*Anal.* Calcd. for $C_{21}H_{20}O_2$: C, 82.8; H, 6.6. Found: C, 82.8; H, 6.3.

To a suspension of 3 g. of the diol in 30 cc. of benzene was added a solution of 0.15 cc. of concentrated sulfuric acid in 60 cc. of methanol. As soon as all of the diol had gone into solution, the **dimethyl ether** of the diol began to crystallize as colorless needles. After purification in the manner described for the other diol ethers, the compound melted at 228–229°; yield 3 g. When a benzene suspension and solution of the total crude diol obtained from 3.56 g. of 5-methyl-1,2-benzanthraquinone was treated with methanol containing 0.2 cc. of sulfuric acid, 3.72 g. (85% on the basis of the quinone) of the diol dimethyl ether was obtained. The diol dimethyl ether gives a deep red color with concentrated sulfuric acid.

*Anal.* Calcd. for $C_{23}H_{24}O_2$: C, 83.1; H, 7.3. Found: C, 83.1; H, 7.3.

**5,9,10-Trimethyl-1,2-benzanthracene** (V).—A mixture of 2 g. of the aforementioned dimethyl ether and 0.28 g. of powdered sodium was allowed to react in 30 cc. of anhydrous ether in the usual manner; most of the diol dimethyl ether remained undissolved. After twenty-four hours the mixture was purple in color and contained a considerable amount of precipitate; the latter was still present after thirty-six hours and proved to be 5,9,10-trimethyl-1,2-benzanthracene (0.85 g., m. p. 127–128°). From the solution an additional 0.71 g. (m. p. 124–126°) of hydrocarbon was isolated, making a yield of 96%. After purification in the manner described for the other hydrocarbons, the 5,9,10-trimethyl-1,2-benzanthracene crystallized from acetone–alcohol in plates or leaflets which possessed a yellowish tinge; m. p. 127–128°. When potassium was employed, the yield of crude, crystalline hydrocarbon was usually not greater than 80%.

*Anal.* Calcd. for $C_{21}H_{18}$: C, 93.3; H, 6.7. Found: C, 93.3; H, 6.2.

**The picrate**, prepared with excess of picric acid, crystallizes from absolute alcohol in beautiful black needles; m. p. 112–113°.

*Anal.* Calcd. for $C_{21}H_{18}\cdot C_6H_3O_7N_3$: N, 8.4. Found: N, 8.5.

**5,9,10-Trimethyl-1,2-benzanthracene-9,10-*endo*-α,β-succinic Anhydride.**—A solution of 0.5 g. of the hydrocarbon and 0.5 g. of maleic anhydride in 5 cc. of benzene was refluxed for one-half hour. The solution which was initially yellow became colorless and deposited crystals of the addition product. After cooling, 0.5 g. of the addition product was filtered off; it crystallizes from benzene in colorless needles; m. p. 250° with previous decomposition. The product obtained by evaporation of the benzene filtrate was completely soluble in hot aqueous potassium hydroxide, an indication that the addition of maleic anhydride to the hydrocarbon had been complete.

*Anal.* Calcd. for $C_{25}H_{20}O_3$: C, 81.5; H, 5.4. Found: C, 82.2; H, 5.1.

## Summary

Three new polycyclic hydrocarbons, 9,10-dimethyl-1,2-benzanthracene, 9,10-diethyl-1,2-benzanthracene and 5,9,10-trimethyl-1,2-benzanthracene, have been synthesized for their possible cancer-producing properties.

Ann Arbor, Michigan Received March 5, 1938

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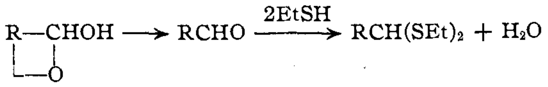
[Contribution from the Chemical Laboratory of The Ohio State University]

# Studies of Cellulose Hydrolysis by Means of Ethyl Mercaptan. II[1]

By M. L. Wolfrom, Louis W. Georges[2] and John C. Sowden[2]

