62**, 2149–2154 (1940); W. B. Hewson, J. L. McCarthy and H. Hibbert, *ibid.*, **63**, 3041–3045 (1941); **63**, 3045-3048 (1941); E. West, W. S. MacGregor, T. H. Evans, I. Levi and H. Hibbert, *ibid.*, **65**, 1176–1180 (1943); K. A. West, W. L. Hawkins and H. Hibbert, *ibid.*, **63**, 3038–3041 (1941).

[4] J. S. Brown, R. D. Heddle and J. A. F. Gardner, *ibid.*, **62**, 3251–3252 (1940).

[5] J. A. Ambler, private communication.

[6] S. I. Aronovsky and R. A. Gortner, *Ind. Eng. Chem.*, **28**, 1270–1276 (1936); **29**, 1431–1434 (1937); H. Y. Charbonnier, *Paper Trade J.*, **114**, No. 11, 31-36 (1942).

[7] H. F. Mark and S. Siggia, U. S. Patent 2,379,917, July 10, 1945.

[8] The cotton fiber used in this work had been mechanically cleaned in a Shirley Analyzer. It was extracted in a Soxhlet extractor for four hours with alcohol and boiled for eight hours with water. The cotton linters used in some experiments had been purified by a commercial firm. The fibers and linters were used in the air-dried condition, it having been found in separate experiments that the small amount of moisture introduced with the sample did not cause a detectable change in the course of the reaction.

[9] Fluidity measurements were made at 25° in British Fabrics Research Committee type viscometers (see "The viscosity of cellulose solutions," H. M. Stationery Office, London, 1932). The cuprammonium solvent contained 15 ± 0.1 g. of copper and 240 ± 5 g. of NH_3 per liter. The dispersions contained 0.5 g. anh. fiber per 100 ml. and the results are expressed in rhes.

methanol containing water, and least for aqueous solutions of acid. This finding recalls earlier work in which it has been shown that, under equal conditions of temperature and acid concentration,[10] alcoholysis of simple glucosides proceeds as much as one hundred times more rapidly than hydrolysis. The curve obtained from the ethanolysis experiment not shown in Fig. 1 was slightly lower than that of methanolysis (Curve A in Fig. 1) during the early stages of the alcoholysis, but it appeared to reach the same ultimate value.

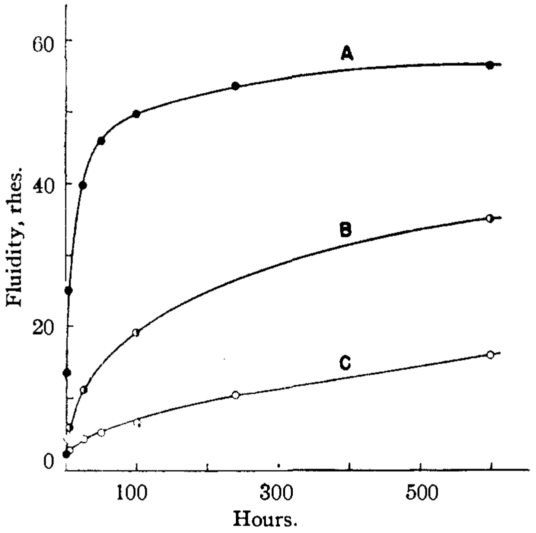

Fig. 1.—The cuprammonium fluidity of cellulose previously treated at 20° for various lengths of time with 0.5 *N* HCl in absolute methanol (Curve A); 0.5 *N* HCl in 90% methanol (Curve B); and 0.5 *N* HCl in water (Curve C).

Copper Number of Alcoholyzed Cellulose.—In contrast with hydrolysis, degradation by alcoholysis does not produce an increase in the copper number[11] of cellulosic material. This finding is to be expected if the conception of the alcoholysis reaction expressed above is correct. Cleavage of the glucose-glucose chain and simultaneous introduction of an alcohol molecule should lead to glucoside formation and not to the production of aldehydic reducing groups. In Fig. 2 is presented the copper number *vs.* fluidity relationship for cotton cellulose degraded by acid-catalyzed methanolysis or hydrolysis. The high-fluidity-methanolyzed samples were usually prepared by autoclaving the linters with methanol containing an initial concentration of 1 to 2% anhydrous hydrochloric acid. The temperatures employed were 100 to 120°. At these temperatures a rapid loss of acid occurred, but since the products did not contain chlorine it is assumed that the loss of acid was due to formation of methyl chloride. The highly degraded hydrolyzed samples were obtained by refluxing or autoclaving linters with 1 to 3% solutions of hydrochloric acid or sulfuric acid in water.

