the solution has been boiled, if it is so desired, the coal may be removed by a glass rod with a hooked end which passes through the glass hook in the coal. One or two pieces about 1 cm. cube are better than many smaller pieces. As powdered anthracite coal has almost no effect, the specific and unusual properties of hard coal in this regard must be due to its structure in the mass. E. C. KENDALL.

MAYO FOUNDATION,
ROCHESTER, MINN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF FOREST PRODUCTS, UNIVERSITY OF WISCONSIN.]

ON THE QUINONE-PHENOLATE THEORY OF INDICATORS. ON THE REACTIONS OF PHENOLSULFONPHTHALEIN, AND ITS BROMO AND NITRO DERIVATIVES, AND THEIR MONOBASIC AND DIBASIC SALTS.[1]

BY E. C. WHITE AND S. F. ACREE.

Received July 27, 1918.

The quinone-phenolate theory of indicators was brought out fully in 1908 by one[2] of the authors of this paper to explain the striking changes of color produced by the addition of alkalies to solutions of aurine, phenolphthalein and analogous substances. The chief color change was assumed to be merely the transformation of the faint yellow quinone-phenol, $—C(:C_6H_4:O)(C_6H_4OH)$, into the quinone-phenolate salt, $—C(:C_6H_4:O)(C_6H_4OK)$, common to all these substances and absorbing the violet, blue, and green and transmitting the red light. The theory proposed was an attempt to correlate (1) the relations between the constitution and color changes of the rosaniline, aurine, and phenolphthalein salts on the one hand and (2) the mathematical relations of the tautomeric forms and the affinity constants and reaction velocities of the various acid and salt groups on the other hand, as had been done by the application of the mass law and conductivity and reaction velocity measurements to the urazole series.[3]

The work of Friedländer[4] and of Nietzki[5] and his students showed clearly that lactoidal colorless phenolphthalein (I) changes into salts of a colored quinoidal form (II),

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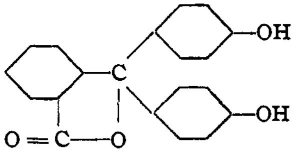
[1] The material presented in this paper and in two earlier articles (THIS JOURNAL, 39, 648 and 40, 1092 (1917)) represents a thesis presented to the Regents of the University of Wisconsin in 1915 by E. C. White, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The experimental work was performed partly in Johns Hopkins University, and partly in the Forest Products Laboratory, Madison, Wisconsin.

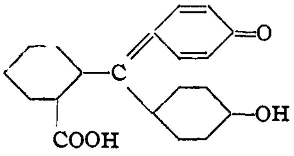
[2] *Am. Chem. J.*, 37, 72 (1907); 39, 155, 528 (1908).

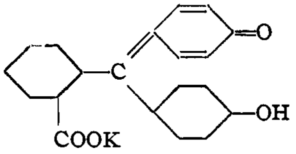
[3] *Ibid.*, 39, 124, 226 (1908).

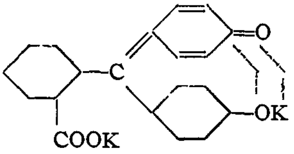
[4] *Ber.*, 26, 172 (1893).

[5] *Ibid.*, 28, 45 (1895); 30, 175 (1897).


(I).


(II).


(III).


(IV).

and thus connected the constitution of these compounds with Ostwald's theory that indicators undergo changes of color because of simple changes in ionization without necessary attendant changes on chemical structure. Hantzsch,[1] and later Stieglitz,[2] developed this view mathematically and used Hantzsch's equation $C_Q \times C_H = K'' \times C_{LH}$ for a tautomeric *monobasic acid.*

Our theory of indicators postulated that a simple change of the *dibasic* lactoidal phenolphthalein into the *monobasic* salt (III) is not sufficient to explain the remarkable colors produced and that the chief source of intense color is due to the presence of both a quinone group and the salt of a phenol (IV). In other words, we treated phenolphthalein as a dibasic acid giving dibasic red salts. Indeed it is hard to understand how anyone could have come to any other conclusion after having read Friedländer's paper showing the analogy between the color changes of aurine and phenolphthalein and their salts, which he assumed to be the *phenol salts* of quinones, $HOC_6H_4C(:C_6H_4:O)(:C_6H_4ONa)$ and $NaOOCC_6H_4—C(:C_6H_4:O)(C_6H_4ONa)$, or after having seen the significance of Nietzki's work showing that the *faint yellow* solutions of the quinoidal carboxyl ester of tetrabromo-phenolphthalein $(C_2H_5OOCC_6H_4)C(:C_6H_2Br_2:O)-(C_6H_2Br_2OH)$, gave the *intensely blue* potassium and silver quinone-phenolate salts $(C_2H_5OOCC_6H_4)C(:C_6H_2Br_2:O)(C_6H_2Br_2OK)$. Notwithstanding these facts, there had been necessarily much confusion and lack of logic and vision in attacking these problems, and it must be realized that there is still great uncertainty concerning many of the dyes used today. Even with the above mentioned aurines, we realized that it was not certain whether the mono- or dibasic salts, or both, give the intense colors, and much interesting light has been shed on this by Paŭlŭs, Schaeffer and Jones. Even though we used as evidence for the theory the intense colors of the ester salts of phenolphthalein discussed above, and those described

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[1] *Ber.*, **39**, 1090 (1906).

[2] THIS JOURNAL, **25**, 1112 (1903). These ideas were abandoned after the appearance of our paper in 1908.

by Green,[1] yet we realized[2] that the intense color might arise from mono- and dibasic salts formed by saponification of the ester group. Meyer[3] and Spengler thought that they *proved* that the deeply colored salt of phenolphthalein is *dibasic* because they found that phenolphthalein dissolves as a *red solution* in approximately two molecules of alkali. The real lack of *proof* in such a case is seen at once when we recall that Slagle[4] and one of us found wide variations in the amount of alkali required to dissolve various indicators and derivatives, the results depending on the solubility and hydrolysis constants. Another example of the inconclusive nature of Meyer's evidence is shown by the fact that phenolsulfonphthalein dissolves in one molecule of dilute alkali as a *yellow monobasic* salt which, however, *looks red* if there is a slight excess of alkali as in Meyer's experiments: in such a case one would incorrectly draw Meyer's conclusion that the solution of the *mono* alkali salt of phenolsulfonphthalein is *red*, whereas it is really *yellow*. In other words a *red mono-* or other salt might have been mixed with the *apparent* dibasic salt which Meyer made, just as *dibasic* sodium sulfate can be colored with a small trace of dye. Baeyer developed his once widely accepted carbonium valence theory on the wrong idea that *p*-oxy-diphenylphthalide in alkaline solutions has a *red color*, which he afterwards found was really caused by a trace of phenolphthalein present as an impurity. Even with all this mass of evidence made uncertain by the possible presence of colored impurities in these compounds, and with the uncertainty whether there must be a *second* ion in combination with the quinone-phenolate salt and its ion, we thought that certainly the quinone-phenolate theory was worthy of investigation. What was most needed was the preparation of a series of *yellow monobasic salts*[5] and *red dibasic salts* of *pure* compounds of the phenolphthalein type, and these we have now made in the phenolsulfonphthalein series, and are studying extensively by the use of spectrophotometric methods and the hydrogen electrode.

