A suspension of 0.020 mole of chloranil and 0.5 g. of palladium black in 400 cc. of water was heated to boiling in nitrogen and 0.011 mole of *iso*butyraldehyde in 100 cc. of water slowly added. The reaction took one hour. After cooling and filtering, the solution was distilled in the usual way. The distillate gave a strong test for α-hydroxy-*iso*butyraldehyde but contained no acetone.

Summary

1. The oxidation of *iso*butyraldehyde by ferricyanide in alkaline solution at 80° yields 2,2,5,5-tetramethyldihydropyrazine and 2,2,5,5-tetramethyl-3,6-dicyanopiperazine and no *iso*butyric acid. From methyl *iso*propyl ketone under the same conditions hexamethyldihydropyrazine is formed. The reaction involves the oxidation of the α-carbon atom and the gain of nitrogen from a fraction of the complex cyanide.

2. The oxidation of *iso*butyraldehyde with ceric sulfate at 80° in acid solution yields acetone and α-hydroxy-*iso*butyraldehyde as well as *iso*butyric acid. The same products are formed in acid solution by potassium permanganate and cobaltic sulfate. Chloranil and palladium yield α-hydroxy-*iso*butyraldehyde.

3. Potassium dichromate in acid solution at 80° oxidizes *iso*butyraldehyde in the α-position, yielding acetone to the extent of 40% in very dilute solutions. The process of α-oxidation is favored by dilution. *n*-Butyraldehyde is also oxidized in the α-position, as shown by the formation of carbon dioxide.

4. Potassium permanganate oxidizes acetaldehyde in acid solution at 80°, yielding carbon dioxide as well as acetic acid if precautions are taken to keep the reactants in *very dilute* solution with an excess of aldehyde.

CAMBRIDGE 38, MASSACHUSETTS

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

THE ABSORPTION SPECTRA OF SOME PHTHALEINS AND SULFONEPHTHALEINS OF PHENOL AND ORTHO-CRESOL[1]

BY R. C. GIBBS AND C. V. SHAPIRO[2]

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In continuation of our previous investigations[3] on the absorption spectra of compounds of the triphenylmethane series, data are now presented for some phthalein and sulfonephthalein derivatives of phenol and *o*-cresol.

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

[2] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1923–1928.

[3] Orndorff, Gibbs and co-workers, THIS JOURNAL, **47**, 2767 (1925); **48**, 1327, 1994 (1926); **49**, 1541, 1545, 1588 (1927); **50**, 819, 1755 (1928).

All of the compounds used in the course of the present research were prepared at this Laboratory under the direction of the late Professor W. R. Orndorff and were of analytical purity.

Some preliminary work here on the ultraviolet absorption of these compounds[4] in various solvents and a few reports on their absorption in the visual region in acid and alkaline solutions[5] have been published.

Phenoltetrachlorophthalein, *o*-cresolphthalein and *o*-cresoltetrachlorophthalein are typical lactoid phthaleins, which yield colorless solutions in neutral solvents. Their absorption spectra in absolute ethanol solution, together with that of phenolphthalein[6] in the same solvent, Fig. 1, are characterized by a pair of bands in the region of frequency numbers, 3500 to 3700. Similar bands have been found for a large number of benzenoid compounds of the triphenylmethane series,[7] of which many are lactones of the phthalein class, but some are carbinols of triphenylmethane derivatives. It is therefore believed that these bands are characteristic not of a single typical atom or group of atoms but rather of the molecule as a whole, when all three benzene nuclei are in their normal, benzenoid state.

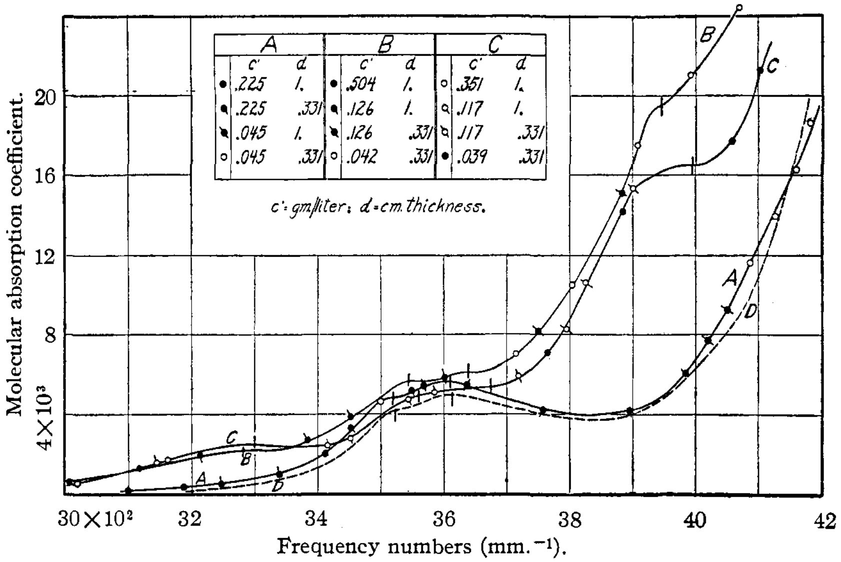

Fig. 1.—Absolute ethanol solutions: *A*, *o*-cresolphthalein; *B*, *o*-cresoltetrachlorophthalein; *C*, phenoltetrachlorophthalein; *D*, phenolphthalein.

