

The following table gives the composition of mixtures for P_H values from 5.2 to 6.8, as taken from a curve constructed from several titrations with a quinhydrone electrode against a saturated calomel cell at 25°.

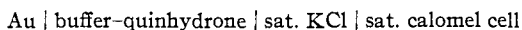
TABLE I

COMPOSITIONS OF MIXTURES (TAKEN FROM CURVE)

Fifty cc. of $N/5$ sodium hydrogen maleate in each case; diluted to 200 cc.

P_H	5.2	5.4	5.6	5.8	6.0	6.2	6.4	6.6	6.8
$N/5$ NaOH, cc.	7.2	10.5	15.3	20.8	26.9	33.0	38.0	41.6	44.4

The base was added from a buret to a maleate solution containing 0.109 g. of quinhydrone. The region of each titration was small, so that the total volume could be kept within limits of 100 ± 3 cc. Potentiometric measurements of the cell



were used for calculation of P_H according to the usual method,² ignoring salt effect and contact potentials. Results from several titrations over different regions, comprising twenty-five measurements, were united into a single curve, from which the above figures were interpolated.

CONTRIBUTION NO. 570 FROM THE
DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

J. W. TEMPLE

RECEIVED FEBRUARY 26, 1929
PUBLISHED JUNE 5, 1929

[CONTRIBUTION FROM THE ROCKEFELLER PHYSICAL AND BAKER CHEMICAL
LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF SOME PHTHALEINS OF THE TRIHYDROXYPHENOLS¹

BY R. C. GIBBS AND C. V. SHAPIRO²

RECEIVED AUGUST 27, 1928

PUBLISHED JUNE 5, 1929

In several previous papers data have been presented on the absorption spectra of the benzeins and phthaleins derived from some of the mono- and dihydroxybenzenes, for example, phenol,³ *o*-cresol,³ resorcinol⁴ and hydroquinol.⁵ The present study of the trihydroxy derivatives includes

² Büllmann and Lund, *Ann. chim.*, 16, 321 (1921).

¹ The investigations upon which this article is based were supported by grants from the Heckscher Foundation for the Advancement of Research, established at Cornell University by August Heckscher.

² Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1923-1928.

³ Orndorff, Gibbs and co-workers, *THIS JOURNAL*, (a) 47, 2767 (1925); (b) 48, 1994 (1926); (c) 49, 1545 (1927); (d) 49, 1588 (1927); (e) 50, 2798 (1928).

⁴ Orndorff, Gibbs and Shapiro, *ibid.*, (a) 48, 1327 (1926); (b) 50, 819 (1928); (c) 50, 1755 (1928).

⁵ Shapiro, *ibid.*, 50, 1772 (1928).

the benzein,⁶ phthalein and sulfonephthalein⁷ of pyrogallol, the phthalein and sulfonephthalein⁸ of hydroxyhydroquinol and the sulfonephthalein of phloroglucinol.⁹

With the extensive data now available a number of significant generalizations have become evident, which clearly indicate that definite conclusions may be drawn from absorption spectra both regarding the structure of these triphenylmethane compounds and their chemical properties, but these will be elaborated in greater detail in a later paper. The effect produced on the chemical properties and on the nature of the absorption by the introduction of hydroxyl groups in the phthaleins is a function both of their number and position. Thus the acidic properties of the sulfonic acid radical in the sulfonephthaleins are greatly influenced by the nature of the substitution in the two phenolic residues. The tendency to form an inner salt may be taken as a qualitative measure of the dissociation constant of the acid group, and a reliable indication of the existence and stability of such a salt is furnished by the similarity of the absorption spectra of the neutral and acid solutions. Thus hydroquinolsulfonephthalein appears as a stronger acid than either phenol- or *o*-cresolsulfonephthalein, for it shows the same type of absorption in aqueous, alcoholic and sulfuric acid solutions,⁵ while the two latter compounds exhibit the inner salt structure in alcoholic solution but the quinoid hydrate configuration in aqueous solution.^{3c} The addition of a molecule of water to form the hydrate necessitates the rupture of the inner salt bond and hence points to a lesser stability of the latter structure in the phenol and *o*-cresol compounds than in the hydroquinol derivative. By an independent method, B. Cohen¹⁰ has demonstrated the weakening of the acidic properties of the sulfonephthaleins due to alkyl substitution in the meta position to the phenolic hydroxyl and it is hoped to check these conclusions by the spectroscopic method outlined above. If it is granted that the introduction of hydroxyl groups serves to enhance the acid properties, it is to be anticipated that the carboxyl radical, ordinarily a very weakly dissociable acid group, will have its dissociation constant so increased in a sufficiently hydroxylated phthalein as to render the formation of an inner salt possible. This has now been realized with hydroxyhydroquinolphthalein, whose solutions in absolute alcohol and in concd. sulfuric acid exhibit closely analogous absorption spectra, which in turn closely resemble those obtained for the corresponding solution of hydroxyhydroquinolsulfonephthalein, as pointed out below. The effect of the position of the hydroxyl groups on these