Not only was the quinone-phenolate group $—C(:C_6H_4:O)(C_6H_4\overset{-}{O}\overset{+}{K})$ thought to be deeply colored but it was pointed out that the intensely colored double compounds discovered by Jackson[6] when he mixed quinones

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[1] *Ber.*, 40, 3724 (1907).

[2] THIS JOURNAL, 38, 2774 (1916).

[3] *Ber.*, 38, 1318 (1905).

[4] *Am. Chem. J.*, 42, 115 (1909).

[5] Although the yellow carboxyl esters of phenolphthalein, $ROOCC_6H_4C(:C_6H_4:O)$-(C_6H_4OH), have been isolated, the corresponding yellow carboxylate salts have not been made. As these must be present in the incompletely neutralized solutions of phenolphthalein and its homologues we expect to measure the concentrations of such mono- and dibasic salts by the spectrophotometric methods which we are now employing.—BRIGHTMAN AND ACREE.

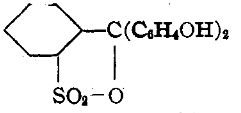
[6] *Am. Chem. J.*, 18, 1 (1894); 34, 441 (1905).

and phenolate salts, for example, $O:C_6H_4:O.2C_6H_5ONa$, may also be present in solutions of the dibasic salt (IV) of phenolphthalein and analogous substances, a fundamental relation overlooked by those acquainted for years with Jackson's work. Whether the combination of the quinone with the phenolate ion or with the nonionized phenolate salt is chiefly responsible for the color change was left for future work.

Equations were developed to show that the "apparent" affinity constants of the indicators involved the equilibrium constants of the different tautomeric forms, and the ionization constants of both the carboxyl group and the phenol group, as had already been proved experimentally with the urazoles. Contrary to the views of Hantzsch and Stieglitz, that a *large* affinity constant for the *carboxyl* group would cause a *greater* tendency to produce the red color or red salt, our equations showed that the addition of a small fraction of a mol. of alkali to a strongly acid carboxyl group would cause the formation of a *greater* amount of the faint yellow carboxyl salt and hence *less* of the (dibasic) phenol salt of such carboxyl salt and *less* intense color. At that time we had developed and applied to the urazoles the equations for only *monobasic tautomeric acids*, but we pointed the way[1] for the extension of these methods to dibasic acids when we could take up the quantitative study of this indicator theory. The equations covering fully the complete theory have now been developed by Birge and Acree and applied extensively in work soon to appear. This theory and our equations have meanwhile been accepted and developed further for special cases in the last few years by Wegscheider, A. A. Noyes, Rosenstein, Biddle, Willstaetter, Bjerrum, Jones, Schaeffer and Paulus, Lubs and Clark, and Cain.

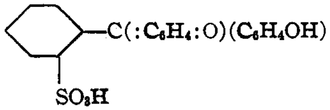
Theoretical Discussion of the Sulfonphthalein Series.

Owing to the necessity for preliminary work on the theory that both the ions and molecules of electrolytes are chemically active, which had to be completed before we could explain the reactions of alkyl halides with salts of indicators, the quantitative study of the quinone-phenolate theory of indicators was delayed until the investigations on the color changes produced by the addition of alkalies to phenolsulfonphthalein and its derivatives were taken up in 1914–15 in understanding with Professor Remsen,[2] who first developed this group in 1890.



Colorless lactoid

(V).



Yellow quinoid acid.

(VI).

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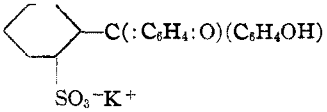
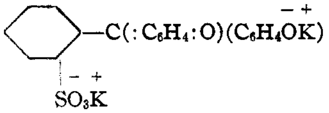
[1] Acree, *Am. Chem. J.*, **39**, 528, 540, 542 (1908).

[2] *Ibid.*, **20**, 257 (1898); **25**, 201 (1901).



Yellow quinoid salt.
(VII).



Intense red quinone-phenolate salt.
(VIII).

The sulfonphthaleins were chosen for further work because it seemed probable that they would yield definite monobasic and dibasic salts and hence give final crucial evidence that the chief cause of the intense color in alkaline solutions is due to the dibasic quinone-phenolate salt (IV) and (VIII), and that the monobasic salt (III) and (VII) postulated formerly by others as a deeply colored salt, would prove to have only a faint yellow color arising from the quinone, in accordance with our theory. These salts were prepared about 4 years ago and since we have now completely substantiated the theory by spectrophotometric methods the work will now be described. The properties of the sulfonphthaleins are almost ideal for a study of this kind. In the first place they are soluble in both water and alcohol, like most sulfonic acids, and unlike the phenolphthaleins. In the second place, the substances are colored in the solid state and in solution and would seem to exist in part at least in the quinoidal condition (VI). This fact reminds us of the deep color shown by fluorescein and eosin, which show a decided contrast to phenolphthalein, which is colorless in the solid state and in solution. If the colored phenolsulfonphthalein exists appreciably in quinoidal form in solution, the fact should be demonstrated readily not only by the color changes but especially by the affinity constants of the sulfonic acid and of the phenol groups as determined by conductivity methods,[1] the hydrogen electrode, catalytic methods, and colorimetric or spectrophotometric[2] methods. A glance at the Formulas V and VI shows that in V we have two phenol groups which are certainly very weak acids. In Formula VI we have a sulfonic acid and a phenol within the same molecule. The sulfonic acids are very strong acids, approaching the mineral acids in affinity constants, and the direct measurement of the conductivities of the solutions of the phenolsulfonphthaleins and the use of the ionic velocities found for such substances should, therefore, give us some measure of the relative per cent of (V) and (VI). This is in decided contrast to the fact that the carboxyl groups of solutions of phenolphthalein, fluorescein, and eosin give so few ions and the conductivities are so small that this direct method can not be used. The conductivities of phenolsulfonphthalein at various concentrations have been used[3] as a direct measure of the per cent. of the quinoidal form in the solution and these results have been verified to some extent by

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[1] White and Acree, THIS JOURNAL, 39, 648 (1917).

[2] White and Acree, *Ibid.*, 40, 1092 (1918).

[3] White and Acree, *Loc. cit.*

corresponding measurements by the use of the hydrogen electrode, and spectrophotometric[1] data for the free acid and its mono- and dibasic salts. Since the lactoidal phenolsulfonphthalein is doubtless colorless, the yellow color given by the monobasic salt (VII) and that given by solutions of the free acid could also be used as a measure of the per cent. of the quinoidal form in equilibrium with the colorless lactoidal substance.

