

value analytically. More rigorous treatment removes the fatty acids from pretreated starch but not from corn amylose itself.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF ORTHO-CRESOLBENZEIN

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In connection with the study being made at Cornell University of the absorption spectra of the pht haleins, the sulfonepht haleins and other triphenylmethane derivatives, it seemed desirable to study the absorption spectra of the benzeins from which the pht haleins and sulfonepht haleins are derived. The absorption of benzaurin (phenolbenzein)^{2a,2c} and a study of *o*-cresolbenzein^{2b} have already been reported.

A complete description of the apparatus and method employed in studying the visible and ultraviolet absorption of a substance is to be found in the earlier paper on benzaurin.^{2a}

When the red-orange crystals of pure *o*-cresolbenzein are dissolved in cold, absolute ethanol, a yellow-orange solution is formed. Several hours are necessary in order to obtain complete solution of the material, and the absorption of this solution is given by Curve *B* in Fig. 1. A week later, and still four months later the solution which had stood in a darkened room gave absorption curves exactly coincident with Curve *B*. Curve *A*, Fig. 1, shows the very similar absorption obtained with the alcoholic solution of benzaurin after the solution had stood ten days and was found to be at equilibrium.

The absorption of fresh alcoholic solutions of fuchson and aurin^{2c} is of an entirely different type from that given by these solutions after they have faded on standing for varying intervals of time. In the fresh solution of these substances absorption is characteristic of the substance in the quinoid state, while the faded solution represents absorption due to the presence of both the quinoid hydrate and carbinol forms of the substance. With benzaurin^{2c} the same change in absorption was found, although the fading proceeded with such great rapidity that it was possible to obtain the absorption characteristic of the fresh solution only by making observations as soon as the substance was entirely dissolved. Even then

¹ From a dissertation presented to the Faculty of the Graduate School of Cornell University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, by S. Alice McNulty, Holder of the Grasselli Fellowship in Chemistry at Cornell University, 1923-1924.

² (a) Orndorff, Gibbs and McNulty, *THIS JOURNAL*, **47**, 2767 (1925). (b) Orndorff and McNulty, *ibid.*, **49**, 992 (1927). (c) Orndorff, Gibbs, McNulty and Shapiro, *ibid.*, **49**, 1545 (1927).

the intensity of some of the absorption bands had decreased considerably. With *o*-cresolbenzein any fading must have occurred immediately, since after obtaining complete solution of the substance in alcohol, no change whatever occurred in the absorption of that solution on standing. Therefore, in view of the close correspondence between the absorption curves for benzaurin and *o*-cresolbenzein (Curves *A* and *B*, Fig. 1) it seems justifiable to assume that the *o*-cresolbenzein exists in alcoholic solution as an equilibrium mixture of the quinoid hydrate and carbinol forms.

The addition of alcohol containing dry hydrogen chloride to the alcoholic solution of *o*-cresolbenzein produces a red-orange color, the solution being quite red in thin layers. The absorption of this solution is entirely different from that of *o*-cresolbenzein in neutral ethanol. Curve *A*, Fig. 2,

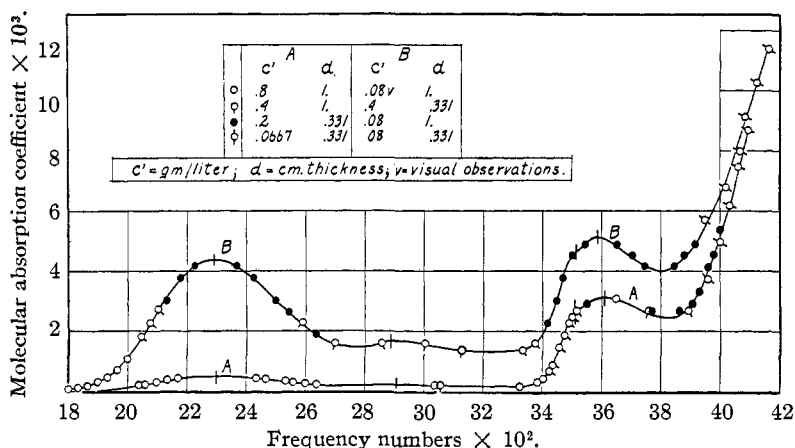


Fig. 1.—*A*, benzaurin in neutral absolute ethanol solution (faded). *B*, *o*-cresolbenzein in neutral absolute ethanol solution.