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[4] Howe, *Phys. Rev.*, **8**, 687 (1916); Howe and Gibson, *Phys. Rev.*, **10**, 767 (1917); Orndorff, Gibbs, Scott and Jackson, *Phys. Rev.*, **17**, 437 (1921).

[5] Formánek and Knop, *Z. anal. Chem.*, **56**, 273 (1917); Moir, *Trans. Roy. Soc. S. Africa*, **7**, 8, 114 (1918); White and Acree, This Journal, **40**, 1092 (1918): Brode, *ibid.*, **46**, 585 (1924); Holmes, *ibid.*, **46**, 629, 633 (1924).

[6] Orndorff, Gibbs and McNulty, This Journal, **48**, 1994 (1926).

[7] Gibbs and Shapiro, *Proc. Nat. Acad. Sci.*, **14**, 251 (1928).

It is extremely unlikely that the methane carbon atom in triphenylmethane derivatives, even when unsaturated as represented by the quinoid state of the molecule, can be the seat of absorption in the wave length range from the visible region down to the ultraviolet at about 2300 Å., as recently suggested by Vogt.[8] The aliphatic hydrocarbons exhibit absorption only in the extreme ultraviolet below 1900 Å. while the simple, unsaturated hydrocarbons have bands in the region of 2200 to 1900 Å.[9] On the other hand, as is well known, benzene shows strong, banded absorption in the middle ultraviolet from 2700 to 2300 Å. and the effect of changing from the benzenoid to the quinoid state with the production of visible color, that is, the production of absorption in the visual region, is well illustrated by comparison of the absorption spectra of hydroquinone and benzoquinone.[10] In a system consisting of several benzene nuclei and a methane, or other simple type of hydrocarbon carbon atom, the absorption will therefore be due entirely to the combined effects of the benzene nuclei. This hypothesis of the negligible part played by the central carbon atom in determining the absorption is neatly confirmed by unpublished results obtained at this Laboratory on the absorption spectrum of a triphenyl derivative of germanium,[11] which was found to be of a type very similar to that of triphenylmethane.

The tetrachlorophthaleins each have two more bands in addition to the pair cited above, one to the side of longer, the other to the side of shorter wave lengths. Comparing phenol- and *o*-cresolphthalein, it is seen that the bands for the latter are shifted toward longer wave lengths and the same relation holds between their tetrachloro derivatives. The effect of chlorine substitution in the phthalic acid residue, however, in spite of a large increase of molecular weight, is to shift the bands toward shorter wave lengths, as is evident if the bands in common for phenol- and phenoltetrachlorophthalein and for *o*-cresol- and *o*-cresoltetrachlorophthalein as given in Table I are compared.

TABLE I

FREQUENCY NUMBERS OF BANDS IN NEUTRAL ABSOLUTE ETHANOL SOLUTION

Phenolphthalein	..	3523	3613	..
Phenoltetrachlorophthalein	3300	3560	3675	3995
o-Cresolphthalein	..	3519	3608	..
o-Cresoltetrachlorophthalein	3281	3544	3638	3945

Phenolsulfonephthalein and *o*-cresolsulfonephthalein, in contrast with the corresponding phthaleins derived from phthalic anhydride, are colored

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[8] Vogt, *Z. physik. Chem.*, **132**, 101 (1928).

[9] Stark and co-workers, *Jahr. Radioakt. und Elektronik*, **10**, 139 (1913).

[10] Klingstedt, *Compt. rend.*, **175**, 365 (1922); **176**, 1550 (1923).

[11] Tabern, Orndorff and Dennis, THIS JOURNAL, **49**, 2512 (1927).

substances whose constitution has been the subject of some debate.[12] Orndorff and Sherwood[12b] have suggested that, because phenolsulfonephthalein is a sulfonic acid derivative of benzaurin, a strongly basic compound, it probably forms an inner salt. In aqueous solution, however, they postulated the addition of a molecule of water, bringing about the formation of a quinoid hydrate. If this theory were correct, it is to be expected that both phenolsulfonephthalein and *o*-cresolsulfonephthalein would exhibit different types of absorption in aqueous and absolute ethanol solution, since in the latter solvent hydrate formation could not occur. It has previously been shown that a sharp differentiation between the quinoid and quinoid hydrate forms, as found in fresh and faded solutions, respectively, of fuchsone, benzaurin and aurin,[13] can be readily obtained by means of their absorption spectra. In the present instance the spectroscopic evidence completely confirms the existence of the quinoid form, or inner salt, in alcoholic, and the quinoid hydrate in aqueous solution. Figs. 2 and 3, respectively, show the absorption curves for phenolsulfonephthalein and *o*-cresolsulfonephthalein in both solvents. Curve A in each case is for the aqueous solution; the curves are entirely similar, with the bands for *o*-cresolsulfonephthalein shifted slightly toward longer wave lengths. For the absolute ethanol solutions Curves B of Figs. 2 and 3 are obtained and they are of a radically different type from the "A" curves. The