⁶ Orndorff and Wang, *THIS JOURNAL*, **47**, 290 (1925); **49**, 1284 (1927).

⁷ Orndorff and Fuchs, *ibid.*, **48**, 1939 (1926).

⁸ M. L. Willard, "Dissertation," Cornell University, 1927.

⁹ We are indebted to Dr. Barnett Cohen of the Public Health Laboratory, Washington, D. C., for the pure sample of this compound.

¹⁰ B. Cohen, *Public Health Reports*, **41**, 3051 (1926).

properties is clearly demonstrated by pyrogallolphthalein, or gallein, which is isomeric with hydroxyhydroquinolphthalein but whose absorption spectrum in absolute ethanol is typical of the lactone structure, indicating that its carboxyl radical has the usual weakly acid function that occurs in the other lactoid phtaleins.

Discussion of the Absorption Spectra

The curves for the absorption spectra of the pyrogallol derivatives in absolute ethanol solution are shown in Fig. 1. Curve A for pyrogallolbenzein, Curve B for pyrogallolphthalein (gallein) and Curve C for pyrogallolsulfonephthalein (sulfonegallein) represent three distinct types of absorption and hence indicate that each of these related compounds possesses a different internal structure. The absorption curve of pyrogallolbenzein bears a general resemblance to the curve obtained for resorcinol-

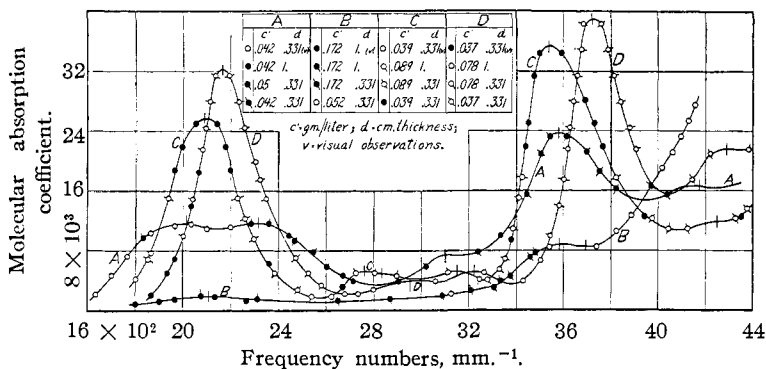


Fig. 1.—Neutral absolute ethanol solutions: A, pyrogallolbenzein; B, gallein; C, sulfonegallein; D, dimethyl ether of sulfonegallein.

benzein^{4a} and is regarded as evidence for the existence of these compounds in the quinoid state and not as quinoid hydrates. In such cases where hydrate formation is definitely known to take place, as previously observed with benzaurin^{3c} (phenolbenzein) and *o*-cresolbenzein,^{3d} fading of the solution occurs due to the setting up of an equilibrium between the colored hydrate and the colorless carbinol, and the absorption in the ultraviolet region is characterized by the presence of several weak bands, of which two have been found to be typical of the benzenoid state in triphenylmethane derivatives.¹¹ Neither fading nor the development of the above typical bands has been observed with pyrogallol- or resorcinolbenzein.

