[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

THE COLORS PRODUCED BY RESORCINOL IN SOLUTIONS OF CERTAIN SALTS AND THE USE OF THESE COLORS AS A MEANS OF DETECTING RESORCINOL IN THE PRESENCE OF OTHER PHENOLS.

BY FRANCIS C. KRAUSKOPF AND GEORGE RITTER.

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Introduction.

It has been found that resorcinol in an ammoniacal solution with zinc salts produces a blue color. This has been used as a colorimetric determination of small quantities of zinc.[1]

In attempting to use this color reaction as a qualitative test for zinc it was found that cobalt, nickel and cadmium also produce characteristic colors. The color produced by cobalt is violet, that by nickel bluish violet, and that by cadmium blue. These colors being similar to that produced by zinc it was found to be impracticable to use this method as a qualitative test for zinc salts.

It was then thought that this color reaction might be used as a means of detecting resorcinol in the presence of other phenols. Since cobalt salts give the most intense coloration, these seemed the most suitable for the purpose.

Accordingly this study is divided into two parts: First, a determination of the conditions under which ammoniacal solutions of these salts and resorcinol will with regularity produce these characteristic colors, and the determination of whether or not other phenols will develop similar colors. Second, the use of these color reactions for the detection of resorcinol in the presence of other phenols.

Pieroni and Girardi[2] found that when a solution of pyrogallol in pyridine, mixed with a pyridine solution of a nickel salt, is diluted with water, various colors are produced, dependent on the relative amounts of nickel, pyrogallol, water and pyridine used. It was also found that salts of silver and mercury, when used in the place of the nickel salts, produced colors of a similar nature.

The authors considered these colors to be caused by the reduction, by means of the pyrogallol, of the salts to the metal in the colloidal state.

It seemed reasonable to suppose that the colors produced by the resorcinol were also due to the reduction of the salt to the metal in the colloidal state. This was confirmed by the fact that the color would not dialyze through parchment, and that the colloidal nature could be easily seen by means of the ultramicroscope.

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[1] Cerdan and De la Puente, *Anales Soc. espan. fis. quim.*, **2**, 98–108 (1913).

[2] *Kolloid Zeit.*, **15**, 159 (1914).

Part I. Experimental.

In order to determine the best conditions under which these characteristic colors develop, an attempt was made to answer the following questions:

Does the depth or shade of the color developed depend upon the salt of cobalt used?

Does the depth of color vary after a certain concentration of cobalt is reached?

Does the depth of color vary after a certain concentration of resorcinol is reached?

What concentration of ammonia is most favorable for the color development?

Knowing that an access of air influences the reaction, will the color develop most uniformly with total, partial, or non-exclusion of air?

What colors, if any, are produced by some of the other phenols?

Solutions Used.—(1) One per cent. solution of each of the following: resorcinol, pyrocatechin, hydroquinone, carbolic acid, pyrogallic acid.

(2) Solutions of cobalt chloride, cobalt nitrate, and cobalt sulfate, each containing 0.0004 g. of cobalt per cc.

(3) Ammonium hydroxide 0.90 sp. gr.

Test solutions as indicated below were prepared in Nessler tubes. These tubes were all of the same size and shape in order to make a fair comparison of the depth and shade of color. These tubes were immediately closed with rubber stoppers and inverted twice to thoroughly mix the liquids. They were then placed in a rack and allowed to stand until the color reaction became pronounced.

Experiment I.—Solutions were made up as follows:

Ammonium hydroxide, 4 cc., resorcinol solution, 1 cc., solution of cobalt sulfate, cobalt chloride, or cobalt nitrate, 1 cc., water to make 50 cc. Allowed to stand 3 hours.

The violet color obtained in all cases was of the same depth and shade, which shows that the various salts of cobalt used have the same effect on the reaction.

Experiment II.—Each solution contained:

Ammonium hydroxide, 4 cc., resorcinol 1 cc., varying amounts of cobalt chloride, water to make 50 cc. Allowed to stand 3 hours.

0.5 cc. of cobalt chloride produced a faint violet color; any amount between 1 cc. and 5 cc. produced the same shade and depth of violet color, which shows that nothing is to be gained by using more than 1 cc. of cobalt chloride solution.

Experiment III.—Each solution contained:

Resorcinol, 1 cc., cobalt chloride, 1 cc., varying amounts of ammonium hydroxide, water to make 50 cc. Allowed to stand 3 hours. Results are seen in Table I.

TABLE I.