The addition of alkalies to solutions of the sulfonphthaleins and the isolation of mono- and dibasic salts has allowed us to differentiate between the colors and spectra of the monobasic[2] salt (VII) and the dibasic salt (VIII) and has given evidence which has decided beyond question whether the monobasic salt or the dibasic salt is responsible for the intense color changes. A consideration of the affinity constants[3] of the sulfonic acids, about 10^{-1}, and of the phenols about 10^{-8} to 10^{-10}, makes it clear that the addition of an alkali to a solution of a mixture of the quinoidal and lactoidal phenolsulfonphthalein would result in the production of practically only the sulfonate salt in the first stages of the titration and that only toward the end of the introduction of one molecule of alkali would the partition of the alkali between the remaining free sulfonic acid and the entirely free phenol result in the production of appreciable quantities of the intensely colored dibasic salt. If the yellow color and spectrum of the solution of the phenolsulfonphthalein arise merely from the presence of the quinone group, uncombined with appreciable amounts of ionized or nonionized phenols, the monobasic salt (VII) should have practically only the same yellow color, which would change to an intense red only after the addition of sufficient quantities of alkali to neutralize a part of the phenol group in (VII) and allow the formation of the quinone-phenolate salt and the intensely colored double compound (IV) and (VIII) arising from the union of the quinoidal group with the phenolate ion or the nonionized phenolate salt. Since it requires 0.85–0.95 mol of alkali to change the yellow acid noticeably into a red salt, whose concentration increases until 2 or more mols of alkali are added, the evidence is fortunately so conclusive that there is no doubt that the monobasic salt (VII) is yellow like the free acid and is only faintly colored in comparison with the intensity of the color of the deep red dibasic salt (VIII); and the absorption spectra substantiate this evidence.

The comparison of the colors of the *free* phenolsulfonphthalein with those given by the *free* tetrabromo and tetranitro derivatives gives us the much needed proof that the chief source of the intense

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[1] White and Acree, *Loc. cit.* and data soon to be published by Guy, Birge, Brightman, Hopfield, Meacham and Acree.

[2] White and Acree, *Science*, **42**, 101 (1915); THIS JOURNAL, **40**, 1092 (1918).

[3] Lubs and Acree, THIS JOURNAL, **38**, 2772 (1916).

color is a combination of the quinone with the phenolate *ion*. If the view were correct that the deep color of phenolphthalein comes from a monobasic carboxyl salt, it follows at once that a solution of phenolsulfonphthalein, with a high conductivity arising from the highly ionized sulfonic acid, should have a deep red color corresponding to the color of the red solution produced by the addition of two molecules of alkali. The facts are against this hypothesis, as the solution is yellow, because of the quinone group. If, on the other hand, the theory is correct that the solution becomes deeply colored only after the formation of *quinone-phenolate ions*, the addition of bromo or nitro groups to the phenol groups should (and does) increase the ionization and conductivity[1] of the phenol and hence causes the solutions of tetrabromo- and tetranitro-phenolsulfonphthalein to have much more of the corresponding blue and red colors given by the dibasic salts. Furthermore, the addition of hydrochloric acid to solutions of the free tetrabromo- and tetranitro-phenolsulfonphthalein should suppress the ionization of the phenol groups and hence change the intense blue and red colors to the faint yellow of the nonionized quinone phenols, which become ionized and deeply colored again when the acid is neutralized with alkalies or diluted with water. The bromophenol groups of the tetrabromo-phenolsulfonphthalein are not as highly ionized as are the nitrophenols and we find that the concentrated solutions show less of the blue. which comes out strongly on diluting the solution or adding alkalies, The nitrophenol groups, however, are much more highly ionized and give enough quinonephenolate ions to form an intensely red color which is very little accentuated by the addition of alkalies to deep layers of the solution studied. The addition of considerable hydrochloric acid suppresses the intense red to the yellow of the quinone-phenol. This yellow color changes into the red again when the solution is diluted with water or neutralized with alkali. Spectroscopic evidence favoring these views has already been published by us and the other descriptive matter is presented in this article.

The sulfonphthaleins are particularly adapted to this study for another reason. Although there is much left to be desired concerning the solubility of these substances, which we shall try to increase by the introduction of more sulfonic acid groups,[2] they are much more soluble in water and in alcohols than are the phenolphthaleins, fluoresceins, aurines, and analogous substances. It is easy to prepare 0.001 N solutions of phenolsulfonphthalein and of its tetrabromo and tetranitro derivatives, and

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[1] THIS JOURNAL, 39, 648 (1917).

[2] This method of increasing the solubility of dyes and indicators by introducing sulfonic acid groups has been emphasized in lectures on dyes for a number of years and will be used as widely as possible, especially in the aurine and phenolphthalein series which are sparingly soluble in water.

Lubs has found thymolsulfonphthalein and its dibromo derivative to be even more soluble. It is, therefore, much easier to measure the colors and affinity constants of the sulfonphthaleins directly than can be done with the phenolphthaleins and this fact makes it much easier to study the changes in color and in affinity constants produced by substituent groups in the benzene sulfonic acid grouping and in the phenol groups. It is possible to introduce negative chloro, bromo and nitro groups, or basic amino or substituted amino groups, or neutral alkyl groups, or acid phenol and sulfonic acid groups, into both the benzene sulfonic acid and the phenol groups of the sulfonphthaleins and obtain a large number of homologues and derivatives of these substances having a wide range of "effective" affinity constants and useful hydrogen ion concentration ranges. This part of the synthetic work is now being prosecuted as rapidly as possible by us[1] and also by Professor Orndorff, who has reached an understanding with us and has begun work along similar lines involving the sulfonphthaleins. The measurement of the "effective" affinity constants of the sulfonphthaleins by both the hydrogen electrode and by very accurate spectrophotometric methods involving studies of "salt effects" was proposed by one of us and extensive investigations, partly completed, are under way.

Experimental.

Preparation of the Acid Ammonium Salt of Orthosulfobenzoic Acid.—This substance, which is the starting point in the preparation of phenolsulfonphthalein, is prepared by the hydrolysis of saccharine. 400 g. of saccharine is suspended in 6 or 7 liters of water to which 500 cc. of conc. hydrochloric acid has been added. The mixture is boiled until all the saccharine has been dissolved, and water is added to replace that lost by evaporation. The commercial saccharine available at present is very pure (ours was obtained from the Monsanto Chemical Works, of St. Louis) and does not deposit the *p*-sulfaminebenzoic acid present as impurity in the material used by Remsen and his students. After solution of the saccharine the liquid is evaporated to about 600 cc., with constant stirring when the volume becomes small. On cooling, most of the acid ammonium salt crystallizes out.

Preparation of the Anhydride of O-sulfobenzoic Acid.—This substance has been variously prepared—by heating the acid, by distilling the acid with phosphorus pentoxide, and by the action of chlorinating agents on the acid salts. The first method is unsatisfactory, for the acid loses its water with great difficulty. The second method also is unsatisfactory, because of the bulk of the pentoxide needed when any considerable quantity of the anhydride is to be prepared, and also because the dehydration

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[1] See Davis and White, *J. Urology*, 2, 107 (1918), for the synthesis of a number of important compounds in the sulfonphthalein, phenolphthalein and other series.

is accompanied by excessive charring. The distillate of the anhydride, moreover, is likely to be dark colored, owing to volatile impurities carried over with it. Both these methods are also open to the objection that the free acid is hard to prepare.