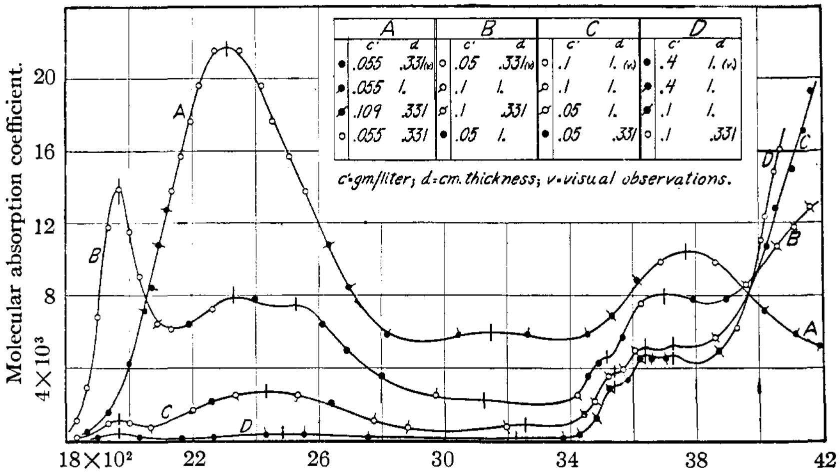

Fig. 2.—Phenolsulfonephthalein—neutral solutions: *A*, aqueous; *B*, absolute ethanol—fresh solution; *C*, solution B—after standing for one year; *D*, diethyl ether—absolute ethanol solution.

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[12] (a) White and Acree, This Journal, **40**, 1092 (1918); **41**, 1190 (1919); (b) Orndorff and Sherwood, *ibid.*, **45**, 490 (1923).

[13] Orndorff, Gibbs, McNulty and Shapiro, This Journal, **49**, 1546 (1927).

assignment of the inner salt configuration to these sulfonephthaleins in ethanol solution is based on the similarity of their absorption curves to those obtained for the sulfuric acid solutions, Figs. 4 and 5. In the latter case salt formation occurs through the neutralization of the basic, quinoid oxygen by the sulfuric acid and it is reasonable to assume that the formation of an inner salt in neutral alcoholic solution by the sulfonic acid radical gives rise to a similar distribution of intramolecular forces, which uniquely determine the nature of the absorption spectrum. It is necessary to work in absolutely dry ethanol and with perfectly dry samples of the sulfonephthaleins in order to obtain this absorption characteristic of the inner salt, as the formation of the hydrate readily takes place in the presence of traces of water. The effect of minute traces of moisture, which cannot after all be completely avoided, is apparent in both of the "B" curves, for a weak band is found in the region of frequency number 2300 which is evidently related to the strong band occurring at the same approximate position for the aqueous solutions. If more water is present, as in a 95% ethanol solution, hydrate formation is complete and the solution has the bright yellow color of an aqueous solution instead of the salmon color in absolute ethanol. This accounts for the type of curve obtained by Howe and Gibson[4] for their "alcoholic" solution of phenolsulfonephthalein, which evidently contained a fair amount of water, since the absorption recorded by them resembles that here presented for an aqueous solution.

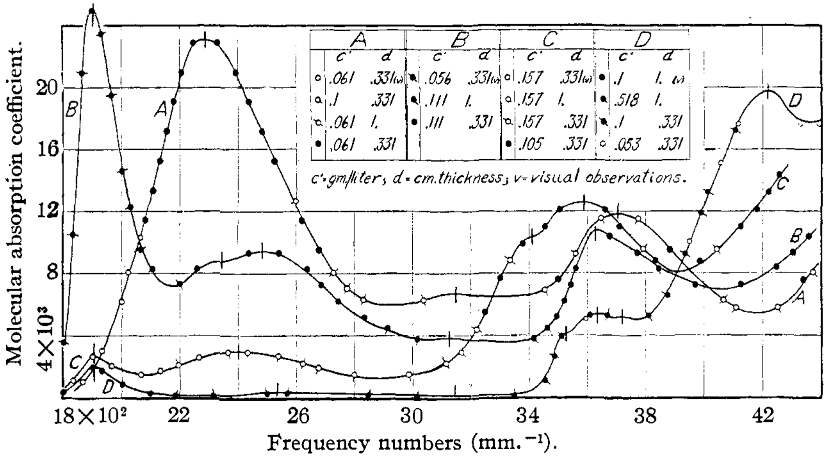

Fig. 3.—*o*-Cresolsulfonephthalein—neutral solutions: *A*, aqueous; *B*, absolute ethanol—fresh solution; *C*, solution *B*—after standing for one year; *D*, diethyl ether—absolute ethanol solution.