In a previous publication[3] from this Laboratory we have reported a study of the course of hydrolysis of the cellulose molecule. This study was performed by allowing a solution of high viscosity cotton linters in fuming hydrochloric acid to hydrolyze at 16° and following the course of hydrolysis by mercaptalation at various time intervals. Ethyl mercaptan is a reagent that will react with the free reducing groups of carbohydrates in high concentrations of mineral acid to form mercaptals or thioacetals.



$$R{-}CHOH \longrightarrow RCHO \xrightarrow{2EtSH} RCH(SEt)_2 + H_2O$$

Sulfur analyses on the resulting mercaptalated hydrolyzed celluloses then gave an estimate of their average molecular size. In the work herein reported, the course of the hydrolysis of the same sample of cotton linters previously studied, was followed in more detail during the first three hours of the hydrolysis by fuming hydrochloric acid at 16°.

The literature concerned with hydrocelluloses and cellodextrins is very large[4] and a great deal of it is concerned with surface alterations of cellulose fibers in relation to textiles. No attempt will be made to review this literature, since so far as we are aware no previous work has been done employing ethyl mercaptan as a reagent for following the course of hydrolysis of the cellulose molecule.

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[1] Presented before the Division of Cellulose Chemistry at the 94th meeting of The American Chemical Society, Rochester, New York, September 9, 1937.

[2] Du Pont Cellulose Research Fellow.

[3] M. L. Wolfrom and Louis W. Georges, This Journal, **59**, 282 (1937).

[4] *Cf.* A. Girard, *Compt. rend.*, **81**, 1105 (1875); E. Heuser and F. Stöckigt, *Cellulosechem.*, **3**, 61 (1922); C. Birtwell, D. A. Clibbens and A. Geake, *J. Text. Inst.*, **17**, T145 (1926).

A cuprammonium viscosity measurement on the sample of high viscosity cotton linters that had been used previously and kept in careful storage, showed that it had remained unaltered and our new results are then comparable with those previously reported.[3] The cellulose was dissolved in fuming hydrochloric acid and allowed to hydrolyze at 16° for a maximum time of three hours. The course of the hydrolysis was followed polarimetrically (Fig. 1). Samples were removed at various time intervals and were mercaptalated with ethyl mercaptan. The acidity was then removed with sodium bicarbonate and the mercaptalated products were recovered by precipitation. Although these products were washed thoroughly, the gelatinous nature of some was such that they entrained considerable sodium chloride. This was corrected for by an ash determination. Precise sulfur analyses were then made on the products and their viscosities in cuprammonium solution were determined. These data are tabulated in Table II. An inspection of Table II will show that good agreement was obtained with the two points in this region previously recorded by the authors.[3]

An exactly similar set of experiments was then performed on another lot of the same cotton linters, except that the mercaptalation was omitted. The hydrolyzed celluloses corresponding to the mercaptalated products were thus in hand and their cuprammonium viscosities were determined (Table III).

The copper numbers (Hägglund–Bertrand) of the mercaptalated and non-mercaptalated hydrolyzed celluloses were determined and are recorded in Table IV. The finding of low but appreciable copper numbers for the mercaptalated products was a matter of some surprise, as visual Fehling's solution tests were considered negative. In comparison with the copper numbers found for the non-mercaptalated products, these values were very low. An interesting ratio is shown for the copper numbers determined on the two parallel products. The constant ratio of 0.2 for the experiments d to n and of 0.4 for the first three points (Table IV), would seem to indicate some regularity, an exact interpretation of which is not possible at the present time. It may be pointed out that incompleteness of reaction with ethyl mercaptan would make the degrees of polymerization, as calculated from the determined sulfur analyses, too high.