The most satisfactory method for the preparation of the anhydride involves the use of thionyl chloride. After we had developed the use of this reagent, which we have applied extensively, we learned that Cobb[1] had used this reagent on the acid potassium salt, and obtained a yield of 80% of the anhydride. The action of the thionyl chloride seems to be confined entirely to the carboxyl group. We have modified this method somewhat, and have obtained nearly theoretical yields, even though the method involves the extraction of the anhydride by means of benzene. We used the acid ammonium salt instead of the potassium salt, and found it unnecessary to use the large amounts of thionyl chloride recommended by Cobb. Enough of the chloride is used just to wet the salt thoroughly. The salt must be finely powdered. The mixture, under a reflux condenser, is heated on the water bath for 3 hours; the excess of the chloride is distilled off *in vacuo*, a small amount of the anhydride being carried along. The residue, consisting of the anhydride and ammonium chloride, forms a hard cake, and the flask must sometimes be broken in order to remove it. It is broken up and extracted with dry benzene. The use of the usual paper thimble is not permissible, as the paper chars badly and contaminates the product. The benzene solution darkens somewhat as the extraction proceeds, but on cooling it deposits beautiful, colorless crystals of the anhydride. Typical preparations gave the following yields:

1. 50 g. acid salt and 80 g. thionyl chloride gave 30 g. anhydride, corresponding to a yield of 80%.
2. 150 g. acid salt and 200 g. thionyl chloride were used. 60 g. of the chloride was recovered. 115 g. of the anhydride was obtained, or 91% of the theory.

Preparation of Phenolsulfonphthalein.—As the product of the action of thionyl chloride on the acid ammonium salt should consist of only ammonium chloride and the anhydride, there appeared to be no reason why we should not proceed directly to the preparation of phenolsulfonphthalein by heating such a mixture with phenol, without previously extracting the anhydride. We made many attempts to prepare the anhydride in this way, but were unsuccessful. The mixture, when heated for 24 hours at 130–135°, formed a red, tarry mass, which on boiling with water became oily. The oil dissolved in alcohol to give an orange solution, from which crystals, presumably of benzoic acid, separated. They were recrystallized several times by dissolving in alcohol and reprecipitating with water, and then showed the melting point of benzoic acid. This

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[1] *Am. Chem. J.*, **35**, 502 (1906).

was not changed by mixing the substance with benzoic acid. We made no further attempts to identify the other substances.

By heating the pure anhydride with phenol, formation of the phthalein readily takes place.[1] 108 g. of the anhydride was mixed with 120 g. of phenol, and heated in an oil bath at 130–135°. The mixture fuses to a yellow liquid as soon as the phenol melts. The color soon becomes deep red, and the liquid slowly becomes opaque and viscous. The maximum viscosity seemed to be reached after about 6 hours' heating; 18 hours further heating produced no appreciable difference. The product displayed a green-red irridescence. The excess of phenol was distilled out with steam, the residue washed with water, dissolved in alkali, filtered from a small amount of insoluble matter, and precipitated with acid. It was then washed again and dried.

We made many attempts to find a means of crystallizing this material. It is only slightly soluble in all the solvents that were tried, with the exception of hot phenol and glacial acetic acid. One g. of the material was dissolved in about 50 cc. of boiling phenol. The solution was allowed to cool as far as possible without solidification, and a large amount of ether was added. A very fine, granular powder separated out, which under the microscope showed poorly crystalline form. This powder was thoroughly washed with ether to remove phenol and dried at 120°. It is more soluble in water than the product obtained by precipitation from alkaline solution, and is lighter in color. The difference in solubility is doubtless due to the smaller size of the particles.

Titrations of Phenolsulfonphthalein.[2]—The powder is soluble in water to the extent of 0.03 g. in 100 cc. Solution is extremely slow, and the water must be boiled vigorously. The solution sometimes shows a slight cloudiness, but the amount of material in suspension from 0.03 g. of the phthalein is not weighable.

The alkali used in the titrations was prepared by dissolving sodium in freshly boiled distilled water. The solution was titrated against hydrochloric acid that had been standardized gravimetrically, and was used immediately against the phthalein solution.

From what has been said in the earlier part of this paper, we should expect that when alkali is added to such a phthalein solution the first reaction would be the formation of a monobasic salt, a sulfonate. This reaction should continue until approximately all of the sulfonic acid is

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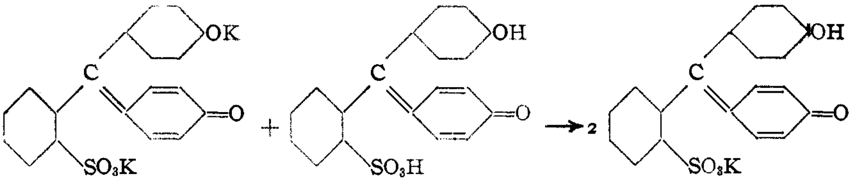
[1] At the suggestion of one of us Mr. L. R. Baldwin has shown that stannic chloride is an excellent condensing agent for the preparation of phenolphthalein from phthalic anhydride and phenol. We expect to use the stannic chloride, and other similar salts easily decomposed by water, widely in the preparation of phthaleins, sulfonphthaleins and similar compounds.

[2] The material used in some of these titrations was kindly furnished by Mr. H. A. B. Dunning of the firm of Hynson, Westcott & Dunning, Baltimore.

neutralized, when the alkali should act on the phenolic hydroxyl and thus form an intensely colored dibasic salt. According to the quinone-phenolate theory, the solution of the monobasic sulfonate should not differ materially in color from that of the free acid; hence, we should be able to add to the solution of the acid approximately one equivalent of alkali without the appearance of a color change, but on further addition of alkali an intense color should appear, due to the formation of the dibasic salt, which contains the quinone-phenolate complex, whereas the free acid and the monobasic salt do not.

A saturated solution of phenolsulfonphthalein in water has an orange color. This is what we might expect from the fact that the dye has a quinone group. If a drop of very dilute alkali is added, an intensely red or purple streamer appears locally, but disappears when the solution is stirred. As more alkali is added the phenomenon is repeated, until at a certain point the solution develops a red tinge which does not disappear on stirring. Two drops of 0.02 *N* alkali, or about 0.10 cc., make this color change marked.

Although we have carefully considered the possibility that some of these color phenomena may arise from impurities in the phenolsulfonphthalein, we believe that the explanation of these color changes is obvious. When a drop of alkali is added to the orange solution, the alkali is *locally* in excess of the phthalein, and some of the intensely colored dibasic salt is formed. As this is stirred up, it is acted upon by the free acid, with the formation of the monobasic salt, which is *not* intensely colored:—



Intensely colored. Yellow. Yellow.

The final appearance of the persistent red color is due to the permanent formation of dibasic salt.