The absorption spectrum of gallein in absolute ethanol, Curve B, is marked by a weak band in the visual region and by two weak bands of nearly equal intensity in the ultraviolet at frequency numbers 3583 and 3693, having a separation of 110 mm.⁻¹. In position, separation and in-

¹¹ Gibbs and Shapiro, *Proc. Nat. Acad. Sci.*, 14, 251 (1928).

tensity these two bands correspond closely with the characteristic pair of bands found for numerous other lactoid phthalein derivatives.¹¹ It therefore appears certain that gallein, despite its color in the solid state and in neutral solution, is present primarily as the lactone. The band at 2107 responsible for the color of the solution may be related to the near ultraviolet band found in the colorless neutral solutions of hydroquinolphthalein⁵ and of phenol- and *o*-cresoltetrachlorophthaleins,^{3c} but shifted into the visual region because of the addition of hydroxyl groups or, what is more likely, it may be due to the presence of a small amount of the quinoid form, in equilibrium with the lactone. The closely related tetrachlorogallein is an almost colorless compound and has been considered by Orndorff and Delbridge¹² as being primarily lactoid, but containing a small percentage of the quinoid modification.

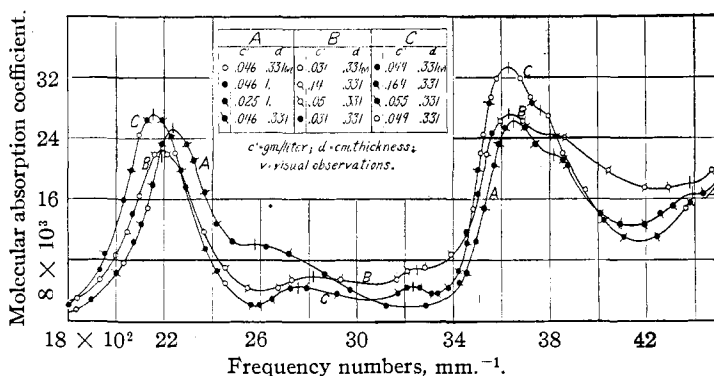


Fig. 2.—Concd. sulfuric acid solutions: A, pyrogallolbenzein; B, gallein; C, sulfonegallein.

Sulfonegallein exhibits absorption, Curve C, which is very similar to that of its sulfuric acid solution, Fig. 2, Curve C. Since in the latter solvent salt formation occurs on the basic, quinoid oxygen atom, this type of absorption is evidently characteristic of a salt structure and hence is the basis for assigning the inner salt configuration to sulfonegallein in neutral ethanol solution. Orndorff and Fuchs¹³ arrived at the same conclusion from the fact that sulfonegallein does not react with hydrogen chloride gas, which indicates that the basic properties have already been neutralized. Sulfonegallein takes on a molecule of water at the oxygen atom of the pyrone ring, giving rise to pyrogallolsulfonephthalein, but the latter compound shows exactly the same absorption as the former in all solvents. The existence of the pyrone ring thus plays no part in determining the optical properties of the compound, a conclusion which was reached previously on comparison

¹² Orndorff and Delbridge, *Am. Chem. J.*, **42**, 183 (1909).

¹³ Ref. 7, p. 1943.

of phenolphthalein and fluoran.^{4b} Curve D of Fig. 1 shows the absorption of the dimethyl ether of sulfonegallein in absolute ethanol and is of the same type as Curve C for sulfonegallein but is shifted bodily toward the ultraviolet. As this evidence indicates that the dimethyl ether must likewise be considered as an inner salt, it follows that methylation of two of the hydroxyl groups has no radical effect on the nature of the molecule.

Figure 2 presents the absorption spectra of the sulfuric acid solutions of the pyrogallol derivatives. The general similarity of the curves is striking and affords sufficient basis for postulating identical quinoid salt structures for the three compounds in this solvent. Attention is called to the characteristic double band, in the region of frequency numbers 3600–3800, which has been found for the sulfuric acid solutions of nearly all phtaleins containing the pyrone ring, such as fluorescein,^{4b} sulfonefluorescein^{4c} and the hydroxyhydroquinol derivatives described below. The hydroquinol and phloroglucinol compounds have proved exceptional in this respect.