The formation of a hydrate in aqueous solution is not observed with all sulfonephthaleins. Hydroquinolsulfonephthalein[14] exhibits the same ab-

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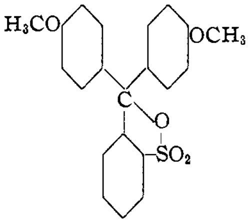
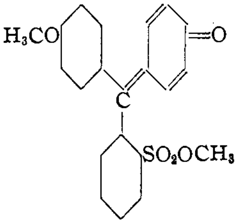
[14] Shapiro, This Journal, 50, 1772 (1928).

sorption in both aqueous and ethanol solution and this is of the acid type, as found for example in concentrated sulfuric acid. The introduction of more hydroxyl groups stabilizes the inner salt configuration, probably by enhancing the acid properties of the sulfonic acid radical. This effect on the acid properties of the phthaleins and sulfonephthaleins due to an increase of the number of hydroxyl groups appears to be quite general and will be discussed in a subsequent paper.

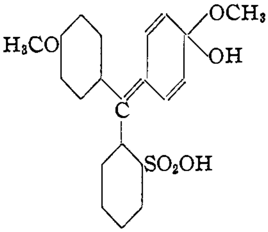
When the alcoholic solutions of phenolsulfonephthalein and *o*-cresolsulfonephthalein are allowed to stand in a dark room for a year in tightly stoppered pyrex bottles, the color decreases considerably in intensity and the solutions no longer give the characteristic color changes of the sulfonephthaleins in acid and alkaline solution. Curve C, Fig. 2, shows the absorption of such a faded solution of phenolsulfonephthalein. The band in the visual region at 1966 has not changed in position but it has only one-twelfth of its original intensity. In the ultraviolet region, however, the character of the bands has been completely modified. This is evidently due to the conversion of the phenolsulfonephthalein into its diethyl ether,[15] for by determining the absorption of the pure diethyl ether in ethanol solution, Curve D is obtained and it runs quite parallel to Curve C. Moreover, the absorption of the diethyl ether solution does not remain constant but slowly approaches that of the faded solution of the sulfonephthalein. There is thus indication that the diethyl ether, which can be obtained in the form of almost colorless crystals[15] and is considered as a lactoid derivative, I, sets up equilibrium in solution with a colored modification, which may be an ether–ester, II, or possibly a mixed quinoid hydrate, III.



I



II



III

The existence of the lactoid form in the equilibrium mixture is confirmed by the presence of the characteristic pair of bands at 3540 and 3639, which have previously been associated with the benzenoid condition of the molecule.[7]

o-Cresolsulfonephthalein likewise fades to a considerable extent in ethanol solution, as shown in Curve C, Fig. 3, with the peak of the band at 1905 decreasing to one-tenth of its original intensity after one year. In the ultraviolet region, however, the absorption increases and new bands

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[15] Orndorff and Shapiro, This Journal, **46**, 2856 (1924).

develop which are not related either to those of the fresh solution, or to those of a freshly prepared solution of the diethyl ether of *o*-cresolsulfonephthalein, Curve D. In fact, at a still later stage (not shown on Fig. 3), the bands at 3411 and 3588 of Curve C had again increased 50% in intensity, with some indication that they were shifting closer together. The absorption of the pure diethyl ether of *o*-cresolsulfonephthalein, Curve D, is similar to that for the ether of phenolsulfonephthalein, except for the presence of a band in the extreme ultraviolet at 4218. It is probable that there is a corresponding band in phenolsulfonephthalein diethyl ether, but further in the ultraviolet and hence beyond the range of our spectrograph, since in general the bands for phenolsulfonephthalein are located to the side of higher frequency numbers with reference to the corresponding bands of *o*-cresolsulfonephthalein. The fading of the alcoholic solution of *o*-cresolsulfonephthalein cannot, therefore, be ascribed to ether formation in view of the relation between Curves C and D, but further observations will be continued on both of these solutions, in particular to follow any changes that may develop in that of the diethyl ether. The positions of the bands in the faded ethanol solutions of the sulfonephthaleins and in the ethanol solutions of their diethyl ethers are presented in Table II.

