SOME NEW SOLVENTS FOR CELLULOSE AND THEIR ACTION ON THIS SUBSTANCE.[1]

By Horace G. Deming.

Received June 20, 1911.

Introductory.

No simple solvent is known for the so-called normal cellulose, of which the cotton fibre is the type. It is precipitated from solution in a modified form,[2] and its esters appear to be not derivatives of normal cellulose, but of hydrocelluloses whose nature has not been determined.[3] The reagents which dissolve cellulose may be classified as follows:

1. Certain solutions of metallic salts in the presence of acids. Zinc chloride in aqueous solution (where some free acid is always present because of hydrolysis) and the same salt in hydrochloric acid solution appear to be the only examples recorded.

2. Certain organic reaction mixtures, in which the cellulose dissolves with the production of esters.

3. Ammoniacal solutions of copper hydroxide, copper carbonate, and cuprous chloride,[4] and solutions of copper hydroxide in the alkylamines.[5]

4. Certain strong mineral acids. Concentrated sulfuric acid, phosphoric acid, and nitric acid (sp. gr. 1.52) were previously known to dissolve cellulose.

This paper will present some new solvents under several of the above heads, with some of the data which have been obtained regarding esterification and hydrolysis of cellulose in such solutions.

The material employed in all cases was an excellent filter paper, such as is used for quantitative determinations (Schleicher and Schüll, No. 595). It contained 0.095 per cent. ash, and its hygroscopic moisture, determined by drying at 110°, was 5.13 per cent. The material contained a little oxycellulose, as was shown by its reducing power with Fehling's solution. Thus 100 grams of material reduced 0.95, 1.18, average 1.05 grams of copper (calculated). The copper reduced in this and in all succeeding experiments was determined by electrolysis from a 10 per cent. sulfuric acid solution, in which the cuprous oxide formed had been dissolved.

Action of Metallic Salts in the Presence of Acids.

A concentrated aqueous solution of zinc chloride dissolves cellulose when warmed slightly. The first stage of the reaction is a swelling of

---

[1] I wish to extend thanks for valuable advice and directions to Professor Louis Kahlenberg, at whose suggestion this work was undertaken.

[2] Schwalbe, "Die Chemie der Cellulose," p. 145.

[3] Ost, *Z. angew. Chem.*, 19, 995 (1906); Häussermann, *Z. Schiess u. Sprengwesen*, 3, 305.

[4] Rosenfeld, *Ber.*, 12, 956 (1879).

[5] *Z. angew. Chem.*, 19, 497 (1906).

the fiber, probably accompanied by hydration, as cellulose which has been previously hydrated by the mercerizing process dissolves in the reagent with unusual ease.[1] The next step in the act of solution is a further modification of the cellulose by the acid, which is always present from the partial hydrolysis of the salt. The following facts support this conclusion:

1. Cellulose dissolves in a solution of zinc chloride in concentrated hydrochloric acid with much greater ease than in a solution of the same salt in water.[2]

2. Hydrocelluloses, produced by the action of dilute acids on cellulose, dissolve in the solution in water to a greater extent than do unaltered celluloses at the same temperature. Rough experiments show that more than half of the hydrocellulose prepared according to Girard[3] is soluble in a cold aqueous solution of zinc chloride at 20°, while less than 10 per cent. of an unaltered cellulose is dissolved in the same time. Hydrocellulose prepared in this way is, however, a mixture of substances, some of which are quite insoluble in the cold reagent.

3. Liquids which dissolve zinc chloride without liberating hydrochloric acid by hydrolysis are unable to dissolve cellulose. The salt for example dissolves readily in pyridine and quinoline, but such solutions do not dissolve cellulose, even at the boiling temperature. Certain celluloses which have been altered by dilute acids are, however, soluble in these reagents. Zinc chloride dissolves to a considerable extent in acetone, ethyl acetate and lactic acid, but such solutions do not dissolve unaltered cellulose. No experiments have been made on the solubility of the altered celluloses in these reagents.