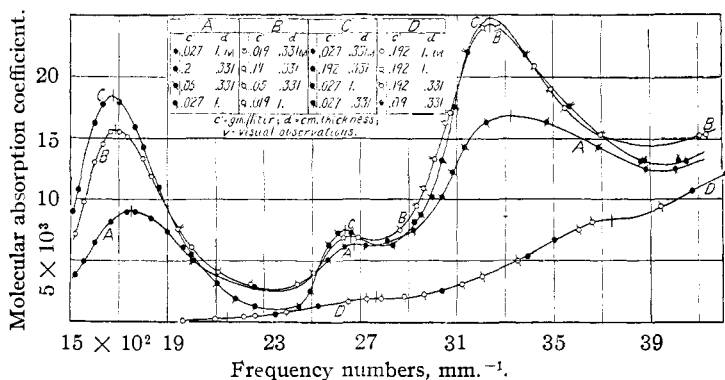


Fig. 3.—Aqueous alkaline solutions: A, pyrogallolbenzein in 5% KOH; B, gallein in 33% KOH; C, sulfonegallein in 33% KOH; D, sulfonegallein—faded.

The freshly prepared aqueous alkaline solutions, pyrogallolbenzein in 5% potassium hydroxide and gallein and sulfonegallein in 33%, also exhibit closely related absorption spectra, as shown in Fig. 3. It is noted in passing that pyrogallolbenzein, like resorcinolbenzein,^{4a} is not soluble in solutions of potassium hydroxide greater than 5%. Unlike resorcinolbenzein and in common with the other pyrogallol compounds, its alkaline solution is not fluorescent and rapidly fades to a very pale yellow in the course of a few days. It is probable that the lesser intensity of the absorption of its freshly prepared solution, Curve A, as compared with Curves B and C for gallein and sulfonegallein, respectively, is due to a somewhat greater incipient fading. However, the similarity in form and position of the bands indicates the existence of basic salts of identical structure in alkaline solu-

tion, even though pyrogallolbenzein, lacking an acidic radical, forms only a *tri*basic salt, while the others are converted into *tetra*basic salts. The fading of these solutions, which was complete in three to four days, is due to the formation of salts of the colorless, benzenoid carbinol, in a manner entirely analogous to the behavior of phenolphthalein in strongly alkaline solution. The absorption spectra of the faded solutions are fairly similar and are characterized by the presence of three shallow bands superimposed on a background of weak general absorption, as illustrated by Curve D for the solution of sulfonegallein measured five days after its preparation. Owing to the difficulty of accurately locating shallow bands of this type, their positions are given only approximately in round numbers. Table I summarizes the locations of all the bands for the above pyrogallol compounds in the various solvents employed.

TABLE I
FREQUENCY NUMBERS OF BANDS IN SOLUTIONS OF PYROGALLOL COMPOUNDS

Pyrogallolbenzein						
Absolute ethanol		2015	2315	3100	3582	4175
Concd. sulfuric acid		2236	2577	3651	3816	4395
5% potassium hydroxide	Fresh	1750	2673	3322		
	Faded	2120	3005	3995		
Gallein						
Absolute ethanol		2107	3583	3693		
Concd. sulfuric acid		2188	2817	3249	3631	3804 4383
33% potassium hydroxide	Fresh	1685	2660	3234		
	Faded	2150	2845	3700		
Sulfonegallein						
Absolute ethanol		2089	2761	2833	3151	3539 4250
Concd. sulfuric acid		2156	2755		3232	3630 3763
33% potassium hydroxide	Fresh	1675	2635	3235		
	Faded	2150	2765	3740		
Dimethyl Ether of Sulfonegallein						
Absolute ethanol		2166	2952	3223	3722	4290