TABLE II

FREQUENCY NUMBERS OF BANDS IN ETHANOL SOLUTIONS OF

Phenol-sulfonephthalein, faded	*o*-Cresol-sulfonephthalein, faded	Phenol-sulfonephthalein, diethyl ether	*o*-Cresol-sulfonephthalein, diethyl ether
1966	1905	1966	1905
2434	2402	2485	2535
3255	..	3225	3145
3540	3411	3540	3527
3639	3588	3639	3634
3727	..	3727	3719
..	..	..	4218

Phenolsulfonephthalein and *o*-cresolsulfonephthalein readily dissolve in concentrated sulfuric acid to form orange colored solutions, in which the sulfonephthalein is presumably present as the sulfate. If hydrochloric acid is added to an aqueous solution of the sulfonephthalein, which is originally present therein as the quinoid hydrate, as we have indicated above, water is split off with the formation of the basic quinoid form, which then reacts to form a hydrochloride. The extent to which this series of reactions proceeds depends, however, on the amount of acid present, and by determining the absorption spectrum at different concentrations of acid it is possible to follow the course of the salt formation. When the solution contains 10,000 molecules of hydrochloric acid to one of the sulfonephthalein, the same absorption bands are found as in the sulfuric acid solutions, but at intermediate concentrations of acid some of the "neutral" bands, that is, those characteristic of the quinoid hydrate form, persist. Phenolphthalein and *o*-cresolphthalein in concentrated sulfuric acid likewise form salts of a quinoid structure which should have the same molecular configuration as those of the sulfonephthaleins and should, therefore, give rise to the same type of absorption spectra. In the case of phenolphthalein, however, it has already been pointed out[6] that the occurrence of sulfonation is a complicating factor in its effect on the absorption spectrum and a similar result has now been found for *o*-cresolsulfonephthalein, as is evident from an inspection of their absorption curves.

Figure 4 shows the absorption curves for the phenol derivatives. Curve A for phenolsulfonephthalein in concentrated sulfuric acid and Curve B for the same compound in aqueous solution with the addition of 10,000 molecules of hydrogen chloride are fairly parallel, with the bands in the sulfuric acid solution shifted uniformly toward longer wave lengths. Curve C is a reproduction of our previously published curve for phenolphthalein in sulfuric acid,[6] with the addition of a band in the extreme ultraviolet at 4280, which has since been found. It is similar to Curves A and B up to frequency number 3200, beyond which the three broad bands are in sharp contrast with the single prominent band of phenolsulfonephthalein at 3771.

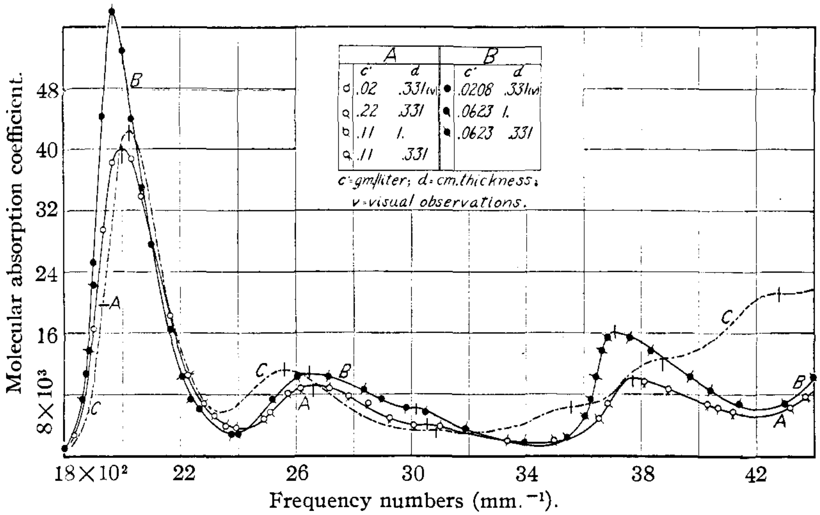

Fig. 4.—Acid solutions: *A*, phenolsulfonephthalein—concd. sulfuric acid; *B*, phenolsulfonephthalein—1 mole:10,000 moles of hydrochloric acid; *C*, phenolphthalein—concd. sulfuric acid.

Figure 5 gives a similar set of curves for the *o*-cresol compounds. Curve A for *o*-cresolphthalein in sulfuric acid corresponds in all respects with the curve for phenolphthalein in the same solvent, Fig. 4. Evidence for progressive sulfonation was also obtained, in that the intensity of the absorption in the visual region was observed to diminish slowly in the course of several days. Curve B for *o*-cresolsulfonephthalein in concentrated sulfuric acid exhibits some peculiarities beyond 3400, in that instead of having a single, well-defined band, as with phenolsulfonephthalein, a shallow double band is produced. In aqueous hydrochloric acid, Curve C, the absorption is normal, with the bands having the same relative positions and intensities as for phenolsulfonephthalein in acid solution and for both sulfonephthaleins in absolute ethanol solution. The data for the positions of the band heads in these several neutral and acid solutions are summarized in Table III.

