*Color Reactions of 3-Methyl-2-benzothiazolone Hydrazone with Phenol Derivatives. I. The Spectrophotometric Microdetermination of Catechol, Hydroquinone and Resorcinol**

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(Received May 27, 1964)

Since Hünig and Fritsch[1] described the oxidative coupling of 3-methyl-2-benzothiazolone hydrazone (MBTH) with various organic compounds, MBTH has been used to detect and determine trace amounts of various types of organic compounds.[2-5]

In the present paper new spectrophotometric procedures for the determination of catechol, hydroquinone and resorcinol with MBTH will be reported.**

Experimental

Reagents.—*Standard Solutions of Catechol, Hydroquinone and Resorcinol (5 μg./ml.)*.—Prepared freshly daily.

3-Methyl-2-benzothiazolone Hydrazone Hydrochloride.—The reagent is commercially available. A 0.4% aqueous solution and a 0.5% methanol solution of the salt were prepared.

Oxidants.—a) 1% (w/v) Ferric Chloride Solution. b) 2% (w/v) Potassium Ferricyanide Solution. — Prepared freshly daily.

Other Reagents.—Methanol. Acetone. Concentrated ammonia. (0.7+100) Ammonia. 8 N Hydrochloric Acid. 10 % Mohr's Salt Solution.—Prepared within 10 min. before use.

Apparatus. — Beckman Model DK-II and DU spectrophotometers. Hitachi ESP-2 spectrophotometer. Coleman Model 14 spectrophotometer.

Results and Discussion

Preliminary Experiments. — The sensitivities and selectivities of the color reactions of catechol, hydroquinone and resorcinol with MBTH are largely dependent on the hydrogen ion concentration and on the conditions of oxidation.

In an ammoniacal medium (pH ~11.5) catechol gives a pink color with MBTH, dissolved oxygen acting as an oxidant for the oxidative coupling. In the same medium, hydroquinone gives a blue color, which fades into brown within 2 min. However, this blue color can be stabilized a further 3 min. by acetone. Resorcinol gives only a weak yellow color under these conditions, and its absorbance is negligibly low at the λ max. of the blue color obtained from hydroquinone.

In a weakly alkaline medium (pH 8~9), catechol, hydroquinone and resorcinol give a red or orange color with MBTH in the presence of ferricyanide. In this condition reproducible results are obtained only for resorcinol.

In the acidic ferric-ferrous redox buffer, catechol gives a violet color with MBTH. Under the same conditions hydroquinone and resorcinol give a weak red or orange color. Thus the medium is more selective for catechol than the ammoniacal medium.

In a higher hydrochloric acid solution (~1.2 N), catechol, hydroquinone and resorcinol give a red or orange color with MBTH in the presence of ferric chloride. These conditions are favorable for the determination of hydroquinone and resorcinol in a mixture of the two.

Taking these results and others into consideration, the following procedures have been elaborated:

TABLE I. SPECTROPHOTOMETRIC DETERMINATION OF DIHYDROXYBENZENE

Dihydroxybenzene	λ_{max} mμ	$\varepsilon\times10^{-4}$	Color	Procedure
Catechol	510	2.8	Pink	1a
Catechol	550	2.4	Vioelt	1b
Hydroquinone	610	1.5	Blue	2
Resorcinol	495	5.2	Orange	4
Resorcinol	515	2.9	Orange	3

Recommended Procedures and The Effect of Various Factors

1) The Determination of Catechol.—a) In an Ammoniacal Medium. — To 2 ml. of a test

* A part of this paper was presented at the 14th Annual Meeting of the Chemical Society of Japan, Kyoto, 1961.

1) S. Hünig and K. H. Fritsch, *Ann.*, **609**, 143 (1957).
2) E. Sawicki, T. R. Hauser, T. W. Stanley and W. Elbert, *Anal. Chem.*, **33**, 93 (1961).
3) E. Sawicki, T. W. Stanley, T. R. Hauser, W. Elbert and J. L. Noe, ibid., **22**, 722 (1961).
4) E. Sawicki, T. R. Hauser, T. W. Stanley, W. Elbert and F. T. Fox, ibid., **33**, 1574 (1961).
5) E. Sawicki, T. W. Stanley, T. R. Hauser and S. McPherson, *Chemist-Analyst*, **50**, 68 (1961).

** Studies of the reaction mechanism of catechol, hydroquinone and resorcinol with MBTH are in progress. Applications of MBTH to the analysis of phenol derivatives will be published elsewhere.