NH_4OH.	1 cc.	2 cc.	3 cc.	4 cc.	5 cc.
Color . . .	brown ppt.	slight violet and brown ppt.	violet and brown ppt.	violet	violet

This shows that if less than 4 cc. of ammonium hydroxide is used with 1 cc. of cobalt chloride, cobalt hydroxide is precipitated and the color is to some extent indistinct. If more than 4 cc. is used the color is not deepened.

Experiment IV.—Solutions contained:

Ammonium hydroxide, 4 cc., cobalt chloride, 1 cc., varying amounts of resorcinol, water to 50 cc. Allowed to stand 3 hours. These results are found in Table II.

TABLE II.

Resorcinol, cc.	0.3	0.5	1	2
Color	faint violet	violet	deep violet	deep violet

This establishes the fact that 1 cc. of resorcinol gives the same results as a larger amount, but less than 1 cc. has a tendency to make the color thin and indistinct.

Experiment V.—Solutions contained:

Ammonium hydroxide, 4 cc., cobalt chloride, 1 cc., resorcinol, 1 cc., water to 100 cc. or to 115 cc.

In the case where the solution was made up to 100 cc., but 15 cc. of air was left above the solution. Where the solution was made up to 115 cc., air was completely excluded from the tube. This was accomplished by fitting a one-hole rubber stopper with a short glass tube drawn to a capillary at one end. By using this stopper some of the liquid was forced out through the capillary tube, thus excluding all air from the liquid. The tube was then sealed by placing the point of the capillary in a Bunsen flame. In order to obtain the same depth of color as in the solutions used before this, it was necessary to allow the tubes containing 100 cc. of solution and 15 cc. of air to stand five hours instead of three. In the tubes from which the air was completely excluded the colors produced were the most satisfactory as far as the shade was concerned. They were exact duplicates of one another in a given time, but the time required was increased from three hours, in the presence of air, to ten when air was excluded.

In cases where air was in contact with the solutions the beautiful violet color would change to a dull green and finally to a brownish black. An ammoniacal solution of resorcinol turns brown when in contact with air, so that this change to green and then to brown was no doubt caused by this color change of the resorcinol itself. However, when the solution was stoppered so as to exclude all air the violet color develops much more slowly, but after reaching a certain intensity retains the same color and depth of color for an indefinite time.

Experiment VI.—Solutions contained:

4 cc. of ammonium hydroxide, 1 cc. of cobalt chloride, 1 cc. of either carbolic acid, pyrocatechin, hydroquinone, or pyrogallic acid and water to 50 cc. Allowed to stand three hours.

The color produced by pyrocatechin, hydroquinone, or pyrogallic acid was brown. Carbolic acid produced no color.

Part II. Experimental.

Having thus become familiar with the characteristic colors of cobalt and resorcinol when solutions of the two are mixed, and with the conditions under which these color reactions best take place, it was thought that these reactions might be used as a means of detecting resorcinol in the presence of other phenols.

Test solutions similar to those shown in Experiments I to VI were prepared in Nessler tubes. At the beginning of each series of experiments a blank sample containing no resorcinol was run. This formed a basis for color comparison with samples containing resorcinol.

The samples in all cases were treated under the same conditions, and allowed to stand the same length of time before the reading was taken. After the sample was prepared, the Nessler tube was immediately closed with a rubber stopper, inverted twice to mix liquids, and then placed into a rack until the color developed. The amounts of each compound per sample and the results are shown in Tables III to V inclusive.

TABLE III.

H_2O. Cc.	Res. Cc.	Pyrocatechin. Cc.	Color.	H_2O. Cc.	Res. Cc.	Pyrocatechin. Cc.	Color.
50	..	1	brown	100	..	1	brown
50	1	1	cherry	100	1	1	cherry
50	1	2	reddish brown	100	1	2	brown
50	1	3	brown	100	1	2	brown

TABLE IV.

H_2O. Cc.	Res. Cc.	Hydroquinone. Cc.	Color.
50	..	1	brown
50	1	1	brown
100	1	1	brown

TABLE V.

H_2O. Cc.	Res. Cc.	Pyrogallic acid. Cc.	Color.
50	..	1	brown
50	1	1	brown
100	1	1	brown

Each test solution in Tables III, IV and V contained in addition 1 cc. of cobalt chloride and 4 cc. of ammonium hydroxide.

These tables show that the presence of hydroquinone, pyrocatechin or pyrogallic acid either prevents the development of the violet color produced by resorcinol alone, or the violet color is completely obscured by the brown color which is produced by the hydroquinone, pyrocatechin, or pyrogallic acid. Since the brown color caused by these phenols appears only when air is in contact with the solution, several solutions similar to the above were prepared with the tubes completely sealed from the air. In these neither the violet color of the resorcinol nor the brown color of the other phenols appeared even on long standing.