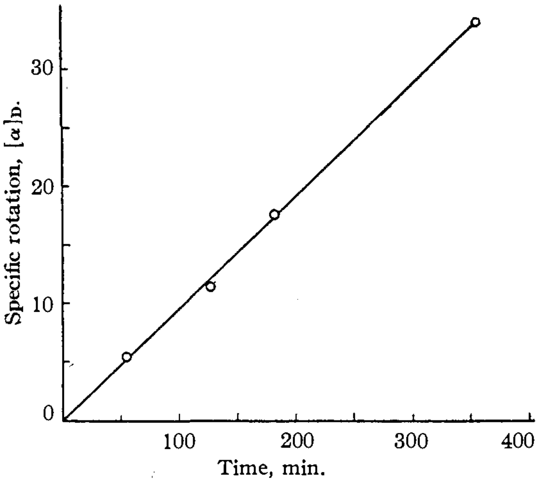

Fig. 1.—Specific rotation of cellulose in fuming HCl ($d^{16}_4$ 1.204; $c$ 4.65; 16°; $l$, 4-dm).

Table I shows the degrees of polymerization in glucose units calculated from the sulfur analytical data on the mercaptalated products and also those calculated from the cuprammonium viscosity data on both the mercaptalated and non-mercaptalated hydrolyzed celluloses, using the equation of Kraemer and Lansing.[5] The agreement in the degrees of polymerization, calculated from viscosity data, between the mercaptalated and non-mercaptalated products is fair, all points save three agreeing within ten units. When the calculated degrees of polymerization of the non-mercaptalated products are plotted against time of hydrolysis, an interesting curve results (Fig. 2).

TABLE I

DEGREE OF POLYMERIZATION (D. P.) IN GLUCOSE UNITS OF MERCAPTALATED AND NON-MERCAPTALATED HYDROLYZED CELLULOSES CALCULATED FROM SULFUR ANALYSES AND CUPRAMMONIUM VISCOSITY DATA

| Time of hydrolysis, min. | Mercaptalated products D. P. by S content | | Non-mercaptalated products D. P. by viscosity |
|---|---|---|---|
| | | D. P. by viscosity | |
| 20 | 114 | 182 | 158 |
| 30 | 89 | 112 | 136 |
| 45 | 87 | 98 | 89 |
| 60 | 80 | 87 | 58 |
| 75 | 66 | 66 | 51 |
| 90 | 31 | 51 | 45 |
| 105 | 29 | 33 | 39 |
| 120 | 26 | 35 | 35 |
| 135 | 27 | 33 | 32 |
| 150 | 23 | 29 | 29 |
| 165 | 24 | 28 | 25 |

A remarkable agreement is shown between the degrees of polymerization calculated from the

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[5] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 164 (1935).

sulfur values and from the viscosity data, on all save the first two points (at twenty and thirty minutes) of Table I. For these first two points, the values from the sulfur analyses are definitely lower than those calculated from the viscosity data. Since an inverse ratio holds between the sulfur content and the degree of polymerization, this cannot be explained by incomplete reaction with the ethyl mercaptan. Incomplete reaction would make the degree of polymerization calculated from the sulfur content too high. It does not seem reasonable that the discrepancy was caused by adsorbed ethyl mercaptan, since the material was subjected to drying *in vacuo* at 63° before analysis and ethyl mercaptan is highly volatile. Nevertheless, this point will require further investigation with such lesser degraded celluloses.

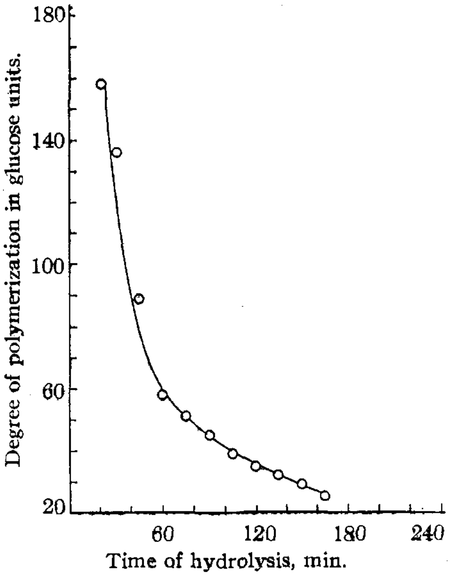

Fig. 2.—Relation between the time of hydrolysis of cotton linters and the D. P. (viscosity method) of the regenerated hydrolyzed celluloses.

Figure 3 shows the extremely rapid initial breakdown in viscosity when the cellulose was dissolved in fuming hydrochloric acid at 16°.