Figure 4 presents the absorption spectra of absolute ethanol solutions of hydroxyhydroquinolphthalein, Curve A, hydroxyhydroquinolsulfonephthalein, Curve B, and phloroglucinolsulfonephthalein, Curve C. The two hydroxyhydroquinol derivatives have almost identical absorption, the phthalein showing slightly greater intensity and having its bands shifted slightly toward the ultraviolet with the exception of the one at 3055, which is to the red side of the corresponding band for the sulfonephthalein. This is the first instance in the course of our study of the phthaleins, where a phthalein and sulfonephthalein of a given phenol have shown the same type of absorption in ethanol solution. Taking into account the fact that their sulfuric acid solutions, Fig. 5, Curves A and B,

also have absorption of this type, it is evident on the basis of the criterion already established and verified, that hydroxyhydroquinolphthalein must possess the structure of an inner salt and hence that its carboxyl

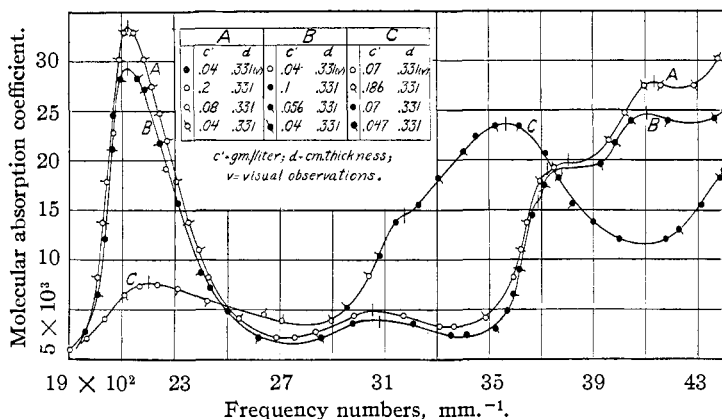


Fig. 4.—Neutral absolute ethanol solutions: A, hydroxyhydroquinolphthalein; B, hydroxyhydroquinolsulfonephthalein; C, phloroglucinolsulfonephthalein.

group has acidic properties equivalent to those of the sulfonic acid radical. Such a marked increase in the dissociation constant of the carboxyl group as the result of substitution in the molecule is, of course, not without prece-

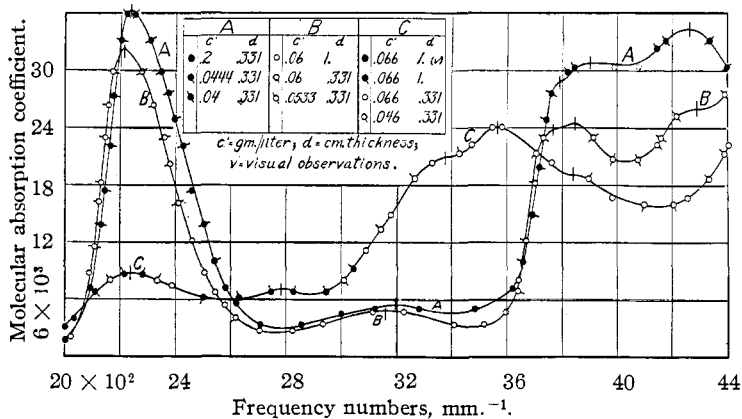


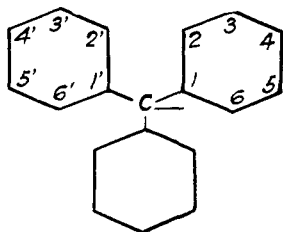
Fig. 5.—Concd. sulfuric acid solutions: A, hydroxyhydroquinolphthalein; B, hydroxyhydroquinolsulfonephthalein; C, phloroglucinolsulfonephthalein.

dent, as note, for example, acetic and trichloro-acetic acids. The objection that the active substituents are far removed from the affected carboxyl group, since they are located in different phenyl nuclei, is met by

considering that any change in the distribution of chemical forces in a given benzene ring is transmitted to the rest of the molecule through its point of linkage, which in this case is the methane carbon atom and this in turn is in the ortho position to the acid radical.