shows the effect of adding 17,100 molecules of hydrogen chloride to one of *o*-cresolbenzein in absolute ethanol. The bands located at frequency numbers 1940, 2465, 3365 and 3656 are well defined. The addition of smaller amounts of hydrogen chloride does not bring out the shoulder at 3365, and all other bands are of less intensity. Increasing the concentration of hydrogen chloride to more than 17,100 molecules serves only to increase the intensity of all the bands that were present in the solution containing 17,100 molecules of hydrogen chloride, except the shoulder in the vicinity of 3365. The change in absorption produced by the addition of hydrogen chloride is probably due to the formation of the hydrochloride of *o*-cresolbenzein, a study of which appears in an earlier paper.^{2b} It is thought that the addition of the acid causes the carbinol to go over to the quinoid hydrate, which then splits off water and forms the colored quinoid hydrochloride of *o*-cresolbenzein.

When the solution used for Curve *A* was allowed to stand for a week it became colorless, and Curve *B* represents its absorption. There are now five bands in the ultraviolet at 3282, 3457, 3561, 3690 and 3782. This curve bears a close resemblance to that for di-*p*-dihydroxytriphenylmethane, which shows five bands at 3465, 3571, 3690, 3782 and 3877. The change of the colored alcoholic acid solution to a colorless one is probably due to the reducing action of alcohol and hydrochloric acid on *o*-cresolbenzein and possibly to even further action in the formation of the diethyl ether of the reduction product of *o*-cresolbenzein. Since the introduction of the methyl group into a compound does not change the general type of absorption curve and because of the similarity between Curve *B* and that for the reduction product of benaurin, Curve

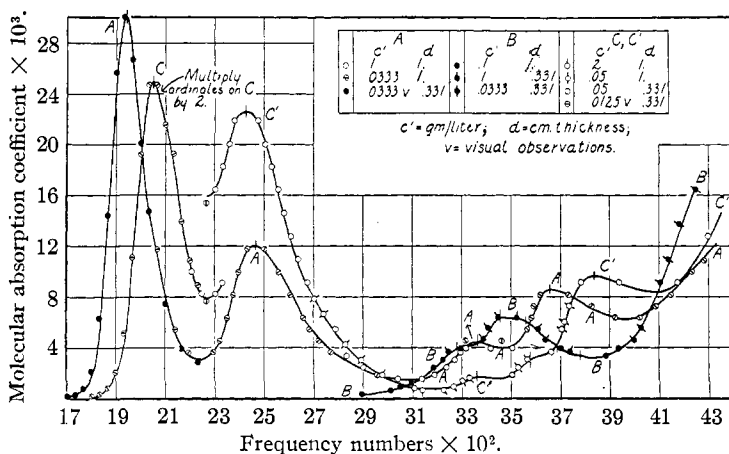


Fig. 2.—*A*, *o*-cresolbenzein in alcoholic HCl solution; 1 mole:17,100 moles of HCl. *B*, solution *A* after standing for one week. *C, C'*, *o*-cresolbenzein in concd. (93%) sulfuric acid.

B seems to indicate the presence of the reduction product of *o*-cresolbenzein, the diethyl ether of this reduction product or possibly a mixture of these two substances. The curves obtained for the colored and colorless alcoholic solutions of benaurin^{2a} in the presence of hydrochloric acid are very similar to the corresponding curves for *o*-cresolbenzein.