## Experimental

**Cellulose Characterization.**—The cuprammonium viscosity of our cotton linter stock[6] in 0.1% solution was redetermined and the degree of polymerization as calculated from the formula of Kraemer and Lansing[5] was found to be 2008. This compares with our value of 1980 found on the same stock in our previous work.[3] The average time of flow in an Ostwald viscosimeter from two trials was 403.5 seconds. The average time of flow of the cuprammonium solvent was 186.6 seconds. The cellulose used throughout the research was this same sample of purified cotton linters, which had been subjected to the customary commercial alkali kier and mild bleaching process.

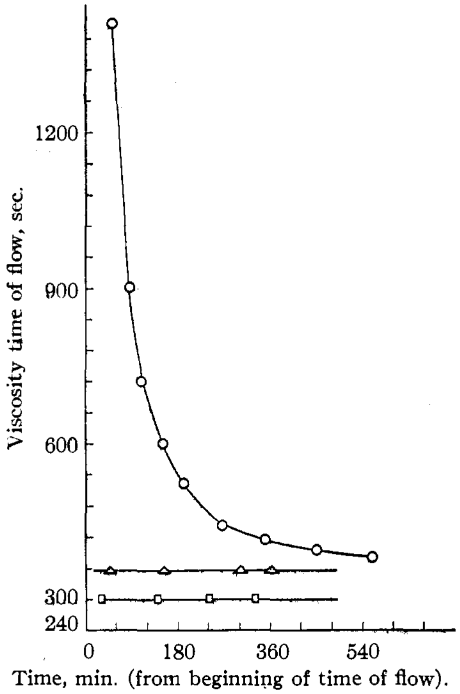

Fig. 3.—Comparison of viscosity at 16°: ○, 5% solution of cellulose in fuming HCl ($d^{16}_4$ 1.204); △, 5% solution of glucose in fuming HCl; □, fuming HCl.

**Preparation of Mercaptalated Hydrolyzed Celluloses.**—The cotton linters (21.0 g.) were dissolved by shaking with fuming hydrochloric acid ($d^{16}_4$, 1.205; 420 cc.) contained in a 1000-cc. glass-stoppered bottle. The solution was maintained at a temperature of about 16° by frequently cooling the bottle in cold water. A portion (60 cc.) of this solution was transferred to a glass-stoppered pressure bottle, purified ethyl mercaptan (8 cc.) was added and the whole shaken mechanically for fifteen minutes in an ice and water bath (0°). The reaction mixture was poured into a suspension of 68 g. of sodium bicarbonate in 200 cc. of water. The excess sodium bicarbonate was neutralized with acetic acid. The material was centrifuged and washed thrice with 100 cc. of water, twice with 100 cc. of ethanol (95%), twice with 100 cc. of acetone, and finally thrice with 100 cc. of petroleum ether (b. p. 30–60°). The product was dried overnight only, in a vacuum desiccator over sulfuric acid and calcium chloride. The same general procedure was used for all the experiments tabulated in Table II. In no case was the fuming acid solution diluted with water for the mercaptalation reaction. In order to determine whether the drying over sulfuric acid was producing further degradation, a portion of the material was dried in a vacuum desiccator without a drying agent, but no significant change in copper number was noted by this modification.

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(6) We are indebted to the Hercules Powder Company for furnishing us with this stock of high viscosity cotton linters.