The absorption spectra of phloroglucinol in absolute ethanol, Curve C, Fig. 4, and in concd. sulfuric acid, Curve C, Fig. 5, while alike in type, are entirely different in character from those of the hydroxyhydroquinol derivatives. In general it has been noted that those quinoid phthaleins which have a different number or arrangement of phenolic hydroxyls, have quite different absorption spectra. Thus each of the sulfonephthaleins derived from the following phenols has its own peculiar absorption: phenol (or 4,4'-dihydroxydiphenylsulfonephthalide), hydroquinol (anhydro-2,2',5,5'-), resorcinol (anhydro-2,2',4,4'-), pyrogallol (2,2',3,3',4,4'), hydroxyhydroquinol (anhydro-2,2',4,4',5,5'-), and phloroglucinol (anhydro-2,2',4,4',6,6'-).¹⁴ *o*-Cresolsulfonephthalein, however, which is a dimethyl derivative of phenolsulfonephthalein and which has its phenolic hydroxyls in the same relative position, 4,4', as phenolsulfonephthalein, shows the same type of absorption spectrum as that compound.^{3e} Similarly the dimethyl ether of sulfonegallein, in which two of the phenolic hydrogen atoms are replaced by methyl groups, absorbs in the same manner as its parent substance (see above). On the other hand, all the lactoid phthaleins, as well as lactoid derivatives of the quinoid phthaleins, have been shown to possess related absorption spectra¹¹ regardless of the number and position of the hydroxyl groups. A possible explanation of this difference in optical behavior on the part of the quinoid and lactoid phthaleins may be that with the former the molecule is in a much less stable condition, as indicated by the generally greater reactivity of such compounds, and that the introduction of active groups, such as hydroxyl, can therefore produce a marked effect on the distribution of interatomic forces with a corresponding effect on the absorption spectrum.

Figure 6 exhibits the absorption spectra of freshly prepared solutions of hydroxyhydroquinolphthalein and -sulfonephthalein and of phloroglucinol-sulfonephthalein in 33% aqueous potassium hydroxide. Curves A and B for the two hydroxyhydroquinol derivatives, respectively, are fairly parallel and are characterized by a relatively complex set of six bands. Both



¹⁴ The numbering of the positions of the hydroxyl groups is based on the schematic structure indicated. Where hydroxyl groups are present in the 2,2'-positions and water is split off to form the pyrone ring, the word anhydro- is prefixed.

solutions fade in a few days to a very pale yellow and their absorption spectra, represented here by that of hydroxyhydroquinolphthalein, Curve C, are found to have practically the same bands, except for the disappearance of the one in the visual region, as curves for the fresh solutions. Owing to the general flattening out of the absorption curve it is much more difficult to locate these bands precisely. This type of behavior is, however, different from that of the other pht haleins on which measurements have been obtainable before fading occurred, since in these cases the absorption

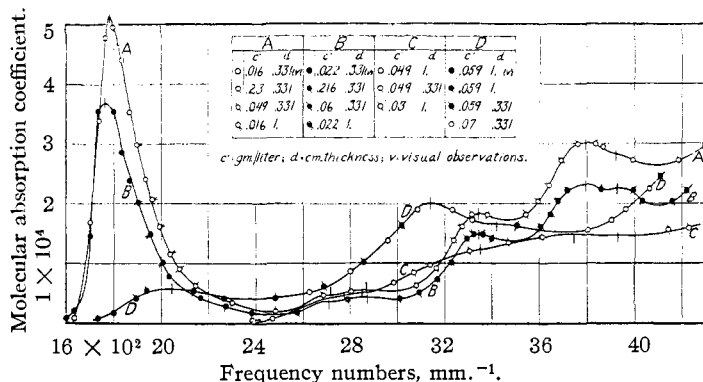


Fig. 6.—33% aqueous potassium hydroxide solutions. A, hydroxyhydroquinolphthalein; B, hydroxyhydroquinolsulfonepht halein; C, hydroxyhydroquinolphthalein—faded; D, phloroglucinolsulfonepht halein.

spectrum was different for the fresh and faded solutions. Phloroglucinolsulfonepht halein in strong alkali yields a solution of an orange-yellow color, quite unlike the well-known red or bluish-red of alkaline solutions of the other pht haleins, and is also exceptional in that no fading was observed over a period of several months. Its absorption, Curve D, is marked by three broad bands.

The positions of the absorption bands for the various solutions of the hydroxyhydroquinol and phloroglucinol compounds are listed in Table II.