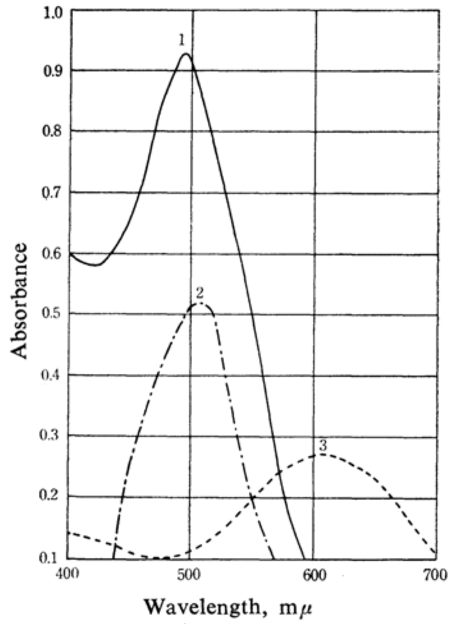

Fig. 1. Visible absorption spectra obtained in determination of catechol, hydroquinone and resorcinol in alkaline solution. 1. Resorcinol, 20 μg. (Procedure 4). 2. Catechol, 20 μg. (Procedure 1a). 3. Hydroquinone, 20 μg. (Procedure 2).

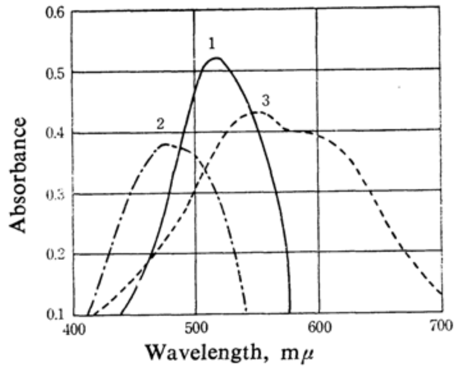

Fig. 2. Visible absorption spectra obtained in determination of catechol, hydroquinone and resorcinol in acid solution. 1. Resorcinol, 20 μg. (Procedure 3). 2. Hydroquinone, 20 μg. (Procedure 3). 3. Catechol, 20 μg. (Procedure 1b).

solution 4 ml. of a 0.5% MBTH methanol solution is added, and then 2 ml. of methanol and 2 ml. of concentrated ammonia. After the mixture has stood for 15 min., the absorbance is read at the wavelength of 510 mμ.

The Effect of Various Factors. — The absorbance reaches a maximum from 10 to 12 min. after the addition of ammonia. Very little change in the absorbance is noticed for a further 30 min. upon the addition of 2∼3 ml. of concentrated ammonia. A lesser amount of concentrated ammonia is not sufficient to stabilize the product, and a decrease in the absorbance is observed after 25 min. upon the addition of 1 ml. of concentrated ammonia. The best results are obtainable with an MBTH hydrochloride concentration more than 0.2%. Beer's law is obeyed from 0 to 10 μg. of catechol. The molar absorptivity is 2.8×10^4 (Table I). The absorption spectrum is given in Fig. 1.

Derivatives of catechol give rise to a pink color. Hydroquinone and its derivatives and *p*-benzoquinone give rise to a brown color. The presence of less resorcinol than the equivalent amount of catechol does not interfere with the determination of catechol.

b) In the Medium of a Ferric-ferrous Salts Solution.—To 4 ml. of a test solution 2 ml. of a 0.4% MBTH aqueous solution is added, and then 1.6 ml. of a 10% Mohr's salt solution and 0.4 ml. of a 1% ferric chloride solution. After the mixture has stood for 5 min., 2 ml. of a acetone is added. The absorbance is read at the wavelength of 550 mμ within 30 min.

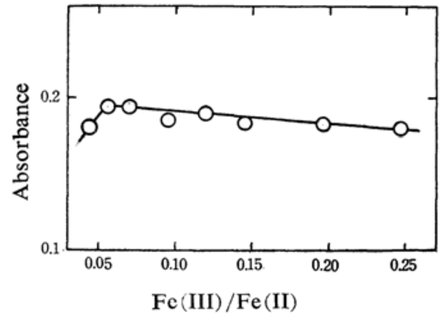

Fig. 3. Effect of Fe(III)/Fe(II) ratio on absorbance in procedure 1b. Catechol, 5 μg.

The Effect of Various Factors.—The absorbance reaches a maximum 4min. after the addition of the ferric chloride solution, and very little change in the absorbance is noticed for the next 6 min. The color is further stabilized for more than 30 min. by acetone. Best results are obtainable with a ratio Fe(III)/Fe(II) of about 0.06 (Fig. 3). The concentration of MBTH hydrochloride must be controlled below 0.1%; otherwise a turbid solution is obtained. The pH of the solution after the addition of all reagents is 3.0. At higher pH values the absorbance decreases and ferric hydroxide precipitates.