TABLE II

MERCAPTALATED PRODUCTS FROM CELLULOSE SOLUTIONS ($c$, 4.65) IN FUMING HYDROCHLORIC ACID ($d^{16}_4$, 1.205) AT 16°

| Expt. Run 1 | Expt. Run 2 | Time of hydrolysis, min. | $[\alpha]^{16}_D$[a] | % ash, as NaCl | Mercaptalated product from 2.8 g. cellulose wt., g.[b] | % S[b] | | $C$[b] | Cuprammonium viscosity, 25°: time of flow in sec. Soln. | Solvent | D. P. by viscosity |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 17[c] | | | | 0.33 | | | | | |
| a | | 20 | + 2.0° | 5.28 | 2.5 | .35 | | 0.1 | 200.5 | 186.9 | 182 |
| | b | 30 | 3.0 | 2.39 | 2.5 | .45 | | .1 | 195.7 | 187.6 | 110 |
| | | | | | | | | 1.0 | 287.5 | 186.5 | 113 |
| c | | 45 | 4.5 | 3.31 | 2.7 | .49 | 0.43 | 0.1 | 194.1 | 186.9 | 98 |
| | d | 60 | 6.0 | 0.40 | 2.5 | .50 | | .1 | 191.7 | 185.4 | 87 |
| e | | 75 | 7.4 | .94 | 2.6 | .66 | .57 | .1 | 191.0 | 186.2 | 66 |
| | f | 90 | 9.0 | .10 | 2.4 | 1.29 | | .1 | 188.8 | 185.4 | 47 |
| | | | | | | | | .5 | 206.3 | 185.4 | 56 |
| g | | 105 | 10.2 | .21 | 2.4 | 1.37 | 1.36 | .1 | 190.0 | 187.6 | 33 |
| | h | 120 | 11.7 | .08 | 2.3 | 1.56 | | .1 | 189.6 | 187.6 | 28 |
| | | | | | | | | .5 | 202.5 | 186.5 | 43 |
| l | | 135 | 13.0 | .13 | 2.3 | 1.42 | 1.56 | .1 | 188.6 | 186.2 | 33 |
| | m | 150 | 14.5 | .10 | 2.1 | 1.71 | | .1 | 189.6 | 187.6 | 28 |
| | | | | | | | | .5 | 197.4 | 186.5 | 30 |
| n | | 165 | 16.0 | .05 | 2.2 | 1.69 | 1.61 | .1 | 189.6 | 187.6 | 28 |
| | | 180[c] | | | | 2.03 | | | | | |

[a] Rotation values from interpolation of curve, Fig. 1. [b] Calcd. on vacuum-dried (63°) and sodium chloride free basis. [c] From previous data of the authors, ref. 3.

The main bulk of solution was kept immersed in a thermostated bath (16 ± 0.1°) except for removal of a sample (60 cc.) at the recorded (Table II) intervals. A separate portion of the same solution was placed in a 2-dm. polarimeter tube and was kept out of the bath long enough to take a reading. Figure 1 has been constructed from these readings. The specific rotations for the solutions at the time of mercaptalation have been interpolated from this curve. Due to the time required to swell the cellulose into solution, it is difficult to determine exactly the initial time of reaction. In accordance with the previous work of this Laboratory and of others,[7] the polarimetric curve is extrapolated to zero rotation, and this point is taken as the initial time.

In order to obtain sufficient material, it was necessary to dissolve a second lot of cotton linters in fuming hydrochloric acid. Precautions were taken that the material was treated exactly as the first lot. The specific rotation of the second lot was found to be +18° at three hours, thus comparing with the rotation of +17.5° found for the first lot at the same time interval.

**Preparation of Non-Mercaptalated Hydrolyzed Celluloses.**—The cotton linters (36.0 g.) were dissolved in fuming hydrochloric acid and treated exactly as described for the preparation of the mercaptalated hydrolyzed celluloses, including the fifteen-minute mechanical shaking at 0°, except that the addition of ethyl mercaptan was omitted. The specific rotation of the acid solution after three hours at 16° was found to be +19°.

TABLE III

NON-MERCAPTALATED HYDROLYZED PRODUCTS FROM CELLULOSE SOLUTIONS ($c$, 4.65) IN FUMING HYDROCHLORIC ACID ($d^{16}_4$, 1.204) AT 16°