TABLE II
FREQUENCY NUMBERS OF BANDS IN SOLUTIONS
Hydroxyhydroquinolphthalein

Absolute ethanol		2124	3055	3726	3804	4135	
Concd. sulfuric acid		2237	3195	3791	3900	4262	
Concd. potassium hydroxide	Fresh	1785	2715	2867	3342	3796	3923
	Faded		2775	2850	3350	3745	3930

Hydroxyhydroquinolsulfonepht halein

Absolute ethanol		2122	3082	3688	3781	4107	
Concd. sulfuric acid		2213	3160	3766	3847	4290	
Concd. potassium hydroxide	Fresh	1763	2709	2872	3343	3795	3928
	Faded		2710	2900	3400	3705	4000

TABLE II (Concluded)
Phloroglucinolsulfonephthalein

Absolute ethanol	2200		3177	3565	
Concd. sulfuric acid	2235	2781	3376	3564	3840
Concd. KOH, fresh	2047	3137	3425		

Both hydroxyhydroquinolphthalein and hydroxyhydroquinolsulfonephthalein behave in an unusual manner, when gradually increasing amounts of potassium hydroxide are added to their neutral absolute ethanol solutions. With most of the colored phtaleins and sulfonephthaleins, it has been observed that over a certain range of alkali concentrations there is a more or less rapid disappearance of the visual band of the neutral solution and a corresponding growth of the band characteristic of the

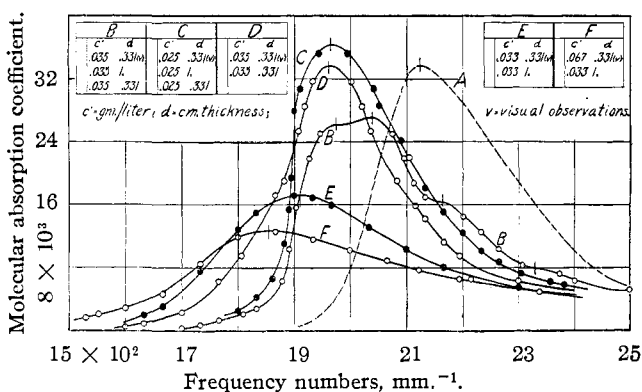


Fig. 7.—Hydroxyhydroquinolphthalein in alcoholic potassium hydroxide: A, neutral solution; B, 1 molecule:2 molecules of KOH; C, 1 molecule:4 molecules of KOH; D, 1 molecule:23 molecules of KOH; E, 1 molecule:87 molecules of KOH; F, 1 molecule:100 molecules of KOH.

alkaline solution.¹⁵ The wave-length positions of the neutral and alkaline bands remain fixed, since they are due to the presence of two different substances, the neutral form and the basic form, and the relative intensities are a measure of their relative concentrations and therefore of the state of equilibrium between them.¹⁶ In the case of the hydroxyhydroquinol derivatives, as illustrated in Fig. 7 by the set of curves covering the visual region for alkaline solutions of hydroxyhydroquinolphthalein, there is, however, an almost continuous shift of the bands toward the red, while the intensities pass through a maximum for an intermediate concentration of alkali. Curve A is a reproduction of the visual portion of the absorption

¹⁵ See references 3a, 3c, 4 and 5; also Brode, *THIS JOURNAL*, **46**, 585 (1924), and Holmes, *ibid.*, **46**, 629 (1924).

¹⁶ Gibbs and Shapiro, *Proc. Nat. Acad. Sci.*, **14**, 694 (1928).