Curve *C, C'* (Fig. 2) shows the absorption for the orange solution of *o*-cresolbenzein in 93% sulfuric acid. This curve probably represents absorption due to the presence of the sulfate of *o*-cresolbenzein, a study of which occurs in an earlier paper,^{2b} just as Curve *A* represents that due to the hydrochloride. The band at 2050 is entirely in the visible region, while the four others are in the ultraviolet at 2425, 3362, 3577 and 3836. The bands at 2050 and 2425 are considerably more intense than the corresponding bands in Curve *A*, due probably to the more complete conversion

of the *o*-cresolbenzein into the sulfate in concd. sulfuric acid. A similar curve is found for benzaurin in 93% sulfuric acid. It has been noted^{2c} that the bands for fuchson, benzaurin and aurin in concd. sulfuric acid uniformly follow Hartley's law, that is, with increasing molecular weight there is a steady shifting of the bands toward the red. In general the bands for *o*-cresolbenzein also fit well into this scheme, being shifted slightly nearer the red region than those for benzaurin, due to the two methyl groups in *o*-cresolbenzein. In fact, this close analogy between most of the well pronounced bands for benzaurin and *o*-cresolbenzein is to be noted in all the solvents studied (Fig. 4).

In Fig. 3 the absorption curves are given for *o*-cresolbenzein in alkaline solutions. When an alcoholic potassium hydroxide solution is added

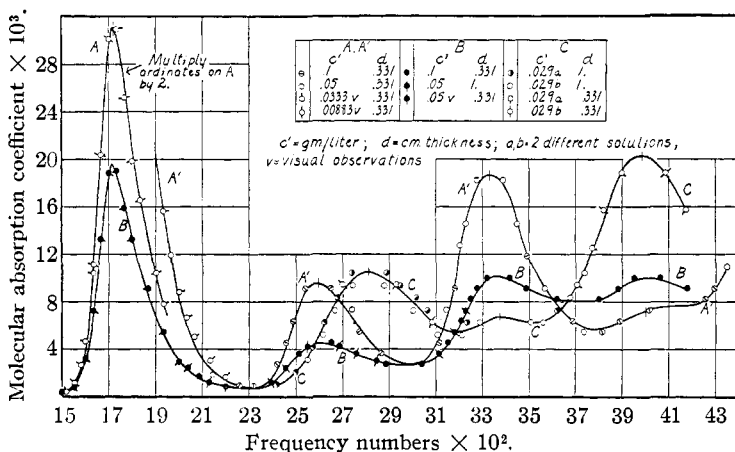


Fig. 3.—*A, A'*, *o*-cresolbenzein in alcoholic KOH solution; 1 mole:30 moles of KOH. *B*, solution *A, A'* after standing one week. *C*, *o*-cresolbenzein in aqueous 33% KOH solution.

to *o*-cresolbenzein dissolved in absolute ethanol, a violet-red solution forms. The absorption of such a solution is represented by Curve *A, A'*, and it is to be noted that the type of curve is similar to that in which acid was added to the alcoholic solution of the benzein. It is believed that in both cases the change is due to the conversion of the carbinol to the quinoid hydrate which then forms either the quinoid potassium salt by loss of water in the presence of potassium hydroxide, or an acid salt of *o*-cresolbenzein when an acid is present. The bands are located at 1720 in the visible region, and in the ultraviolet at 2595, 3330 and 4000. In a similar alcoholic alkaline solution benzaurin also showed four bands at 1765, 2640, 3380 and 4005.^{2a}

After the solution used in *A, A'* had stood for a week it became much lighter in color, and gave the absorption represented by Curve *B*. In

general, this curve shows decreased absorption except at 4000, where the band increases in intensity and becomes more definitely developed. The absorption of a colorless solution of *o*-cresolbenzein in 33% aqueous potassium hydroxide is given in Curve C, in which case absorption is most probably due to the presence of the colorless dipotassium salt of the carbinol form. The bands are located at 2810, 3373 and 3985, while those for benzaurin are at 2900, 3380 and 4050. Examination of the curves in Fig. 3 seems to indicate that the cause of the fading in the case of the colored alcoholic alkaline solution after standing for one week is the partial