In alkaline solution, phenolsulfonephthalein and *o*-cresolsulfonephthalein exhibit their characteristic bluish-red color, due to the formation of the quinoid, di-basic salt. There are, however, two conditions under which this color is subject to modification. In the first place, at very low concentrations of alkali, corresponding to two molecules of the base to one of the sulfonephthalein and at low concentrations of the sulfonephthalein, hydrolysis occurs to a marked extent owing to the weak nature of the acid.

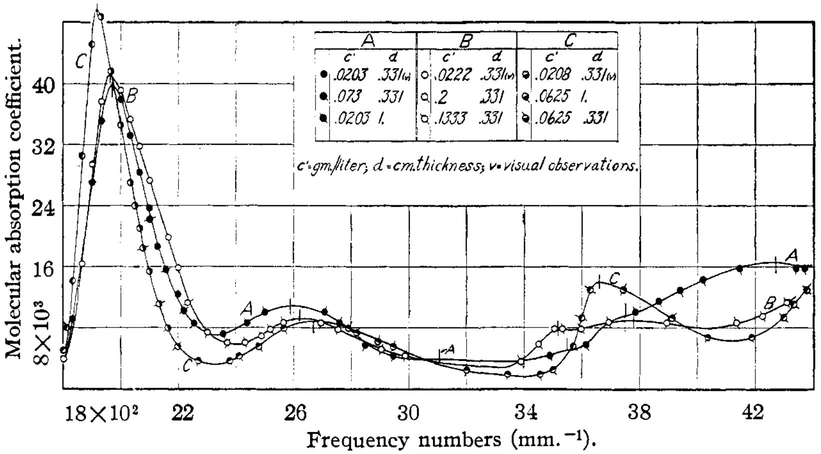

Fig. 5.—Acid solutions: *A*, *o*-cresolphthalein—concd. sulfuric acid; *B*, *o*-cresolsulfonephthalein—concd. sulfuric acid; *C*, *o*-cresolsulfonephthalein—1 mole : 10,000 moles of hydrochloric acid.

This is brought out in Fig. 6, Curves A and A', for the absorption of an aqueous solution of phenolsulfonephthalein containing the theoretical amount of alkali for producing the dipotassium salt. Curve A was for a solution containing 0.0609 g. of phenolsulfonephthalein to the liter and it will be noted that for the thinnest cell available, 0.331 cm., it was not possible to obtain the peak of the band in the visual region at 1782 indicated on the curve by a broken line. Upon diluting to a concentration of 0.0203 g. to the liter, the solution changed from its bluish-red color to an orange and the absorption in the visual and near ultraviolet regions, Curve A', showed a large decrease in the intensity of the band at 1782 and a simultaneous increase of that at 2300, which is the

TABLE III

FREQUENCY NUMBERS OF BANDS IN NEUTRAL AND ACID SOLUTIONS

Distilled water						
Phenolsulfonephthalein	..	2310	..	3148	..	3768
o-Cresolsulfonephthalein	..	2290	..	3148	..	3705
Absolute ethanol						
Phenolsulfonephthalein	1966	2330	2527	3125	3516	3700
o-Cresolsulfonephthalein	1905	2345	2483	3125	..	3629
Concentrated sulfuric acid						
Phenolphthalein	2025	2560	3085	3555	3875	4280
Phenolsulfonephthalein	2000	2659	3055	..	3771	..
o-Cresolphthalein	1970	2590	3105	3550	3752	4271
o-Cresolsulfonephthalein	1964	2623	..	3518	3780	..
1 mole of phenolpthalein: 10,000 moles of hydrochloric acid						
Phenolsulfonephthalein	1965	2647	3016	3709	..	..
o-Cresolsulfonephthalein	1920	2672	..	3663	..	..

first band in the neutral aqueous solution, Fig. 1, Curve A. At a ratio of 100 molecules of potassium hydroxide to one of phenolsulfonephthalein, Curve B, the full alkaline color developed and was then stable at all practical dilutions. It is now apparent on examining Curve A for the higher concentration of the sulfonephthalein in solution with two molecules of alkali that even under these conditions hydrolysis is effective, for traces of two of the neutral bands still persist at 2250 and 3642.

The same phenomenon occurs with *o*-cresolsulfonephthalein in an aqueous solution containing two equivalents of potassium hydroxide, Fig. 6, Curve A, except that the *o*-cresol compound appears to be somewhat more susceptible to hydrolysis, for at a concentration of 0.061 g. to the liter the absorption curve has the same contour as that for phenolsulfonephthalein at a concentration of 0.0203 g. to the liter. It was found on examining a solution containing 0.1 g. of *o*-cresolsulfonephthalein to the liter, that the intensity of the first two bands was reversed, that at 1745 becoming much stronger than the one at 2287. With 100 molecules of potassium hydroxide present, the absorption becomes stable at all practical dilutions and Curve B is obtained, which is entirely comparable with that of phenolsulfonephthalein obtained under similar conditions. In each case there are three bands, with those for *o*-cresolsulfonephthalein shifted uniformly toward longer wave lengths.