| Expt. | Time of hydrolysis, min. | $[\alpha]^{16}_D$[a] | % ash, as NaCl | Product from 2.8 g. cellulose wt., g.[b] | $C$[b] | Cuprammonium viscosity; 25°; time of flow in sec. Soln. | Solvent | D. P. by viscosity |
|---|---|---|---|---|---|---|---|---|
| a′ | 20 | +2.0° | 3.34 | 2.5 | 0.1 | 196.0 | 184.1 | 163 |
| | | | | | .75 | 289.8 | 186.2 | 153 |
| b′ | 30 | 3.0 | 2.57 | 2.7 | .1 | 195.9 | 185.9 | 136 |
| c′ | 45 | 4.5 | 0.95 | 2.7 | .1 | 193.3 | 186.8 | 89 |
| d′ | 60 | 6.0 | .25 | 2.7 | 1.0 | 232.3 | 186.2 | 58 |
| e′ | 75 | 7.4 | .22 | 2.6 | 0.1 | 190.5 | 186.8 | 51 |
| | | | | | 1.0 | 223.8 | 185.0 | 50 |
| f′ | 90 | 9.0 | .24 | 2.6 | 0.1 | 190.1 | 186.8 | 45 |
| g′ | 105 | 10.2 | .10 | 2.4 | .1 | 189.8 | 186.8 | 41 |
| | | | | | 1.0 | 214.9 | 186.2 | 37 |
| h′ | 120 | 11.7 | Trace | 2.4 | 0.1 | 189.3 | 186.7 | 35 |
| l′ | 135 | 13.0 | 0.18 | 2.3 | .1 | 188.8 | 186.6 | 31 |
| m′ | 150 | 14.5 | Trace | 2.2 | 1.0 | 209.4 | 185.0 | 32 |
| | | | | | 0.1 | 188.7 | 186.6 | 29 |
| n′ | 165 | 16.0 | Trace | 2.2 | .1 | 188.4 | 186.6 | 25 |

[a] Rotation values from interpolation of curve, Fig. 1.

[b] Calcd. on vacuum-dried (63°) and sodium chloride free basis.

**Ash and Sulfur Analyses.**—The ash content of the mercaptalated and non-mercaptalated hydrolyzed celluloses was determined by careful ashing of 0.5-g. samples with concentrated sulfuric acid in a platinum crucible. The results were calculated in terms of sodium chloride and are tabulated in Tables II and III.

All of the sulfur values were determined according to the Parr bomb method. Two samples of 0.25 g. each were fused separately, dissolved in the same solution, the iron from the crucible removed by precipitation and reprecipitation, and the barium sulfate precipitated from a total volume of 800 cc. After standing for eighteen hours, the barium sulfate was filtered through a porous-bottomed

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[7] *Cf.* H. Hibbert and E. G. V. Percival, THIS JOURNAL, **52**, 3995 (1930).

porcelain crucible which had been treated previously with a mixture of hot aqua regia. This treatment brought the crucibles to constant weight. If, after weighing the barium sulfate, the latter was removed mechanically and the crucible heated again with aqua regia, the weight of the crucible could be checked within the accuracy of the balance used (±0.2 mg.). In all cases, a crucible of the same kind was used as a tare for weighing. A blank determination showed that all reagents used were sulfur-free. Very satisfactory sulfur analyses were thus obtained and are tabulated in Table II, which also show good agreement with the two sulfur values previously determined[3] in this region.

From the sulfur analyses, the degree of polymerization in glucose units was calculated by the following close approximation

$$\text{D. P.} = \frac{100 \times 2\text{S}}{\%\text{S} \times \text{C}_6\text{H}_{10}\text{O}_5} = \frac{40}{\%\text{S}}$$

The data so obtained are tabulated in Table I.

**Cuprammonium Viscosities.**—An amount of 50 mg. of sample, corrected for moisture content as determined in a separate sample and corrected for any sodium chloride content, was weighed accurately and dissolved in 50.0 cc. of cuprammonium solvent, prepared according to the standards of the Cellulose Division of the American Chemical Society. The viscosity was determined in a calibrated viscosimeter of the Ostwald type at 25 ± 0.03°, and all the customary precautions were observed. The viscosimeter had a volume at 10.5 cc.; its capillary length was 9.3 cm.; and the mean head was 13.3 cm. The viscosity of the solvent was taken at the same time. The results are tabulated in Tables II and III. The recorded times of flow represent an average of two trials, all agreeing within ±0.2 second. The viscosity of the solvent was determined simultaneously in duplicate (agreement ±0.2 second) and the recorded variations were caused by changes taking place in the solvent on standing for relatively long periods of time. A number of check determinations were made at higher concentrations.