The Limiting Fluidity and Methoxyl Content of Alcoholyzed Cellulose.—Davidson[12] has recently emphasized the fact that, on long-continued hydrolysis, cellulose approaches a maximum or limiting cuprammonium fluidity value which is well below the fluidity of the cuprammonium solvent. Although cellulosic material disappears on drastic hydrolysis, the fluidity of that part which remains undissolved in the aqueous acid does not exceed the limiting value. A higher limiting fluidity has been found for mercerized cellulose than for native cellulose. A similar situation is encountered upon alcoholysis of cotton cellulose; and furthermore the limiting fluidity values correspond very closely with those obtained upon hydrolysis. Under the conditions employed for measurement of fluidity,[9] the limiting values upon methanolysis appear to be approximately 60 rhes for native cellulose and approximately 70 rhes for mercerized cellulose. The corresponding values for hydrolyzed celluloses are 59 and 69 rhes, respectively.

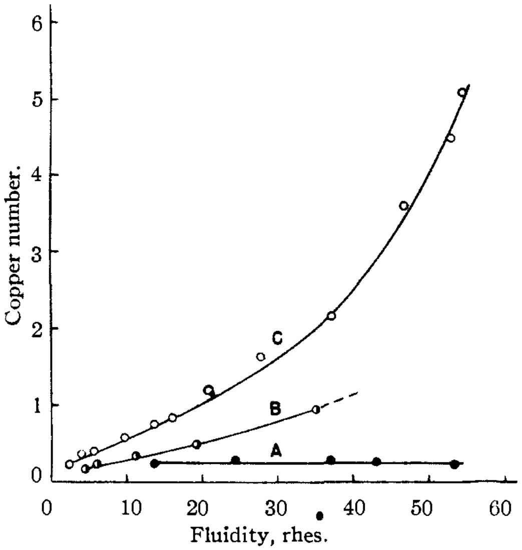

Fig. 2.—The copper number-fluidity relationship for cellulose degraded by acid in absolute methanol (Curve A); 90% methanol (Curve B); and water (Curve C).

The material which has been methanolyzed to maximum fluidity has been found to yield measurable amounts of methoxyl when subjected to standard methoxyl analyses.[13] Methanolyzed native cotton linters yield approximately 0.58% and methanolyzed mercerized linters, 0.87% methoxyl. By the same technique purified cotton linters, starch, sucrose, and National Bureau of Standards glucose all yield low but fairly reproducible methoxyl values of approximately 0.2 to 0.34%. The methoxyl value of methanolyzed cellulose is thus definitely above that of non-methanolyzed cellulose. Long-continued extraction of methanolyzed linters with water in a Soxhlet apparatus failed to remove any methoxyl from the cellulose, but hydrolysis for 24 hours with 0.5 *N* hydrochloric acid reduced the methoxyl content from 0.54 to 0.25%, and at the same time increased the copper number from 0.24 to 8.6. This is the type of behavior which would be expected if glucosidic methoxyl groups were replaced by hydroxyl groups by hydrolysis.

TABLE I

COMPARISON OF THE ALKALI-SOLUBILITY OF METHANOLYZED AND HYDROLYZED COTTON FIBER

	Fluidity[a] rhes	% Alkali soluble[b]
Methanolyzed cotton fiber	56.5	2.4
Hydrolyzed cotton fiber	56.8	45.6

[a] See footnote 9. [b] The sample was placed with 100 parts of 1% NaOH in a test-tube immersed in a boiling water bath for six hours. The undissolved residue was collected on a sintered glass filter, rinsed with water, dilute acid, water, and dried to constant weight.