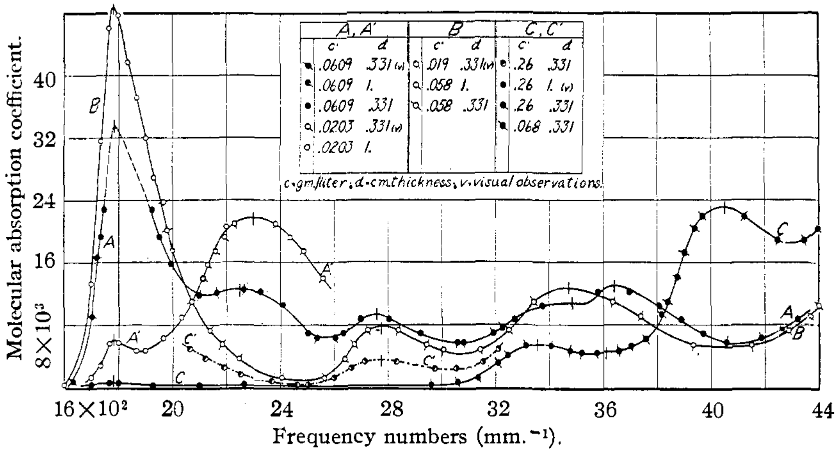

Fig. 6.—Phenolsulfonephthalein in aqueous alkaline solutions; *A*, *A′*, 1 mole:2 moles of potassium hydroxide; *B*, 1 mole:100 moles of potassium hydroxide; *C*, *C′*, 33% potassium hydroxide—two days after preparation of solution.

As both phenolsulfonephthalein and *o*-cresolsulfonephthalein are commonly used as indicators for the absolute determinations of *P*H values, it is evident that when working with alkaline solutions of low concentration, if only slightly buffered or unbuffered, it is essential to carry out comparisons with the standard solutions under very nearly identical conditions of concentration of the alkaline medium and of the indicator. The use of the partially neutralized indicator, as recommended by Clark,[16] is evidently an improvement in the light of the above data, but the caution

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[16] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, **1922**, p. 80.

still applies for very low alkali concentrations. It is, furthermore, not safe, in view of the hydrolysis of the dibasic salts of the indicators, to assume as Brode[17] has done in the development of his spectrophotometric method for the determination of hydrogen-ion concentration, that Beer's law always holds over a range of concentrations.

The second of the two conditions under which the alkaline color of these sulfonephthaleins is modified is in the presence of high concentrations of alkali. In aqueous solutions containing 33% potassium hydroxide, the deep red color of phenolsulfonephthalein rapidly fades to a pale pink in two days, while *o*-cresolsulfonephthalein requires six months to reach the same stage. This fading, which is common to all phthaleins in strongly alkaline solutions, is due to the formation of the colorless tripotassium salt of the carbinolcarboxylic acid. With phenolsulfonephthalein an attempt was made to record the absorption of its solution in 33% potassium hydroxide immediately after its preparation but, owing to the rapidity of the fading, consistent data could not be obtained. Curve C′, Fig. 6, represents a portion of the data thus obtained and brings out the band at 2774, which is missing in Curve C for the same solution, two days later. In the ultraviolet region, Curve C shows three bands, whereas in the solution containing 100 molecules of alkali to one of phenolsulfonephthalein there is only one in the same region.

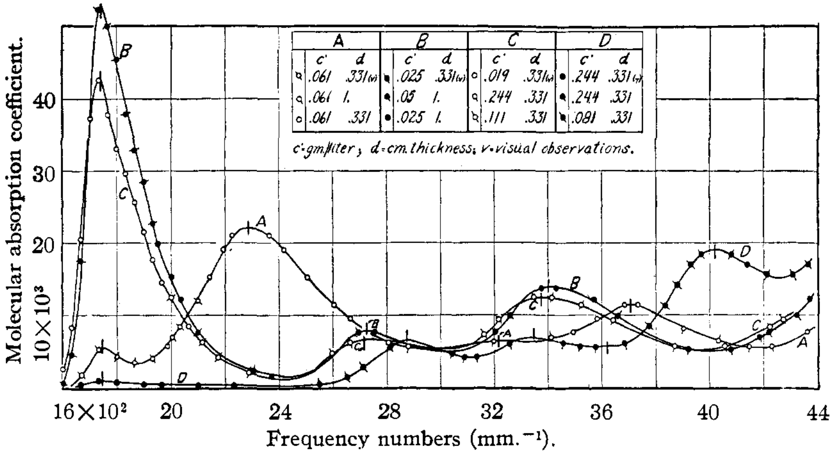

Fig. 7.—*o*-Cresolsulfonephthalein in aqueous alkaline solutions: *A*, 1 mole:2 moles of potassium hydroxide; *B*, 1 mole:100 moles of potassium hydroxide; *C*, 33% potassium hydroxide—fresh solution; *D*, solution *C*—after standing for six months.