From the viscosity measurements, the degree of polymerization in glucose units was calculated by the equation of Kraemer and Lansing

$$\text{D. P.} = 260\ [\eta]$$

$[\eta]$ = intrinsic viscosity = $\ln_e \eta_r/C$

$\eta_r$ = relative viscosity, $C$ = concentration in g. per 100 cc.

A sample calculation is shown for the top figure in the third column of Table I, wherein the calculated degrees of polymerization are tabulated.

$$\text{D. P.} = \left[260 \ln_e \frac{200.5}{186.9}\right] \Big/ 0.1 = 182$$

The data in the last column of Table I are plotted in Fig. 2.

**Copper Numbers.**—The copper numbers were determined according to the Hägglund–Bertrand[8] method. The Bertrand solution was first heated to boiling and the sample (0.25 to 0.50 g.) added. The results are tabulated in Table IV. The mercaptalated hydrolyzed cellulose of experiment (a) in Table IV, showing a copper number of 1.84, was recovered, washed well with water and acetone and treated a second time according to the Hägglund–Bertrand procedure. A copper number of only 0.21 was then obtained. A sample of glucose diethyl mercaptal yielded a zero copper number.

TABLE IV

COPPER NUMBER[a] (HÄGGLUND–BERTRAND) OF MERCAPTALATED AND NON-MERCAPTALATED HYDROLYZED CELLULOSES

| Time of hydrolysis, min. | Mercaptalated products Run 1 | Run 2 | Copper no.[b] | Non-Mercaptalated products Expt. | Copper no.[b] | Ratio of copper numbers |
|---|---|---|---|---|---|---|
| 20 | a | | 1.84 | a' | 4.96 | 0.37 |
| 30 | | b | 2.52 | b' | 7.06 | .36 |
| 45 | c | | 3.33 | c' | 8.37 | .40 |
| 60 | | d | 3.07 | d' | 12.90 | .24 |
| 75 | e | | 2.99 | e' | 16.15 | .19 |
| 90 | | f | 3.92 | f' | 18.64 | .21 |
| 105 | g | | 3.19 | g' | 20.83 | .15 |
| 120 | | h | 4.49 | h' | 22.09 | .20 |
| 135 | l | | 4.92 | l' | 25.39 | .19 |
| 150 | | m | 5.91 | m' | 26.29 | .22 |
| 165 | n | | 5.49 | n' | 28.37 | .19 |

[a] Copper no. = grams of copper reduced from cupric to cuprous state by 100 g. of sample.

[b] Calcd. to a moisture-free and sodium chloride free basis.

**Viscosity of a 5% Solution of Cellulose in Fuming Hydrochloric Acid.**—The viscosity change of the fuming hydrochloric acid solution of the cotton linters was determined directly at 16° with an Ostwald type viscosimeter and is diagrammed in Fig. 3.

The authors are indebted to E. I. du Pont de Nemours and Company, Inc., for the fellowship grant which has made this research possible.

## Summary

1. The hydrolysis of 5% solutions of cellulose in fuming hydrochloric acid at 16° during the first three hours has been studied in some detail. The optical rotation changes of the cellulose solution during this time have been observed. Mercaptalated products have been prepared by treating the cellulose solution at 0° with ethyl mercaptan at stated time intervals. The corresponding regenerated hydrolyzed-cellulose products were prepared.

2. Sulfur analytical data indicated that the degrees of polymerization of the mercaptalated products varied from 114 to 23 glucose units.

3. The degrees of polymerization calculated, according to the equation of Kraemer and Lans-

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[8] E. Hägglund, *Cellulosechem.*, **11**, 1 (1930).

ing, from the cuprammonium viscosity data for both the mercaptalated and non-mercaptalated hydrolyzed celluloses, were in good agreement throughout with those calculated from the sulfur analytical data, except for the very early stages of the hydrolysis, wherein the sulfur data gave lower results.

4. The mercaptalated hydrolyzed celluloses showed a low copper number, varying from 1.8 to 5.5. The copper numbers of the non-mercaptalated hydrolyzed celluloses varied from 5.0 to 28.4. The copper number ratios for these two series of products showed an apparent regularity.