The following data show the amount of alkali required to produce the permanent color change. Approximately 0.02 *N* alkali was found to be suitable for the titrations. In the column headed "cc. NaOH, theory" are given the number of cc. of alkali corresponding to one molecular equivalent with respect to the phthalein.

Titrations 1–6, inclusive, were made with material obtained from Hynson, Westcott and Dunning, the others were made with material of our own preparation, 10, 11 and 12 having been crystallized from phenol by the method already described. (Most recent preparations have required 0.93 to 0.95 mol alkali and further purification will be attempted for the very exact spectrophotometric data.—S. F. A.)

No.	Wt. of phthalein.	Vol. of solution. Cc.	Cc. NaOH, theory.	Cc. NaOH found.	% of 1 mol. eq.
1	0.0314	300	4.28	3.75	87.6
2	0.0310	150	4.28	3.73	87.1
3	0.0288	125	3.99	3.43	87.2
4	0.0322	200	4.40	3.77	85.6
5	0.0176	20	2.40	2.10	87.5
6	0.0420	150	5.73	4.97	86.6
7	0.0131	100	1.73	1.51	87.2
8	0.0389	300	5.95[1]	4.76	80.0
9	0.0329	300	5.03	3.96	78.7
10	0.0297	...	4.54	4 11	90.5
11	0.0252	...	3.86	3.49	90.4
12	0.0329	...	5.04	4.41	87.5
				Av.,	86.3

The fact that less than one equivalent of alkali is required is explained as follows: as more and more of the sulfonic acid is neutralized, the ionization of the remaining sulfonic acid is suppressed, and its acidity is, in effect, lowered. When approximately 95% of one molecular equivalent of alkali has been added, there are present about 100 parts of phenol hydroxyl to every 5 parts (*at most*, depending on the purity) of sulfonic acid still unneutralized. Since the ionization of this remaining free sulfonic acid is reduced by the presence of the sulfonic acid salt already formed, the phenol can at this point visibly compete with the sulfonic acid for the alkali. Hence, further addition of alkali results in the formation of the phenolate group, with the consequent appearance of intense color. These figures vary, of course, with the purity of the compound and the substituent groups, as has been shown by Lubs and Acree.[2]

These titrations show, then, that we can add nearly one molecular equivalent of alkali before the appearance of a color change; in other words, the monobasic salt does not differ in color to any appreciable extent from the free acid.

Monopotassium Salt.—We have, moreover, *isolated* monobasic salts of phenolsulfonphthalein, although we are not sure that they are perfectly pure. In every case the color of the *solutions* of these salts is *orange;* the addition of alkali to these solutions produces an *intense purple color,* due to the formation of the dibasic salt. When solid phenolsulfonphthalein is stirred up with enough strong potassium hydroxide to dissolve it, the intense purple color is developed, but if an excess of the phthalein is now added, the solution, on stirring, becomes

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[1] A new standard alkali solution was used in this and succeeding titrations, which accounts for the fact that 8 required a larger *volume* of alkali than did 6, although Sample 8 was smaller than Sample 6.

[2] Lubs and Acree, THIS JOURNAL, 38, 2772 (1916).

orange-red, and more of the phthalein dissolves. Such a solution, in which no more phthalein would dissolve, was filtered, and the rather viscous filtrate was evaporated to dryness on the water bath. The loss of water was slow, especially towards the end of the process. A glassy, brittle, dark-red residue was obtained. The material, after being finely ground in an agate mortar, was dried to constant weight at 120°. It was analyzed for potassium by converting it to potassium sulfate. As the digestion with conc. sulfuric acid was extremely difficult, the material was first ignited in a platinum crucible until the ash was perfectly white; this was dissolved in dil. sulfuric acid, carefully evaporated to dryness, and again ignited. It was found that the ash formed by the first ignition gained practically no weight by the treatment with sulfuric acid; hence it must have consisted almost entirely of sulfate.

Potassium salt, 0.1510, 0.3877. K_2SO_4, 0.0327, 0.0821.
Calc. for $C_{19}H_{13}O_5SK$: K, 9.98. Found: 9.71, 9.50.

Although the potassium content is a little low for the monobasic salt, there is probably a trace of the dibasic salt present also, for the color of the solution of the substance, while distinctly orange, is noticeably deeper than that of the free acid or of a solution of the free acid to which as much as 75% of one molecular equivalent of alkali has been added. When we consider how intensely colored the dibasic salt is, we see that a very small amount of it would affect the color of the monobasic salt very considerably. However that may be, the color of the product is so far different from that produced when more alkali is added to it that there can be no doubt as to the wide difference between the colors of the monobasic and dibasic salts.

In accounting for the low potassium content, we must consider that phenolsulfonphthalein is somewhat soluble in water, and the method of preparation of our monobasic salt permits the solution of a certain quantity. This lowers the potassium content of the product. The substance is, then, most likely contaminated with small amounts of dibasic salt and of free acid. The coexistence of the latter two would not be surprising, for we have the same condition when there has been added 86 to 95% of one equivalent of alkali in the titrations already described.

The monobasic salt is readily soluble in water and in alcohol, but insoluble in ether. If ether is added to the alcoholic solution an emulsion is formed, and on standing the salt forms a sticky mass on the sides of the vessel, and does not crystallize.

Mono-silver Salt.—When a water suspension of silver oxide and phenolsulfonphthalein is shaken up a purple color develops at first. If an excess of silver oxide is present, the purple color (dibasic salt) remains for a time, but soon a brown sludge forms, which is so finely divided that it passes through filter paper. This is probably due to the reducing effect of the phenol group upon the oxide. If, on the other hand, an excess of the phthalein is used, the purple color gives way to an orange one, and all the silver oxide dissolves. The solution, when filtered and evaporated in the same manner as the potassium salt, gives a material identical in appearance with that salt, and showing the same solubility and color of solution. On ignition it gives metallic silver, although we might expect that silver sulfide or sulfate would be formed from a silver salt of a sulfonic acid. The analyses follow:

Subs., 0.2556, 0.4153. Ag, 0.0591, 0.0958.
Calc. for $C_{19}H_{13}O_5SAg$: Ag, 23.39. Found: 23.12, 23.06.

Mono-calcium Salt.—Calcium carbonate in excess was shaken up with a water suspension of phenolsulfonphthalein and allowed to stand, with frequent shaking, for several days. The orange-colored solution was filtered and evaporated as in the other cases. A sample dried to constant weight was ignited, evaporated with sulfuric acid, and ignited again.

Subs., 0.1085; $CaSO_4$, 0.0210.
Calc. for $(C_{19}H_{13}O_5S)_2Ca$: Ca, 5.6. Found: 5.3.

This salt was similar to the other monobasic salts in every respect.

Pyridine Salt.—Phenolsulfonphthalein readily dissolves in pyridine. An excess of the latter was used, the solution was filtered and evaporated on the water bath. (The use of an excess of the dye gives a viscous mass from which the excess cannot be filtered.) The salt formed a soft, tarry mass, whose solution resembled in color that of the other salts. When heated to 110–120° it became hard and dry, but still smelt of pyridine. This odor did not disappear even when the salt was allowed to stand over sulfuric acid in a vacuum, and the attempt to remove the free pyridine by heating the material at 120° for a long time resulted in decomposition.