As the fading was so much slower in the case of *o*-cresolsulfonephthalein in 33% potassium hydroxide, it was possible to obtain the absorption of the fresh solution, Curve C, Fig. 7, and it will be noted that except for a

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[17] Brode, This Journal, **46**, 587 (1924).

slight decrease in intensity, which is probably due to an incipient fading, the bands are very close to those for an aqueous solution of *o*-cresolsulfonephthalein containing 100 molecules of potassium hydroxide, Curve B. At the end of six months, however, when the solution had changed to a pale pink, the absorption, Curve D, had likewise changed completely in character, yielding a curve very like that of phenolsulfonephthalein after two days, except that there remains a well defined band at 2874, for which there is no counterpart in the faded solution of the latter substance. The relatively greater stability of *o*-cresolsulfonephthalein in strongly alkaline solution, as indicated by the above data, renders it more desirable than phenolsulfonephthalein as an indicator under such conditions. The relation between the bands in the various alkaline solutions of these two sulfonephthaleins is well brought out in Table IV.

Table IV

Frequency Numbers of Bands in Aqueous Alkaline Solutions of Phenolsulfonephthalein and *o*-Cresolsulfonephthalein

	1 mole: 2 moles of KOH	1 mole: 100 moles of KOH	33% KOH	33% KOH, faded
Phenolsulfonephthalein	1782	1782	1782	1782
	2250 (2300)			
	2756	2774	(2774)	
	3487	3474	(3378)	3355
	3642			3610
			(4058)	4052
o-Cresolsulfonephthalein	1745	1745	1742	1745
	2287			
		2725	2715	2874
	3215	3402	3373	3346
	3705			3620
				4021

Summary

1. The absorption spectra of phenoltetrachloro-, *o*-cresol-, and *o*-cresoltetrachlorophthaleins are discussed in their relation to that of phenolphthalein. Evidence is presented to support the view that the absorption of triphenylmethane compounds is due primarily to the joint effect of the three phenyl nuclei and not to the central methane carbon atom.

2. A consideration of the absorption spectra of phenolsulfonephthalein and *o*-cresolsulfonephthalein in neutral aqueous and ethanol, and in sulfuric acid solutions, leads to the conclusion that they possess the inner salt structure in ethanol solution but the quinoid hydrate in aqueous solution.

3. The absorption spectra of these sulfonephthaleins in weakly alkaline solutions bring out the progress of hydrolysis of the dibasic salts at low concentrations. The implications of this fact with respect to their use as indicators are pointed out.

4. In concentrated alkaline solutions, both phenolsulfonephthalein and *o*-cresolsulfonephthalein are converted largely into the colorless tribasic salts of the carbinolcarboxylic acid, although the reaction proceeds very much more rapidly with the former.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

DI-NORMAL-BUTYL ETHER AS A SOLVENT FOR THE GRIGNARD REAGENT

BY C. S. MARVEL, A. T. BLOMQUIST AND L. E. VAUGHN

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The need for a solvent with a higher boiling point than that of diethyl ether for the preparation and use of the Grignard reagent has long been felt. The low boiling point of diethyl ether with the consequent loss of it in handling and danger of the formation of explosive mixtures of its vapor and air has limited the use of the Grignard reagent in commercial work to very rare cases. Numerous papers describing the use of higher aliphatic ethers, various phenyl ethers and high boiling hydrocarbons have appeared in the literature.[1]

It seemed likely that a suitable substitute for diethyl ether would be di-*n*-butyl ether, which has occasionally been used as a solvent in the Grignard reaction. This ether may be prepared in a pure condition easily and cheaply fron *n*-butyl alcohol and its boiling point is high enough so that it can be conveniently handled without excessive loss due to evaporation. Furthermore, distillation alone gives an ether free from moisture and butyl alcohol, thus avoiding the difficulties met in the purification of ordinary ethyl ether. While it has been suggested as a solvent in this reaction, there is very little information in the literature concerning the yields of the Grignard reagents from different halogen compounds or of the yields of products that may be obtained from Grignard reagents in this solvent. Gilman and McCracken[1] report a yield of 55.9% of phenylmagnesium bromide from bromobenzene and magnesium in di-*n*-butyl ether.

The present investigation has shown that the yields of the Grignard reagent from several typical halogen compounds when di-*n*-butyl ether is the solvent are nearly equal to those obtained in diethyl ether. It has also been shown that in a typical reaction of the Grignard reagent, such as that with carbon dioxide, as good a yield of product can be obtained in di-*n*-butyl ether as when diethyl ether is used. For a reaction such as that between the Grignard reagent and ethylene oxide, where an elevated temperature is needed to complete the reaction, di-*n*-butyl ether is more

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[1] A review of this topic is given in a recent paper by Gilman and McCracken, *Rec. trav. chim.*. **46**, 463 (1927).