---

[10] W. Voss and W. Wachs, *Ann.*, **522**, 240–261 (1936).

[11] Copper numbers were determined by the micro method described by T. F. Heyes, *J. Soc. Chem. Ind.*, **47T**, 90 (1920).

[12] G. F. Davidson, *J. Textile Inst.*, **34T**, 87–96 (1943).

[13] The methoxyl analyses were made by Alva Faust, employing Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, 5th ed., 1940, pp. 647–648. The phenol was omitted and samples were weighed directly into glass micro beakers.

Alkali Solubility of Alcoholyzed Cellulose.—Hydrolyzed cellulose is known to undergo extensive degradation by hot aqueous alkalies. Data given in Table I show that methanolyzed cotton cellulose does not undergo such an effect. This finding provides support for the view expressed by others that the loss of weight suffered by hydrocellulose in hot, dilute alkali is a function of reactivity, and not of solubility.[12] Alkaline solutions heated with hydrocellulose become discolored, whereas when heated with alcoholyzed cellulose they show no discoloration.

RECEIVED APRIL 11, 1946

Dehydrogenation of 1,4-Pentanediol

BY L. P. KYRIDES AND F. B. ZIENTY

The availability of 1,4-pentanediol (I) prompted the study of the dehydrogenation[1] of this glycol. Using a typical copper chromite hydrogenation catalyst,[2] and operating in the liquid phase under reflux, two moles of hydrogen were evolved and γ-valerolactone (II) was produced in 80% yield (an unexpected result). When the reaction mixture was slightly acidified with an organic acid and a downward condenser was used, as much as 30% of γ-acetopropanol[3] (III) was produced together with some (II).

Several derivatives of (III) were prepared (Table I).

TABLE I

Derivative	Recrystn. solvent	M. p.,[a] °C.	Formula	% Nitrogen[b] Calcd.	% Nitrogen[b] Found
(I) Bis-*p*-nitrobenzoate	Me_2CO-EtOH	150–151	$C_{19}H_{18}N_2O_8$	7.0	6.8
(III) Semicarbazone	EtOH	154–155[c]	$C_6H_{13}N_3O_2$	26.4	26.5
(III) Thiosemicarbazone	H_2O	102–103	$C_6H_{13}N_3OS$	24.0	23.9
(III) Acetate semicarbazone[d]	H_2O	125–126	$C_8H_{15}N_3O_3$	20.9	21.0
(III) Acetate thiosemicarbazone[d]	MeOH	117–118	$C_8H_{15}N_3O_2S$	19.3	19.3

[a] All melting points are corrected. [b] The analyses were performed by Mrs. J. D. Nevins of the Monsanto Analytical Laboratory. [c] Paul, *Bull. soc. chim.*, **53**, 426 (1933), reported 155–157°. [d] Prepared from (III) acetate, b. p. 88–89° (7 mm.). Slobodin, Zigel and Yanishevskaya, *C. A.*, **39**, 702 (1945), reported b. p. 100–115° (22 mm.). Palomaa, *Chem. Zentr.*, **84**, II, 1959 (1913), reported 211–213°. Bergel, U. S. Patent 2,358,618 (September 19, 1944), reported b. p. 96–99° (12 mm.), 103–104° (14 mm.) and 110–112° (17 mm.).

Experimental

Dehydrogenation of (I). (a) **In Absence of Organic Acids.**—A mixture of 104 g. (1 mole) of (I), 4 g of copper chromite catalyst[2] and 0.15 g. of powdered reagent sodium hydroxide was stirred vigorously and heated under reflux. At 200° a lively evolution of hydrogen occurred and the temperature soon dropped to 190–192° where the dehydrogenation proceeded smoothly. The evolution of gas (39 liters or two moles on the (I) reacted) ceased in about three hours. The reaction mixture was cooled to about 30°, filtered from the catalyst and distilled under reduced pressure, producing 79 g. (87%) of (II), b. p. 90–92° (16 mm.), n^{26}_D 1.4290, d^{25}_4 1.047[4], and 12 g. of unreacted (I), b. p. 124–126° (16 mm.) or 120–121° (14 mm.). The (II) was analyzed by titration with alkali.