An attempt was made to prepare a pyridine salt by allowing the phenolsulfonphthalein to stand over pyridine in a desiccator. The substance attracted much pyridine, finally forming a liquid mass like that obtained in the previous experiment.

Ammonium Salts of Phenolsulfonphthalein.—These salts were prepared by the action of dry ammonia gas upon weighed quantities of the sulfonphthalein. The ammonia was generated by placing a mixture of lime and ammonium chloride in a desiccator, which also contained over this mixture a dish holding a large amount of sodium wire. The sulfonphthalein changed from a red to an almost black color very soon after it was placed in the atmosphere of ammonia, and this dark material dissolved in water with the intense purple color characteristic of the *dibasic* salt. When the dark material was allowed to stand in the air or over sulfuric acid, it gave off ammonia and slowly changed color back to the red of the original phthalein. This red material was evidently the **mono-ammonium** salt, for it was readily soluble in water, giving an *orange* solution, and on analysis gave the proper per cent. of nitrogen.

These changes are readily explained. When the phthalein is in the presence of excess of ammonia, a *dibasic* salt is formed, which is intensely colored and gives intensely colored solutions. It contains an ammonium *sulfonate* group and also a ammonium *phenolate* group. We should expect the former to be very stable, and the latter to be stable only in the presence of ammonia. Indeed, we might predict that the extent to which the ammonium phenolate would break up into the free ammonia and the phenol residue would depend upon the temperature and the pressure of the ammonia in the atmosphere in which the salt was placed. If it was placed over sulfuric acid, the ammonia given off would be continuously absorbed by the acid, and all of the ammonium phenolate would finally be decomposed. A monobasic ammonium sulfonate should be left, and according to the quinone-phenolate theory it should and does dissolve in water with approximately the same color as the free phthalein.

The quantitative results obtained show clearly that the dark material is the dibasic salt, and that the red material formed again when the dibasic salt is placed over sulfuric acid is the monobasic salt. Weighed samples of the phthalein were placed over the ammonia mixture and allowed to stay there until the maximum gain in weight was reached. Standing overnight was sufficient. It was found that the samples lost in weight slightly after this period; this loss is not surprising in view of what was said above in regard to the equilibrium conditions existing between the ammonium phenolate and its decomposition products. After the maximum weight had been thus attained, the sample was transferred to a sulfuric acid desiccator and allowed to stay there until minimum weight was attained. All weighings were made by quickly transferring the material to a tightly closed weighing glass, as the salts are very hygroscopic. Minimum weight was reached after standing over sulfuric acid for about two weeks.

Subs., (phenolsulfonphthalein) 0.1962, 0.2814. Gain, NH_3, 0.0190, 0.0270.
Calc. for $C_{19}H_{12}O_5S(NH_4)_2$: Gain, 9.60. Found: 9.68, 9.59.

After standing over sulfuric acid these gains were reduced to (I) 0.0100 g. or 5.09%; (II) 0.0137 g. or 4.86%. Monobasic NH_4 salt requires 4.80%.

In order to study the effect of substituent groups on phenolate formation, and consequently on color, we have prepared bromination and nitration products of phenolsulfonphthalein. The bromine and nitro groups are strongly negative, and their introduction into the phenol residue in ortho position with reference to the hydroxyl increases the acidity of the phenol. We should therefore expect a more ready formation of intense color than in the case of phenolsulfonphthalein.

Tetrabromo-phenolsulfonphthalein.—Remsen and Sohon[1] obtained a dibromo substitution product by the action of bromine on phenolsulfonphthalein, and were unable to obtain a tetrabromo derivative even when sufficient bromine was present. The experiments of Remsen and his students with other sulfonphthaleins also led to the preparation of compounds with only two substituted bromine atoms. We have, however, obtained a well defined tetrabromo substitution product. Evidently the experimental conditions used in the excellent work of Remsen and Sohon differed from ours in an unknown way.

In one experiment 7 g. of sulfonphthalein, 5 cc. of bromine and 150 cc. of acetic acid were used. The solid material did not dissolve even on long standing, but changed over to an orange-colored, well crystallized material. When filtered off, this appeared pinkish. It was subjected to further treatment with bromine under the same conditions as before, and the appearance did not change. The acetic acid—bromine solution from the yellow material was evaporated on the water bath. A dark red, tarry mass was formed. For this reason it is not advisable to use a large amount of acetic acid in the preparation of the tetrabromo derivative; the material contained in solution crystallizes out only very slowly, and attempts to obtain it by concentration invariably result in decomposition.

A much more satisfactory method is the following: Five g. of phenolsulfonphthalein is suspended in 40 cc. of glacial acetic acid. The acid is heated almost to boiling and there is added little by little a solution of 5 cc. of bromine in 20 cc. of glacial acetic acid, while keeping the original mixture just below the boiling point. Evolution of hydrobromic acid begins as soon as the first of the bromine is added. The phenolsulfonphthalein gradually dissolves, and in its place a crystalline precipitate of the tetrabromo derivative settles out. Yield 7.5 g. These crystals are almost colorless, but when they are filtered they acquire a pink color as soon as the acetic acid is drained from them. This color changes to orange, but is removed if the crystals are again moistened with the acid, returning again when the material is drained. This phenomenon does not appear to be one of oxidation and removal of the oxidation product by acetic acid, for it appears when the wet crystals are dried in a current of carbon dioxide. After a time the dry crystals assume a flesh color, which seems to be uniform and which has not changed after keeping for more than two years.

The product thus prepared, and washed free of bromine with acetic acid, is pure, giving the following analysis after drying in the air:

Subs., 0.1464; AgBr, 0.1628.

Calc. for $C_{19}H_{10}O_6SBr_4$: Br, 47.7. Found: 47.3.

The material can be recrystallized from boiling glacial acetic acid, but

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[1] *Loc. cit.*

a large amount of acid is required and solution is slow. A more satisfactory solvent consists of a mixture of acetic acid and acetone, in the latter of which the substance is very soluble. The recrystallized substance showed the same bromine content as did the first crystals.

Subs., 0.1902; AgBr, 0.2115.
Calc. for $C_{19}H_{10}O_5SBr_4$: Br, 47.7. Found: 47.3.

The behavior of this substance when heated in the capillary tube is characteristic. At about 210° a greenish sublimate appears, and the substance becomes a deeper orange in color. This then melts sharply at 270–271°, with decomposition and gas evolution. We intend to investigate this substance further.

Di-ammonium Salt of Tetrabromo-phenolsulfonphthalein.—This salt was prepared in the same manner as was the mono-ammonium salt of phenolsulfonphthalein. It was found that tetrabromo-phenolsulfonphthalein absorbed an amount of ammonia much in excess of that required for a dibasic salt; the product formed by the absorption was allowed to stand over sulfuric acid until minimum weight was reached. The gain indicated a stable *dibasic* salt. This is what we might expect, for the bromophenol is a stronger acid than the phenol of phenolsulfonphthalein, and can therefore hold the ammonia more firmly.