With carbolic acid and resorcinol present the solutions developed no color, even when in contact with air. This would indicate that the presence of the other phenols had an inhibiting effect upon the development of the violet color of resorcinol.

It is also shown that in the presence of these other phenols, resorcinol cannot be detected by this method.

Having found that resorcinol cannot be detected by the method indicated in Tables III to V, an attempt was made to produce colors by which it might be done. It was discovered that by decreasing the amount of ammonium hydroxide and adding a few cubic centimeters of alcohol to a test sample containing resorcinol, allowing it to stand about three minutes, and then shaking, a dark green color is produced.

The reaction of carbolic acid treated in this manner gives a colorless solution. Pyrocatechin, hydroquinone, and pyrogallic acid, when present in considerable amounts, develop a brown color.

Solutions similar to those shown in Tables III to V were prepared in Nessler tubes, only that the amount of ammonium hydroxide was decreased and a few cubic centimeters of alcohol were added. The tubes containing these test solutions were immediately closed with a rubber stopper, and after being allowed to stand from three to five minutes, were vigorously shaken.

The portion of each ingredient per sample and the results are shown in Tables VI to IX.

TABLE VI.

Res. Cc.	Pyrocatechin. Cc.	Color.	Res. Cc.	Pyrocatechin. Cc.	Color.
..	1	brown	1	10	dark green
1	1	dark green	1	20	dark green
1	4	dark green	0.5	20	brownish green

Table VI shows that in 50 cc. of solution, 0.005 g. of resorcinol can be detected in the presence of 0.220 g. of pyrocatechin.

TABLE VII.

Res. Cc.	Hydroquinone. Cc.	Color.
..	1	brown
1	1	dark green
1	10	green
1	20	brownish green

TABLE VIII.

Res. Cc.	Carbolic acid. Cc.	Color.
..	1	colorless
1	1	greenish yellow
1	10	greenish yellow
1	20	greenish yellow
1	30	yellow tinge

TABLE IX.

Res. Cc.	Pyrogallic acid. Cc.	Color.
..	1	brown
1	1	cherry
1	8	cherry
1	20	slightly cherry

Besides the contents shown in the tables, each test solution contained

1 cc. cobalt chloride, 0.3 cc. ammonium hydroxide,[1] 3 cc. of 95% alcohol, and water to make 50 cc.

Table VII shows that in 50 cc. of solution, 0.010 g. of resorcinol can be detected in the presence of 0.200 g. of hydroquinone.

Table VIII shows that in 50 cc of solution, 0.005 g. of resorcinol can be detected in the presence of 0.300 g. of carbolic acid.

Table IX shows that in 50 cc. of solution, 0.010 g. of resorcinol can be detected in presence of 0.200 g. of pyrogallic acid.

Summary.

(1) Resorcinol in an ammoniacal solution of cobalt salts produces a color distinct from that produced by the other phenols tried.

(2) The best conditons for uniformity of this color development have been determined.

(3) The exclusion of the air from the test solution increases the length of time required for color development.

(4) The presence of certain other phenols either inhibit the formation of the resorcinol color, or else obscure it by the colors they themselves produce. Consequently, resorcinol cannot with certainty be detected with an ammoniacal solution of cobalt by the method indicated in Tables III to V, if these other phenols are present.

(5) Resorcinol as low as 0.001 g. per 50 cc. sample, if shaken with a weak ammoniacal solution of a cobalt salt and a few cubic centimeters of alcohol, develops a dark green color. Pyrocatechin, hydroquinone, and pyrogallic acid under same conditions develop a brown color, carbolic acid produces a colorless solution.

(6) The presence of the other phenols tried does not prevent the formation of the dark green color developed by resorcinol. Thus small amounts of resorcinol can be detected in the presence of comparatively large amounts of certain other phenols.

MADISON, WIS.

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

PREPARATION OF BROMOACETYLGLUCOSE AND CERTAIN OTHER BROMOACETYL SUGARS.

BY J. K. DALE.

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In a recent article[2] E. Fischer published a method for the preparation of bromoacetylglucose which consisted essentially in the action of a saturated solution of hydrobromic acid gas in glacial acetic acid upon glucose pentacetate. Since bromoacetylglucose is an important compound, serving as the basis for the synthesis of many derivatives of glucose, it does not

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[1] In Table IX the amount of ammonium hydroxide was 2 cc. for each test solution.

[2] *Ber.*, 49, 584 (1916).