After showing the necessity for the presence of free acid, it seemed likely that solutions of other salts of a weak base and a strong acid might dissolve cellulose in aqueous solution, or at least in solution in concentrated hydrochloric acid. Many such cases were found, and are recorded below.

Water added in small quantities to crystals of antimony trichloride produces a clear solution, which dissolves cellulose in the cold, and more quickly on warming. A solution of the same salt in aniline does not dissolve cellulose even on boiling, but one in concentrated hydrochloric acid effects solution in the cold.

Strong solutions of mercuric chloride and bismuth chloride in concentrated hydrochloric acid make splendid solvents for cellulose even in the cold. Four parts of stannous chloride dissolved in one part of water

---

[1] Ger. Pat., 11886, 118837.

[2] *Chem. Ztg.*, **18**, 441 (1894); *Chem. News*, **63**, 66 (1891).

[3] *Ann. chim. phys.*, [5] **24**, 350 (1881).

bring cellulose into solution when warmed to 100°, while the same salt in concentrated hydrochloric acid is effective in the cold.

Antimony pentachloride, tin tetrachloride, and titanium tetrachloride mixed with a small amount of hydrochloric acid dissolve cellulose. In the case of the last mentioned solution one can best observe the fact that the cellulose fibers swell up and become transparent before dissolving.

Cobalt chloride, auric chloride, uranyl chloride, cerous chloride, and chromic chloride are less efficient. To secure a clear solution in such cases it is necessary to filter the liquid through an asbestos felt which has been washed with concentrated hydrochloric acid, as portions of the fibers remain undissolved. Aqueous hydrochloric acid solutions of cadmium chloride, cuprous chloride, thallic chloride and vanadium chloride are relatively poor solvents, but all dissolve some cellulose. Manganous chloride, cupric chloride and nickel chloride were employed in the form of the hydrated salts, which were dissolved in concentrated hydrochloric acid. In each case they are without action. Silver chloride, lead chloride, thallous chloride, thoric chloride, aluminum chloride, phosphorus chloride, and arsenic trichloride all fail to dissolve cellulose in acid solution. These results are possibly due, in some cases, to the fact that the salt is but poorly soluble in the concentrated acid. Zirconium chloride in concentrated hydrochloric acid solution dissolves but little cellulose, except at high temperatures where the organic material is so far decomposed as no longer to permit of recovery by dilution with water.

The action of bromides in acid solution is complicated by the fact that hydrobromic acid has such a powerful effect on cellulose. The decomposition of the latter by hydrobromic acid gas in ethereal solution, with the production of brommethylfurfural, is well known.[1] A concentrated aqueous solution of hydrobromic acid dissolves cellulose almost instantly with profound decomposition, but the following observations were nevertheless made. Aqueous zinc bromide dissolves cellulose, but zinc fluoride is but slightly soluble and so fails to act. Bismuth bromide and mercuric bromide dissolved in hydrochloric acid dissolve cellulose at concentrations where an equivalent amount of hydrobromic acid would disintegrate the fibers without dissolving them. The same is true of the iodides of zinc and mercury in hydrochloric acid solutions, which dissolve cellulose readily. Lead iodide and bismuth iodide dissolved in hydriodic acid dissolve cellulose, but the concentrated acid itself has considerable solvent power.

Neutral solutions of the halogen salts of the alkalies and alkaline earths are unable to effect solution, but what has been said would lead one to expect some of these solutions to dissolve cellulose which has been previously altered by the action of acids. This is actually the case, and a

---

[1] Fenton and Gostling, *J. Chem. Soc.*, 79, 361, 807 (1901).

subsequent report will deal with the action of such reagents on various modified celluloses. As an example may be mentioned the fact that a solution of calcium chloride boiling at 130° will at that temperature dissolve the modified cellulose precipitated from the formic-hydrochloric acid reagent described later. The hydrocellulose of Girard is soluble in the calcium chloride solution to a large extent at the same temperature.