5. A determination has been made of the viscosity changes taking place at 16° in a 5% cellulose solution in fuming hydrochloric acid with increasing time of hydrolysis.

COLUMBUS, OHIO RECEIVED JANUARY 22, 1938

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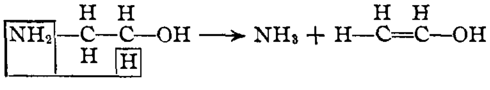
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE, COLLEGE OF THE CITY OF NEW YORK]

# Alkanolamines. IV. Reducing Properties of the Amino Alcohols

BY CHESTER B. KREMER AND BERNARD KRESS

The ability of the ethanolamines to reduce organic compounds and aqueous solutions of silver, lead and mercury salts, has been the subject of recent investigations.[1,2] It was thought of interest to determine the ability of other amino alcohols to act as reducing agents and to compare their action with that of the ethanol compounds. A list of the alcohols studied may be obtained by reference to Tables I and II. In addition to these, pentanolamine, diethylaminoethyl alcohol and the cyclic amines morpholine and phenylmorpholine were investigated.

While it has been proposed[1] that in these reactions the amino alcohol is decomposed into ammonia and an aldehyde, no mechanism for such a decomposition has been given. The presence of ammonia in many of these reactions is detected readily. The decomposition may very well parallel that of the esters of amino acids wherein ammonia is liberated and an unsaturated, nitrogen-free compound results. Accordingly, we would have for monoethanolamine



$$\boxed{NH_2}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{\boxed{H}}{C}}-OH \longrightarrow NH_3 + H-\overset{H}{C}=\overset{H}{C}-OH$$

Ammonia and acetaldehyde (enol form) are here seen to be the end-products. The mechanism appears plausible and the presence of aldehyde has been proved.

The fact that morpholine reduces aqueous solutions of certain metal salts to a slight degree, led to the carrying out of a series of reactions with this material, and also with phenylmorpholine. In all cases studied the morpholines failed to effect reduction of organic compounds.

An interesting observation was made in comparing the reducing ability of alcohols containing a tertiary amine group. Whereas triethanolamine, as well as triisopropanolamine, proved to be good reducing agents, diethylaminoethyl alcohol was extremely weak in action. More interesting, was the fact that the latter compound reduced solely to the azoxy state, a result not duplicated by any other amino alcohol studied.

All of the reductions were carried out upon either nitrobenzene or *m*-chloronitrobenzene; both in the presence and absence of added alkali. Alkalinity of medium, length of heating, temperature of refluxing and the molar ratio of the reactants materially affect the yields and nature of the end-products.

TABLE I

| Amino alcohol | Yield of reduction products, %<br>3,3′-Dichloro-azobenzene | *m*-Chloroaniline |
|---|---|---|
| Monoethanolamine | 30–40 | 60–70 |
| Monopropanolamine | 15–18 | 30–35 |
| Monoisopropanolamine | 20–25 | 60–70 |
| Monoisobutanolamine | 12–14 | 20–22 |

TABLE II

| Amino alcohol | NaOH | Approximate yield, %<br>Azobenzene | Aniline |
|---|---|---|---|
| Monoethanolamine | None | 10 | 12 |
| Diethanolamine | None | 27 | 10 |
| Diethanolamine | 5 g. | 50 | 5 |
| Triethanolamine | None | 10 | 7 |
| Triethanolamine | 5 g. | 55 | Trace |
| Monoisopropanolamine | None | 20 | 25 |
| Monoisopropanolamine | 5 g. | 60 | Trace |
| Diisopropanolamine | None | 25 | Trace |
| Triisopropanolamine | None | 12 | 5 |
| Monopropanolamine | None | 5 | Trace |
| Monoisobutanolamine | None | Trace | Trace |

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[1] M. Meltsner, C. Wohlberg and M. J. Kleiner, THIS JOURNAL, **57**, 2554 (1935).

[2] M. Meltsner, L. Greenstein, G. Gross and M. Cohen, *ibid.*, **59**, 2660 (1937).