At lower pH values (pH 1∼2) the violet color turns pink. In a solution containing ferric ions but not ferrous ions, catechol instantaneously gives a violet color with MBTH, and this color rapidly turns dark brown. In these two cases the reaction is no

TABLE II. DETERMINATION OF HYDROQUINONE AND RESORCINOL IN THE PRESENCE OF EACH OTHER

Hydroquinone, added μg.	Resorcinol, added μg.	Absorbance at 510 mμ	Net absorbance for resorcinol*	Calculated absorbance for resorcinol**	Recovery of resorcinol %
2.5	2.5	0.175	0.115	0.110	105
5.0	2.5	0.235	0.115	0.110	105
10	2.5	0.350	0.110	0.110	100
2.5	5.0	0.285	0.225	0.220	102
5.0	5.0	0.345	0.225	0.220	102
10	5.0	0.455	0.215	0.220	98

* Calculated from the following equation: Absorbance at 510 mμ $-0.024\times$ μg. of hydroquinone.
** Calculated from the calibration curve for resorcinol constructed by procedure 3.

longer selective for catechol, the sensitivities of the reaction of hydroquinone and resorcinol being comparable with that of catechol.

Beer's law is obeyed from 0 to 15 μg. of catechol. The molar absorptivity is 2.4×10^4 (Table I). The absorption spectrum is given in Fig. 2.

The presence of 2 μg. of hydroquinone or 5 μg. of resorcinol does not interfere with the determination of catechol. Derivatives of catechol give rise to a violet or blue color.

2) The Determination of Hydroquinone.—To 3 ml. of a test solution 3 ml. of a 0.5% MBTH methanol solution is added, and then 1 ml. of concentrated ammonia. After 1 min. 3 ml. of acetone is added to the solution. The absorbance is read at the wavelength of 610 mμ within 3 min.

The Effect of Various Factors. — The maximum absorbance is reached 40 sec. after the addition of ammonia, and very little change in the absorbance is noticed for the next 50 sec. The color is further stabilized for 3 min. by acetone. Acetone takes part also in making the solution clear. The absorbance is depressed in a methanol concentration more than 30%(v/v). Best results are obtainable with a 0.15% MBTH hydrochloride concentration and the addition of 1 or 2 ml. of ammonia. An increase or decrease in the concentration of MBTH or ammonia results in a decrease in the absorbance. Beer's law is obeyed from 0 to 10 μg. of hydroquinone. The molar absorptivity is 1.5×10^4 (Table I). The absorption spectrum is given in Fig. 1.

Catechol interferes with the reaction between hydroquinone and MBTH. Derivatives of hydroquinone and *p*-benzoquinone give rise to a blue color. The presence of resorcinol up to 100 μg. does not interfere with the determination of hydroquinone.

3) The Determination of Hydroquinone and Resorcinol in a Mixture of the Two. — To 4.5 ml. of a test solution 3 ml. of a 0.4% MBTH aqueous solution is added, and then 1.5 ml. of 8 N hydrochloric acid and 1 ml. of a 1% ferric chloride solution. Then the solution is heated for 2 min. in a water bath at 80°C. The solution is cooled in running tap water. Using a reagent blank as reference, the absorbance is read within 30 min. at the wavelength of 510 mμ, which corresponds to the sum of hydroquinone and resorcinol.

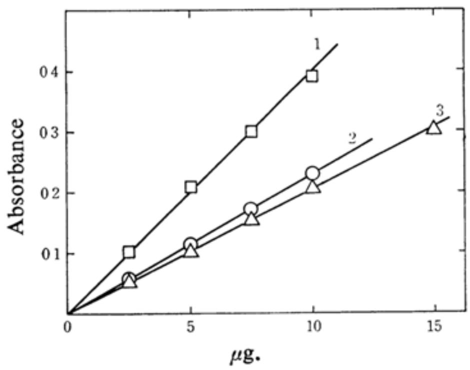

Fig. 4. Calibration curves for hydroquinone and resorcinol. 1. Resorcinol at 510 mμ (Procedure 3). 2. Hydroquinone at 510 mμ (Procedure 3). 3. Hydroquinone at 610 mμ (Procedure 2).