The chlorides of the alkalies and alkaline earths do not dissolve cellulose in hydrochloric acid, perhaps on account of the fact that the salts are but sparingly soluble in the acid. One might expect to find that solutions of these salts in other acids would dissolve cellulose. In fact solutions of calcium chloride, calcium bromide, barium chloride, magnesium bromide, lithium chloride and potassium bromide in formic acid, or in mixtures of the latter with hydrochloric acid do dissolve cellulose. A similar but less decided action is obtained with solutions of lithium chloride and calcium chloride in trichloracetic acid.

Precipitation takes place when solutions of cellulose in any of the above reagents are poured into water, but the action is often not complete until after several days. The product must be entirely free from acid if it is to possess stability. Washing is best effected by separating the precipitate in a centrifuge, shaking it up with water and separating again. After several such operations a few drops of normal alkali will render the wash-water neutral. Final separation is made on a Büchner funnel.

The dried product is an extremely hard, hornlike mass, almost colorless if prepared with care, and resembling the cellulose recovered from solution in Schweizer's reagent. The yield from solution in antimony trichloride dissolved in concentrated aqueous hydrochloric acid at room temperature was about 60 per cent. of the weight of the original material, when the product was precipitated by dilute acids within one hour from the time of solution. The air-dried sample contained 10.0 per cent. moisture, determined by drying in the air at 105°. It also contained 0.40 per cent. ash, and was easily soluble in concentrated hydrochloric acid, partly soluble in cold 10 per cent. sodium hydroxide solution, and very slowly soluble in Schweizer's solution. Its reducing power was determined as directed by Schwalbe,[1] except that a smaller sample was weighed out and boiled with 150 cc. of Fehling's solution. A 0.4040 g. sample gave 0.0716 g. copper, corresponding to a copper number of 20.8, corrected for moisture and ash.

The rate of hydrolysis of the cellulose appears to vary with the nature of the salt which has aided in effecting its solution. The action proceeds to a stage where the material can no longer be precipitated by water, and results in the production of considerable glucose, as shown by the osazone test. The absence of large quantities of dextrins among the final products

---

[1] *Z. angew. Chem.*, 23, 924 (1910).

of the cellulose hydrolysis is indicated by the low rotatory power of the solutions. For example, 0.80 g. cotton, dried at 110° and dissolved in a solution of 25 g. pure antimony trichloride and concentrated hydrochloric acid, showed a rotation of +0.83° in a 1 dcm. tube, after making up to 50 cc. with the concentrated acid and allowing to stand for 17 hours before polarizing. $[\alpha]_D = 51.9°$.

Some results were obtained regarding the hydrolysis of cellulose in other reagents mentioned above, but no discussion or quantitative description will be attempted until the work is complete.

Esterification and Hydrolysis in Formic Acid Solution.

Details for the esterification of cellulose in the presence of different condensing agents will be found in the recent text-books of Schwalbe[1] and Piest.[2] Cellulose formates prepared with the use of sulfuric acid as a catalyzer were studied by Woodbridge.[3] Recent patents call for the use of zinc chloride[4] or gaseous hydrochloric acid,[5] but the products of the reaction have not been investigated.

A cellulose ester was prepared by the solution of 3.0 g. of filter paper in 100 cc. of formic acid which had been saturated at room temperature with dry hydrochloric acid gas. The product precipitated after four hours was slowly soluble in formic acid, slightly soluble in pyridine, and insoluble in the other reagents which dissolve the different cellulose acetates. If allowed to remain in the acid liquid for 24 hours before precipitating, the ester thus formed is saponified, yielding a modified cellulose identical with that obtained from the mixture of hydrochloric acid, formic acid, and calcium chloride described below.