Subs., 0.2472, 0.2526. Gain, NH_3, 0.0141, 0.0126.
Calc. for $C_{19}H_8O_5SBr_4(NH_4)_2$: Gain, 5.1. Found: 5.7, 4.9.

Preparation of Tetranitro-phenolsulfonphthalein.—Five g. of phenolsulfonphthalein is dissolved in 30 cc. of cold conc. sulfuric acid. Solution is slow, and must be aided by shaking. A dark red solution results. Conc. nitric acid is added a little at a time until the precipitate first formed no longer dissolves on agitating the mixture. The solution is then poured into a moderate amount of water (about 100 cc.). A voluminous, bright yellow precipitate separates out. Where the solid is in contact with water a red color appears, but as the red portion is stirred up and comes in contact with acid it becomes yellow. The pasty precipitate is filtered on the pump; if allowed to stand long before filtration it goes over to a colloidal form, and this material cannot be filtered. The precipitate is washed with water. Complete drying by suction is impossible, as the water is held tenaciously. The material is purified by crystallization from boiling acetic acid, or better from a mixture of acetic acid and acetone. The crystals are minute, glistening flakes, which when dry have a canary yellow color.

The substance showed no sharp melting point, slowly passing to a shellac-like material above 200°. It was analyzed for nitrogen by the Kjeldahl method, thiosulfate being used as a reducing agent.

Subs., 0.2653, 0.2494. Cc. 0.0714 N H_2SO_4, 26.7, 27.5.
Calc. for $C_{19}H_{10}O_5S(NO_2)_4$: N, 10.5. Found: 10.0, 11.0.

Di-ammonium Salt of Tetranitro-phenolsulfonphthalein.—This salt was prepared in the same manner as the other ammonium salts already described. Here again the substituted phenol is a sufficiently strong acid to hold ammonia firmly, and a dibasic salt is therefore formed.

Subs., 0.2407, 0.1869. Gain, NH_3, 0.0158, 0.0127.

Calc. for $C_{19}H_8O_5S(NO_2)_4(NH_4)_2$: Gain, 6.3. Found: 6.5, 6.7.

The Color Changes of Tetrabromo-phenolsulfonphthalein and of Tetranitro-phenolsulfonphthalein, and their Interpretation.—(*a*) Tetrabromo-phenolsulfonphthalein is soluble in water to the extent of at least 0.7 g. per liter. A solution of this concentration has a dark, dirty red color. *This changes to an intense blue when alkali is added to the solution, or when the solution is diluted.* If alkali is added to a *very dilute* solution of tetrabromo-phenolsulfonphthalein, already deep blue, *no noticeable change in color takes place.*

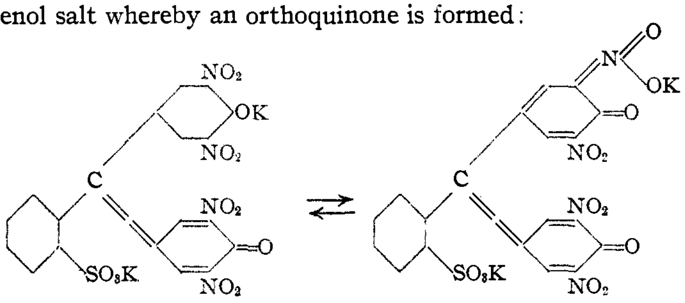
The addition of any strong acid to a blue solution of tetrabromo-phenolsulfonphthalein causes a gradual change of the color through various lighter shades, and the solution finally becomes deep yellow.

These color phenomena can all be explained on the assumption that it is the *quinone-phenolate ion* (or the complex that the phenolate ion forms with the quinone group) that is the cause of intense color. The substitution of bromine atoms in ortho position to the phenol hydroxyl of phenolsulfonphthalein increases the acidity of the phenol; hence there is an appreciable formation of phenolate ions in a water solution of the tetrabromo-compound, whereas the phenol of the unbrominated compound is so weak an acid that it gives no appreciable quantity of phenolate ions, and the solution is *not* intensely colored, but becomes so only on the addition of alkali. The extent of the ionization of the bromophenol would be increased by dilution of the solution or by the addition of alkali, hence either of these processes intensifies the color of the solution.

The addition of acid to a blue solution of tetrabromosulfonphthalein *gradually* changes the color to yellow because the ionization of the phenol is suppressed more and more as the hydrogen ion concentration increases.

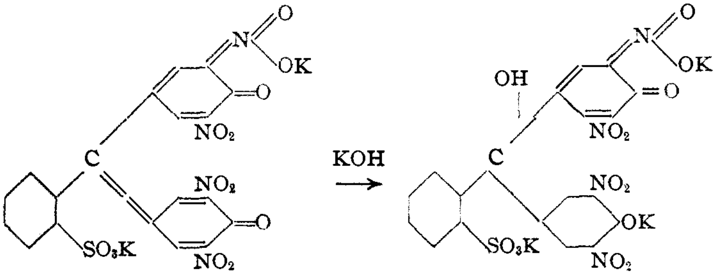
(*b*) Tetranitro-phenolsulfonphthalein, a yellow powder, dissolves in water (or alcohol) with the production of a beautiful purple-red solution. The color resembles that of a solution of phenolsulfonphthalein to which two molecular equivalents of alkali have been added. Evaporation of the solution of the tetranitro compound gives back the yellow powder. If two equivalents of alkali are added to the solution, *absolutely no visible change in color takes place in deep layers. The solution shows precisely the same absorption band before and after the addition of alkali in a 30 cm. tube.* As these deep layers of the acid give enough quinone-phenolate ions to absorb the green light, thin layers will be used in the spectrophotometric work. A solution of the *tetrabromo* compound of the same normality *does* show a change in color when alkali is added. This is true because a solution of the bromo compound contains a considerable amount of *undissociated* phenol and much less of *phenolate ions*, and the blue, violet and green is not all absorbed; the addition of the alkali causes a further conversion of the phenol molecules into these ions, and hence greater absorption. The dinitrophenol group of the tetranitro-phenolsulfonphthalein is a much stronger acid than the corresponding dibromophenol, and is therefore more fully dissociated in solution. It therefore requires the addition of much more acid to the tetranitro than to the tetrabromo derivative to suppress the ionization of the phenols and change the deep color back to yellow. Consequently, the addition of alkali to a solution of the nitro compound does not so greatly increase the concentration of the phenolate ions, and there is therefore no appreciable increase in the intensity of the color in the deep layers which already absorb practically all the green.

If a considerable amount of alkali is added to the solution of the nitro compound the color changes from purple-red to yellow. Addition of acid brings back the intense purple-red color. It seems likely that this fading may be connected with two processes: (1) a rearrangement of the nitrophenol salt whereby an orthoquinone is formed:



Intense red. Yellow.

and (2) with a hydration effect whereby the paraquinone is destroyed with the formation of a tribasic salt:[1]



Yellow.