Refering to the content of hydroquinone previously determined by procedure 2 and to standard curves for resorcinol and hydroquinone constructed by this procedure (Fig. 4), the amount of resorcinol in mixtures with hydrquinone can be calculated by the following equation:

$$\mu\text{g. of resorcinol} = (\text{absorbance at 510 m}\mu - 0.024\times\mu\text{g. of hydroquinone})\times22.7$$

The Effect of Various Factors. — At room temperature the absorbance increases gradually, reaches a maximum, and decreases. After two minutes' heating in a water bath at 80°C, the reaction proceeds to completion, and no further change in absorbance is observed, even after the solution has stood for 30 min. at room temperature. The optimum range of the hydrochloric acid concentration is from 1.0 to 1.6 N for resorcinol and about 1.2 N for hydroquinone

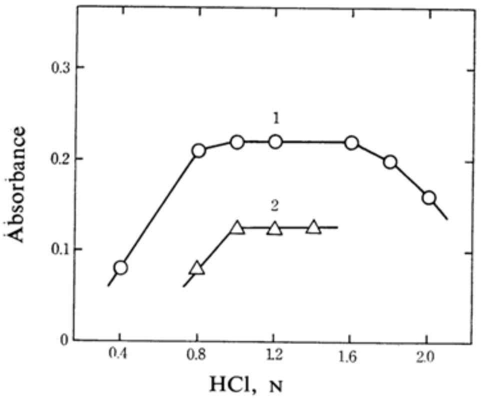

Fig. 5. Effect of acidity on absorbance in procedure 3. 1. Resorcinol, 5 μg. 2. Hydroquinone, 5 μg.

hydroquinone (Fig. 5). The optimum concentration of ferric chloride is from 0.10 to 0.14%. Best results are obtainable with an MBTH hydrochloride concentration more than 0.10%. Beer's law is obeyed from 0 to 7.5 μg. for resorcinol and from 0 to 10 μg. for hydroquinone. The molar absorptivity for resorcinol is 2.9×10^4 (Table I). Absorption spectra are given in Fig. 2.

Derivatives of dihydroxybenzene such as catechol give rise to an orange or red color.

Results of the recovery test for resorcinol in mixtures with hydroquinone are given in Table II. As is shown in the last column of the same table, the recoveries of resorcinol are from 98 to 105%.

4) The Determination of Resorcinol. — To 3 ml. of a test solution 0.5 ml. of a 0.5% MBTH

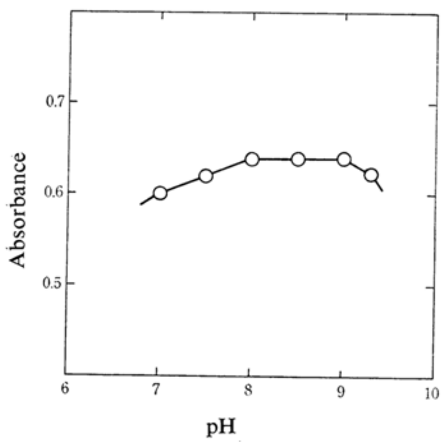

Fig. 6. Effect of pH on absorbance in procedure 4. Resorcinol, 10 μg.

methanol solution is added, and then 4.5 ml. of methanol, 1 ml. of (0.7+100) ammonia and 1 ml. of a 2% ferricyanide solution. The pH of the solution must be 8∼9. The absorbance is read at the wavelength of 490 mμ within 30 min.

The Effect of Various Factors.—The absorbance reaches a maximum a few minutes after the addition of the ferricyanide solution. Very little change in the absorbance is noticed for the next 30 min. The optimum range of the MBTH hydrochloride concentration is from 0.02 to 0.03% in the methanol concentration of about 50%(v/v). A turbid solution is obtained with a higher MBTH concentration. The optimum pH range is from 8 to 9 (Fig. 6). The use of an ammonia - ammonium chloride buffer is not recommended, the absorbance being depressed in the buffer. The concentration of potassium ferricyanide should be kept very close to 0.02%; otherwise precipitation occurs. Beer's law is obeyed from 0 to 10 μg. of resorcinol. The molar absorptivity is 5.2×10^4 (Table I). The absorption spectrum is given in Fig. 1.

Phenol derivatives give reddish colors.

Summary

New spectrophotometric procedures for determining microgram amounts of catechol, hydroquinone and resorcinol with MBTH have been described. The sensitivities and selectivities of the reactions are largely dependent on the pH and on the conditions of oxidation: 1) In an ammoniacal medium MBTH gives a stable pink color with catechol and, with hydroquinone, a blue color which is stabilized by acetone. Resorcinol gives only a faint color under these conditions. 2) When ferricyanide is used as an oxidant in a weakly alkaline solution, MBTH gives a sensitive orange color with resorcinol. 3) In an acidic ferric-ferrous redox buffer, MBTH gives a violet color with catechol. At pH 3 the reaction is selective for catechol. 4) Ferric chloride in 1.2 N hydrochloric acid is favorable for the determination of hydroquinone and resorcinol in a mixture of the two.

We are grateful to Professor Motoharu Tanaka for his invaluable advice and criticism.

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