When calcium chloride is substituted for the hydrochloric acid gas the cellulose is esterified, and a portion is dissolved. The calcium chloride probably aids the esterification by bringing the cellulose into solution in the way previously noted. The amount of cellulose dissolved by this method is, nevertheless, small.

The dissolved ester is precipitated by the addition of alcohol or water, but the reaction mixture may be diluted with concentrated hydrochloric acid without causing a precipitate to form. This observation suggests the use of a mixture of hydrochloric acid, formic acid, and calcium chloride to dissolve cellulose. The product recovered from such a solution is not an ester, but a modified cellulose produced by the saponification of an ester by the mineral acid.

It may be mentioned that a mixture of 30 cc. of formic acid (sp. gr.

---

[1] "Die Chemie der Cellulose," Berlin, 1910.

[2] "Die Cellulose," Stuttgart, 1910.

[3] THIS JOURNAL, 31, 1067 (1910).

[4] U. S. Pat. 655,082; Ger Pat. 219,163.

[5] Ger. Pat. 189,837.

1.22), 70 cc. hydrochloric acid (sp. gr. 1.40), and 10 g. calcium chloride will dissolve 1.5 g. of cellulose within fifteen minutes, while a mixture of the two acids alone will effect no solution in twenty-four hours. Addition of as little as four grams of calcium chloride to the acid mixture will cause almost complete solution within half an hour. We may conclude that there is some specific action of the metallic salt, since the addition of an equivalent amount of hydrochoric acid gas does not bring about solution.

In order to investigate the modified cellulose recovered from the solution in this reagent, 25 cc. of concentrated hydrochloric acid were mixed with 25 cc. of formic acid and 5 grams of calcium chloride. About 2.5 g. filter paper dissolved in the liquid to a clear syrup in about one hour. The material was precipitated with water, washed with the aid of a centrifuge, and dried for several weeks in a vacuum at room temperature over sulfuric acid.

Analysis by combustion gave the following figures:

Calculated for $(C_6H_{10}O_5)_6.H_2O$: C, 43.63; H, 6.26.
Ash, 0.37%. Found: C, 43.42, 43.50; H, 6.05, 5.93.

Material dried in this way evidently contains a slight excess of water over that contained in normal cellulose.

A second sample was prepared in the same way as before, except that the material was allowed to remain dissolved in the acid mixture for three hours before precipitating. The acid-free sample was dried in an air oven at 110° for three hours, when its weight was practically constant. Analysis by combustion gave:

Calculated for $C_6H_{10}O_5$: C, 44.44; H, 6.17.
Ash, 0.55%. Found: C, 44.19, 44.00; H, 6.17, 6.24.

Ost[1] found the figures 44.26 and 6.25 for cotton cellulose, from which we may conclude that the modified cellulose under consideration has the same percentage composition as the former, or differs from it by an amount too small to be detected by elementary analysis.

The modified cellulose prepared as described above is slowly soluble in Schweizer's reagent and in concentrated hydrochloric acid if freshly precipitated. On drying, it becomes insoluble in cold concentrated hydrochloric acid, and dissolves in Schweizer's reagent only on standing for a number of days. About 45 per cent of the material will dissolve in cold 10 per cent. sodium hydroxide solution in three days. It is not permanently stained with iodine unless first moistened with sulfuric acid, when it receives a deep blue color. It is soluble in the acid solvents for normal cellulose, but is distinguished from the latter by its marked reducing power and ready hydrolysis.

---

[1] *Z. angew. Chem.*, 19, 993 (1906).

No. 1. 1.5189 g. substance gave 0.1256 g. copper. Corrected copper number 20.6. No. 2. 0.4443 g. substance gave 0.1862 g. copper. 0.6137 g. substance gave 0.2533 g. copper. Corrected copper number 42.88, 42.46. No. 3. 0.2154 g. substance gave 0.0296 g. copper. 0.2154 g. substance gave 0.0256 g. copper. Corrected copper number 12.1, 10.2.