curve for the neutral solution. Curve B for two molecules of potassium hydroxide to one of the phthalein has a lesser intensity and there are present a prominent double band and two weak shoulders in place of the single band of the neutral solution. For four and twenty-three molecules of alkali, Curves C and D, there are now present again only single bands but shifted to the region of frequency number 1990 while the maximum of intensity has been reached at Curve C. Thereafter further additions of alkali, 87 molecules for Curve E and 100 molecules for Curve F, produce a rapid shifting of the band toward the red together with a marked decrease of intensity. Coincident with these changes in absorption, there is first an increase and then a disappearance of fluorescence. The neutral solution shows faint fluorescence, but with the addition of alkali up to twenty-three molecules, this becomes quite intense, corresponding to the increased absorption at this concentration. Abruptly with the shift of the band from its position on Curve D to that of Curve E, the fluorescence completely disappears. If there are assumed several changes in molecular configuration during the addition of the potassium hydroxide and therefore a correspondingly complex set of equilibrium conditions, it is possible at least qualitatively to interpret the above data. It was demonstrated above that hydroxyhydroquinolphthalein in neutral ethanol solution possesses the structure of an inner salt. In the presence of an amount of alkali insufficient to form the tetrabasic salt, it is conceivable that the molecule would revert to the condition of the free acid, which would have a different type of absorption from that of the inner salt. It is therefore significant, inasmuch as hydroxyhydroquinolphthalein may be regarded as dihydroxyfluorescein, that Curve B for two molecules of potassium hydroxide, half the theoretical amount, closely resembles the curves for neutral solutions of resorcinolbenzein^{4a} and fluorescein,^{4b} both quinoid compounds and the latter a free acid. With four and twenty-three molecules, salt formation is completed and the fluorescence is at a maximum, but with more alkali a decisive change must be produced in the molecule, corresponding to the creation of a new type of absorption and the loss of the fluorescence. Since the hydroxyhydroquinolphthalein can be reprecipitated from the non-fluorescent solution by the addition of acid, this last change is reversible and hence must be in equilibrium with the other two processes—the rupture of the inner salt bond and the formation of the tetrabasic salt. The ultraviolet spectrum, which consists of three well-defined bands for the solution containing four molecules of potassium hydroxide, undergoes no unique changes such as are found in the visual region, but with increasing alkali concentrations the bands become shallower until in the presence of 100 molecules it is difficult to locate them with accuracy. For completeness all of the bands for the various alkaline solutions are listed in Table III.

TABLE III
 FREQUENCY NUMBERS OF BANDS IN ALCOHOLIC ALKALINE SOLUTIONS OF HYDROXY-
 HYDROQUINOLPHTHALEIN

Ratio to KOH							
1:2	1975	2039	2165	2330	3018	3657	4125
1:4	1965				2911	3612	4093
1:23	1962				2950	3600	4092
1:87	1911				2995	3558	3987
1:100	1855				2900	3450	3950

Summary

1. Data and curves are presented on the absorption spectra of various phthalein derivatives of pyrogallol, hydroxyhydroquinol and phloroglucinol. Correlations are drawn with data previously obtained for phthaleins of the mono- and dihydroxybenzenes.

2. The effect on the chemical properties and absorption spectra of the phthaleins, due to the introduction of hydroxyl groups, is discussed.

3. Gallein, which is colored in both the solid state and in neutral solution, is shown to be primarily lactoid in structure, but probably in equilibrium with a small amount of the quinoid modification.

4. The unusual behavior of hydroxyhydroquinolphthalein in weakly alkaline solutions both as regards its absorption and fluorescence is described and a possible explanation is advanced.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

THE PREPARATION OF AMINONAPHTHOLS

BY WILSON F. BROWN, JOHN C. HEBDEN AND JAMES R. WITHROW

RECEIVED SEPTEMBER 4, 1928

PUBLISHED JUNE 5, 1929

1-Amino-7-naphthol and 1-amino-6-naphthol were needed for work in progress. An investigation was therefore conducted for the preparation of these compounds by caustic fusion of the respective α -naphthylamine-sulfonic acids.

Among other things, the results indicated that 1-amino-6-naphthol could be prepared from α -naphthylamine-6-sulfonic acid by caustic soda fusion. The melting point of the picrate of 1-amino-6-naphthol was not the same as that given in the literature. Further, 1-amino-7-naphthol was prepared in good yield (average of 58%) by caustic soda fusion of α -naphthylamine-7-sulfonic acid.

Literature

The Cassella Company¹ gave an example of the preparation of 1-amino-7-naphthol by caustic fusion from α -naphthylamine-7-sulfonic acid. In

¹ German patent 69,458; *Friedländer*, 3, 476 (1890).