Anal. Calcd. for $C_5H_8O_2$: mol. wt., 100.1; *MR*, 24.7. Found: mol. wt., 100.0: *MR*, 24.6.

Addition of a small amount of potassium hydroxide, monobasic sodium phosphate, alundum or decolorizing charcoal (Darco) to the reaction mixture produced an 87–90% yield of (II).

(b) **In Presence of Organic Acids.**—Under slightly acid conditions, such as could be attained by the addition of 0.003–0.005 mole per cent. of a non-volatile fatty acid like stearic acid,[1] to the reaction mixture, water and a low-boiling organic material could be distilled off and condensed in appreciable amounts. The mechanism in this reaction probably involves dehydrogenation of the secondary alcohol group in (I) to form (III), which, in its cyclic form,[5] dissociates into water and 2-methyl-4,5-dihydrofuran[6] (IV) which distil over and subsequently recombine to form (III).[7] The reaction of (IV) with water is slow (24–48 hours) and may be accelerated by stirring, but will proceed instantly, and even with violence, in the presence of a small amount of mineral acid, such as hydrochloric acid.

In order to separate the (III) from the (II) formed in the reaction, the crude reaction products were distilled slowly at atmospheric pressure using a short column. The volatile dissociation products of (III) distilled over, leaving the (II) behind in the still. (II) and (III) have similar boiling points under atmospheric pressure.

Reaction in an atmosphere of hydrogen was without benefit in producing (III). Activated copper made by decomposition of cupric carbonate in (I) caused some dehydrogenation to (II), but no (III) was obtained. A nickel hydrogenation catalyst caused extensive dehydration of (I), and produced only about 15% of (III).

RESEARCH LABORATORIES
MONSANTO CHEMICAL CO.
ST. LOUIS 4, MISSOURI

RECEIVED FEBRUARY 27, 1946

---

[1] Kyrides and Zienty, U. S. Patent 2,382,071 (August 14, 1945); *C. A.*, **40**, 90 (1946).

[2] Calingaert and Edgar, *Ind. Eng. Chem.*, **26**, 878 (1934).

[3] Several other examples of the formation of keto alcohols by dehydrogenation of glycols are described in the literature: McNamee and Blair, U. S. Patent 2,143,383 (January 10, 1939), *Chem. Zentr.*, **110**, I, 4842 (1939); Hilger, U. S. Patent 1,955,882 (April 24, 1934), see *Chem. Zentr.*, **104**, I, 2172 (1933); Neish, *Can. J. Research*, **23B**, 67 (1945); Holmes, U. S. Patent 2,036,940 (April 7, 1936), *Chem. Zentr.*, **107**, II, 402 (1936).

[4] Schuette and Sah, THIS JOURNAL, **48**, 3165 (1926), reported n^{25}_D 1.4301 and d^{25} 1.04608.

[5] Buchman, THIS JOURNAL, **58**, 1804 (1936).

[6] Lipp, *Ber.*, **22**, 1199 (1889).

[7] Marshall and Perkin, *J. Chem. Soc.*, **59**, 882 (1891). Paul, *Bull. soc. chim.*, **53**, 419 (1933), produced γ-acetopropanol by addition of water to 2-methylene-tetrahydrofuran in the presence of sulfuric acid. Knunyantz, Chelintzev, and Osetrova, *C. A.*, **28**, 4382 (1934), reported b. p. 115–116° (30 mm.) for γ-acetopropanol, while we found b. p. 85–86° (10 mm.)

Solubility Product of Silver Selenocyanate at 25°

BY G. R. WAITKINS AND C. R. MCCROSKY

Subsequent to studies dealing with selenocyanic acid and the gravimetric analysis of $SeCN^-$ as silver selenocyanate (AgSeCN)[1] it became of interest to determine the solubility of this silver salt.

A solubility product of 6.9×10^{-15} (K_{sp} average of four determinations) was found for silver selenocyanate at 25 ± 0.1° using the cell: Ag/

---

[1] Waitkins, M. S. Thesis, Syracuse University, 1934.