Sample No. 1 had remained in the acid liquid for two hours before being precipitated. It had been mixed with silica to aid washing, and contained 59.93 per cent. ash and 2.12 per cent. moisture, determined at 110.°.

Sample No. 2 had been in solution for 36 hours, in a mixture of 100 cc. of formic acid (sp. gr. 1.22), 100 cc. water, 300 cc. of hydrochloric acid (sp. gr. 1.20), and 50 g. anhydrous calcium chloride. It contained 0.27 per cent. ash and 3.94 per cent. moisture.

Sample No. 3 had been in solution two hours. Its reducing power was determined approximately by pipetting off 50 cc. of an acid-free suspension of freshly precipitated material. The total weight of the solid matter was determined in another sample of 50 cc. The ash content was 30 per cent.

The correction for the copper solution absorbed by the filter paper used in separating the cuprous oxide was taken as 0.0037 g. in all determinations. It is evident that the reducing power of the material under consideration is increased by long contact with the acid solvent, or even by drying in the air.

To compare the rate of hydrolysis of normal cellulose with that recovered from solution in the reagent under study, samples were weighed out and boiled for four hours with normal hydrochloric acid, the reducing power of the filtrate being determined with the following results: 3.1291 g. S & S paper No. 595 gave 0.5133 g. copper; 0.4285 g. modified cellulose, 0.4346 g. copper. This corresponds to a hydrolysis of about 8 per cent of the filter paper, as compared with 50 per cent. of the modified cellulose.

From what has been stated it is evident that a solution of cellulose will be rapidly hydrolyzed by the strong acid present. Samples which have not been diluted with water are no longer precipitated by water after twenty-four hours. Only about 80 per cent. of the material can be recovered, even if precipitation takes place within one hour.

We may conclude that dextrins of high rotation are absent from the first products of hydrolysis, because the substances not precipitated by water show a very low optical activity. For example, with 10.2 g. dry filter paper, about 7.9 g. were precipitated by water after being in solution for about one hour. The filtrate was concentrated under 35 mm. pressure, and most of the calcium removed by sulfuric acid. After diluting with water and concentrating again under diminished pressure, a solution was obtained which showed a rotation of +0.37° in a 2 dcm. tube, after the volume had been made up to 200 cc. This is about one-third of the rotation which would be produced by an equal amount of glucose.

Longer action of the strong acid solution results in the production of considerable amounts of glucose. A solution of eight grams of filter paper after four days produced no precipitate when poured into water. The greater part of the calcium chloride and acid was removed as described above, then the solution was neutralized with sodium carbonate and allowed to evaporate at room temperature to a moist cake. This was treated with absolute alcohol to precipitate the remaining salts, which were extracted several times with boiling 95 per cent. alcohol. After the removal of the alcohol the product was fermented with compressed yeast in a current of purified hydrogen. The carbon dioxide evolved weighed 1.120 grams, this being a yield of about 30 per cent. fermentable sugar, calculated as glucose. Glucose was isolated in large quantities as the osazone (m. p. 204° to 206°) and as the pentabenzoate (m. p. 179° after crystallization from alcohol). A fermentation experiment was successful when carried out without first removing the inorganic salts by means of alcohol, but the action was much slower.

The presence of the isomaltosazone of Fischer[1] was indicated by the fact that the saccharin liquors become brown during concentration if the temperature is allowed to rise much over 50°, and by the fact that an osazone was obtained which was soluble in hot water.[2]

Considerable amounts of furfural and a little acetic acid were obtained in the distillate collected during concentration under diminished pressure. If a solution of the cellulose in the acid mixture is heated for four hours to 100° in a pressure flask, about 44 per cent. of the material is converted into a black insoluble mass, of which about 10 per cent resembles the so-called humic acids in being soluble in 4 per cent. ammonia. The water-soluble portion of the original material consists of a mixture of organic acids not yet determined.

Solutions of Cellulose in the Mineral Acids.