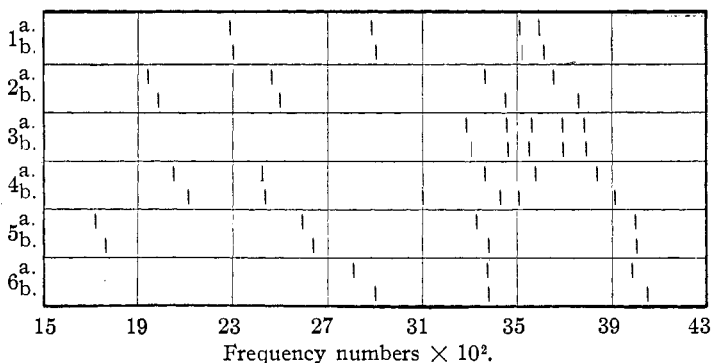


Fig. 4.—Frequency numbers of bands in various solutions of *o*-cresolbenzein and benzaurin (See Table I).

transformation into this dipotassium salt of the carbinol. Curve C is of the same type as that of *o*-cresolbenzein dissolved in absolute ethanol. This similarity supports to some degree the supposition that in an alcoholic solution some of the *o*-cresolbenzein is present in the carbinol form.

Fig. 4 summarizes in graphic form the relative positions of the bands for *o*-cresolbenzein and benzaurin in similar solvents and, together with Table I, brings out the agreement with Hartley's law.

TABLE I
FREQUENCY NUMBERS OF ABSORPTION BANDS

1. In neutral absolute ethanol					
a.	<i>o</i> -Cresolbenzein.....	2290	2886	3511	3592
b.	Benzaurin (faded soln.).....	2300	2902	3520	3613
2. In alcoholic hydrochloric acid					
a.	<i>o</i> -Cresolbenzein (1 mole):17,100 moles of HCl.....	1940	2465	3365	3656
b.	Benzaurin (1 mole):17,400 moles of HCl.....	1985	2500	3450	3760 approx.
3. Same solutions one week later					
a.	<i>o</i> -Cresolbenzein.....	3282	3457	3561	3690 3782
b.	Benzaurin.....	3308	3463	3549	3693 3788

TABLE I (Concluded)
4. In 93% sulfuric acid

a. <i>o</i> -Cresolbenzein.....	2050	2425	3362	3577	3836
b. Benzaurin.....	2112	2437	3430	3507 ^a	3910

5. In alcoholic potassium hydroxide

a. <i>o</i> -Cresolbenzein (1 mole):30 moles of KOH.....	1720	2595	3330	4000
b. Benzaurin (1 mole):60 moles of KOH.....	1765	2640	3380	4005

6. In 33% aqueous potassium hydroxide

a. <i>o</i> -Cresolbenzein.....	2810	3373	3985
b. Benzaurin.....	2900	3380	4050

^a The existence of this band is somewhat doubtful.

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Summary

1. Curves showing the absorption spectra of solutions of *o*-cresolbenzein in neutral absolute ethanol, alcoholic hydrogen chloride, alcoholic potassium hydroxide, 93% sulfuric acid and 33% aqueous potassium hydroxide have been prepared and discussed.

2. The probability has been suggested that the absorption spectra of *o*-cresolbenzein in neutral absolute ethanol is due to the presence of an equilibrium mixture of the quinoid hydrate and carbinol forms of the benzein; in acid solutions to a hydrochloride or sulfate of *o*-cresolbenzein; in the colored alkaline solution to the quinoid potassium salt of *o*-cresolbenzein; and in strongly alkaline solution (33%) to the dipotassium salt of the carbinol.

3. A chart showing the position of maximum absorption expressed in frequency numbers for all the bands in the solutions studied, together with corresponding data for benzaurin, has been prepared.

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