In comparing the solubility of the modified celluloses obtained above with that of normal cellulose it is found that the former resemble the latter in being soluble in phosphoric acid, sulfuric acid, and nitric acid (sp. gr. 1.52). Independent observation was made of the fact recently announced[3] that phosphoric acid will dissolve cellulose even when strongly diluted with acetic acid.

Cellulose treated with a solution of chlorosulfonic acid in chloroform

---

[1] *Ber.*, **23**, 3687; **28**, 3024.

[2] Compare Storer, *Chem. Zentr.*, **1900**, II, 1069.

[3] Ger. Pat. 227,198 (1910).

is converted to a dark liquid which is rapidly decomposed by the moisture of the air. Arsenic acid dissolves cellulose slowly in the cold, but more readily on warming. Selenic acid dissolves a little cellulose on heating, which is reprecipitated when the concentrated acid is poured into water

Discussion.

The solution of cellulose by the solvents here presented is closely connected with some phenomena which have long been known. The specific attraction which cellulose possesses for certain metallic salts was noticed by Runge[1] and by Crum,[2] who observed that cotton which had been dipped into solutions of alum, ferric acetate, and similar salts was able to fix a portion of the metal within itself as hydrated oxide or basic salt. A part of the acid present in the salt is liberated in this way and exerts the effect which dilute acids in general produce when they dry upon cellulose.

Cellulose will even fix noteworthy quantities of copper, lead, titanium and mercury when immersed in dilute solutions of the salts of these metals.[3] In certain stronger solutions the adsorption compound of cellulose and salt swells up, yielding a product resembling mercerized fiber. This indicates either that the surface condition of the cellulose is altered by the adsorption of the salt, or that the latter is removed from solution in a hydrated form. This phenomenon was studied by Müller with a solution of basic lead acetate,[4] by Cross and Bevan with zinc chloride,[5] and by Hübner and Pope with solutions of potassium iodide, potassium-mercuric iodide, and barium-mercuric iodide.[6] This swelling is the first stage in the solution of the cellulose in the solvents here presented. It is simply one manifestation of that attraction between the cellulose and the salt plus water, which may finally bring the fiber into solution.

In addition to the many examples already given of solution of cellulose in the presence of acids it may be added that potassium thiocyanate, melted down with a few drops of water, will dissolve cellulose at 200°.[7] Solution in this case is effected in a solution which has an alkaline reaction. In all other cases studied solution took place in acid media.

Cross and Bevan have attempted to explain the solution of cellulose in the zinc chloride reagent by stating that the process is analogous to that involved in the formation of double salts.[8] Nevertheless no such compound has ever been isolated. The assumed "amphoteric character

---

[1] "Farbenchemie," Berlin, 1834; Schwalbe, "Die Chemie der Cellulose," p. 82.

[2] *Ann.*, **55**, 223 (1845).

[3] Schwalbe, *Loc. cit.*, **80**, 81.

[4] "Die Pflanzenfazer," p. 16.

[5] "Cellulose," p. 8.

[6] *J. Soc. Chem. Ind.*, 23, 401 (1904).

[7] Compare the conflicting statements in the literature: *Lpz. Färberztg.*, **55**, 19; Abstract, *Z. angew. Chem.*, **19**, 689 (1906); Schwalbe, *Loc. cit.*, p. 155.

[8] Cross and Bevan, "Cellulose," p. 14.

of the cellulose molecule" is still unproven, since it has its chief support in facts which may find an explanation as capillary phenomena. The idea has also been advanced that such solutions are due to the formation of alcoholates, but this theory is hardly admissible, since such compounds would be broken down by the strong acid employed. The most probable explanation for this class of cellulose solvents is, accordingly, the one first presented, which seeks to connect the process of solution in the reagents discussed with the phenomena of hydration and absorption in the presence of certain salts.

Summary.

It has been shown that cellulose in the form of filter-paper is soluble in concentrated aqueous solutions of certain salts, such as antimony trichloride, stannous chloride and zinc bromide. In solution in the aqueous hydrohalogen acids these salts and many others dissolve cellulose with extreme ease, as do also a few salts in formic acid and trichloroacetic acid.

The solution of the cellulose in these reagents is connected with facts previously known in a manner which may be summarized as follows:

Cellulose attracts metallic salts in solution to an extent depending on its mechanical structure and degree of hydration, on the nature and concentration of the salt, and on the temperature. This attractive force is opposed by that existing between the salt and its solvent, hence the final result is a distribution of the salt between the fiber and the solution. In concentrated solutions the attraction between the adsorption complex and the solvent may manifest itself in one of two ways, *viz.*: either the complex becomes hydrated, or else the reciprocal attraction of the solvent for the complex may bring the latter into solution. The latter effect obtains only where a high temperature is employed, or where some agent is present which, like certain dilute acids, can bring about union with water.

In support of the above view, it has been shown that cellulose modified by acids becomes soluble in certain reagents, such as an aqueous solution of calcium chloride, which are unable to dissolve cellulose not so modified. Chlorosulfonic, arsenic and selenic acids have been shown for the first time to possess the power of dissolving cellulose.

Celluloses dissolved in the acid solutions of the salts studied may be precipitated as amorphous compounds distinguished from the original material by their marked reducing properties and ease of hydrolysis. These substances have been described simply as modified celluloses until their relation to each other and to the so-called hydro- and hydralcelluloses can be determined.

One of the formates of cellulose has been studied with regard to the type of cellulose produced by its saponification by the agency of concentrated hydrochloric acid. Further action of this material converts the cellulose

into water-soluble products, and finally into glucose, but no evidence is at hand to show that the production of this sugar can be made quantitative.

The writer desires to reserve for a future paper the study of the reducing power, dyeing capacity, and hydrolysis of the celluloses precipitable from the reagents presented, in order to determin their relations to each other, to various other modified celluloses, and to the parent substance. A further study of the process of hydrolysis will be made to ascertain what substances are present in the final stage where glucose is produced. It is hoped that some of the reagents discussed may prove useful in separating and studying various modified celluloses.

CHEMICAL LABORATORY,
UNIVERSITY OF WISCONSIN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE ACTION OF SUBSTITUTED HYDRAZINES ON β-ORTHOTOLUQUINONE.

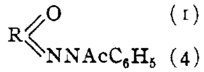
BY WILLIAM MCPHERSON AND CECIL BOORD.

Received July 3, 1911.

Notwithstanding the many investigations carried on with a view of determining the constitution of the hydroxyazo compounds and their derivatives, the question still remains an open one, except in the case of the acyl derivatives of the members of the para series.[1] These derivatives are prepared by the action of the acyl chlorides or the corresponding anhydrides on the parent hydroxyazo compounds. The problem to be solved in connection with their constitution resolves itself simply into one of determining whether the acyl group is joined to oxygen or to nitrogen as indicated in the two following formulas:

$$R\left\langle\begin{array}{ll}OAc & (1)\\ NNC_6H_5 & (4)\end{array}\right.$$

Formula I.



$$R\left\langle\begin{array}{ll}=O & (1)\\ NNAcC_6H_5 & (4)\end{array}\right.$$

Formula II.

That formula I correctly represents the constitution of these derivatives was proved by the preparation of compounds having the constitution expressed in formula II. These compounds represented by formula II, in which the acyl group is joined to nitrogen, proved to be not identical but isomeric with the acyl derivatives of the corresponding parahydroxyazo compounds; hence in the latter compounds the acyl group must be joined to oxygen as shown in formula I above. The compounds of the type represented by formula II were prepared by the action of the unsymmetrical acylphenylhydrazines on the paraquinones as represented in the following equation:

---

[1] McPherson, *Am. Chem. J.*, 22, 364; McPherson and Gore, *Ibid.*, 25, 485.