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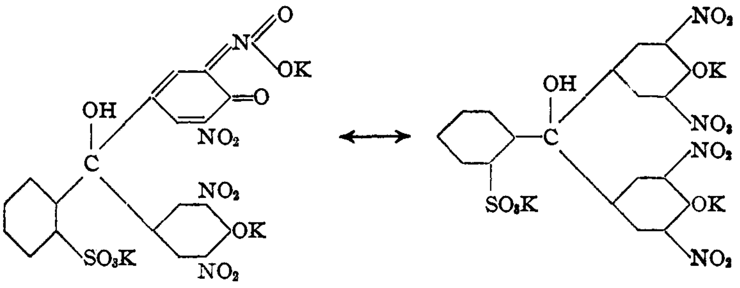
[1] Cf. Green and Perkin, *J. Chem. Soc.*, **85**, 398 (1904); Kober and Marshall, This Journal, **33**, 1779 (1911).



Yellow(?). Colorless.

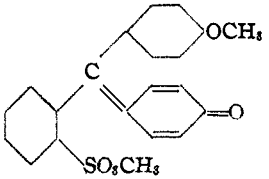
The second nitrophenolate thus formed might rearrange into a second orthoquinone, and the yellow color of the solution could then be accounted for by the presence of two orthoquinones, which are not intensely colored. It is obvious that the bleaching by alkalies may be a very complicated process, and that the addition of acid to the solution simply reverses these reactions.

When a drop or two of strong hydrochloric acid is added to a solution of the free tetranitro compound no appreciable color change takes place. As more acid is added the color fades to yellow. *Addition of water to the yellow solution brings back the purple-red* color. The hydrochloric acid suppresses the ionization of the nitrophenol, hence the color fades. The ions and the color return when the solution is diluted.

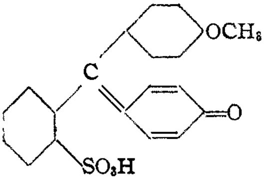
Action of Diazomethane on Phenolsulfonphthalein.—The phenolsulfonphthalein was suspended in ether and treated with diazomethane until the powder had become yellow and no longer gave any trace of color with alkali. Only a small part of the yellow material was found to be in solution. This slowly separated out in the form of minute crystals, which melted sharply at 158°. Further evaporation of the solution did not give more of the crystalline material; a dark red, tarry substance was left when the mother liquid was evaporated to dryness. The crystals did not change their melting point when they were recrystallized from carbon tetrachloride, so they were assumed to be pure. The bulk of the yellow powder, which had not dissolved in the ether, showed a melting point of of 150–154°. Recrystallization gave a product which melted sharply at 158°. The mother liquor from this substance usually deposited nothing until it had been evaporated to complete dryness, when the dark red material mentioned above was left. Attempts to crystallize this red material failed.

The substance which melts at 158° is insoluble in cold water and in cold alkali solution, even though it be very concentrated. When boiled with water it slowly dissolved, giving a deep yellow or orange solution, which gave no color on addition of alkali. On boiling some of the substance with alkali it dissolved very slowly, and the solution developed a pale red tinge. The substance dissolved readily in conc. hydrochloric acid with a deep red color. Green and King[1] prepared an ester-hydrochloride of phenolphthalein which was deep red, whereas the ester itself was yellow.

The color of the substance indicates that it is a *quinoid* ester. Its insolubility in cold alkali solutions shows that it cannot be a mono-ester, for such an ester would have one free acidic group and would be soluble in alkali. It is to be assumed for the present that it is a quinoid di-ester of the constitution



and further work now in progress will throw more light on its structure. Such an ester would be the normal product of the action of diazomethane on quinoidal phenolsulfonphthalein. It would be expected that the sulfonic ester would be very readily saponified by alkali and hydrolyzed by water, and that the resulting mono-ester



would be soluble in alkali with approximately the same color as a solution of free phenolsulfonphthalein. The fact is, however, that the di-ester must be boiled with water or alkali to effect solution.

The attempt to determine the amount of sulfur in this compound by Carius' method failed. A colorless, crystalline substance was formed in the tube, and it was not decomposed even after heating for 4 days at 250–300°. The limited amount of the material at our disposal made other analyses impossible.

Action of Diazomethane on Tetrabromo-phenolsulfonphthalein.—The bromine derivative was treated with diazomethane until it no longer gave any trace of blue color with alkali. A bright yellow powder was formed. By recrystallization from benzene a product was obtained which seemed to become semi-fluid between 155 and 160°. This then solidified, a contraction being noted, and the new material, which had a slightly deeper color, melted at 232–234°. Further crystallization from benzene eliminated the change at 155–160°, and the material then melted sharply at

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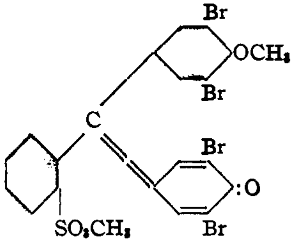
[1] *Loc. cit.*

234–235°. This point was not changed by further crystallization. The pure product was similar to the crude product in solubility and behavior towards alkali. It was insoluble in water and alkali, and even vigorous boiling did not affect the material in any way. It was soluble in alcohol and in acetic acid, very slightly soluble in ether. It is possibly a quinoid ester of the structure



and we are now investigating the constitution further. It seems strange, however, that a sulfonic ester should be stable in the presence of boiling solutions of alkali.

Conclusions.

1. Methods have been described for the preparation of phenolsulfonphthalein, tetrabromo-phenolsulfonphthalein, and tetranitro-phenolsulfonphthalein, and their properties and color changes have been described.

2. Although monobasic carboxylate yellow salts of phenolphthalein have not been isolated, the corresponding monobasic yellow salts of the phenolsulfonphthalein series have been made and described by us and later by Lubs and one of us. These salts have been studied spectrophotometrically and shown to resemble the free acids very closely. They cannot be the causes of the intense color changes.

3. The dibasic intensely colored salts of the phenolsulfonphthalein series have been made by us and by Lubs and one of us and studied extensively spectrophotometrically. They are shown to be the cause of the intense color changes.

4. These dibasic salts have been shown by conductivity, titration and spectrophotometric methods to be practically solely quinone-phenolate salts possessing the characteristic chromophoric group $—C(:C_6H_4:O)(C_6H_4O^-K^+)$, which is also the seat of the color changes in aurine, phenolphthalein and similar substances. The sulfonphthaleins studied give practically no colorless lactoidal salts.

5. The color of the dibasic salts, and of the tetrabromo- and tetranitro-phenolsulfonphthalein, all of which give quinone-phenolate ions, show that the nonionized quinone-phenol, $—C(:C_6H_4:O)(C_6H_4OH)$, is orange or yellow, whereas the quinone-phenolate ion, $—C(:C_6H_4:O)(C_6H_4O^-)$ is intensely colored and is the chief cause of the intense color changes. The

non-ionized quinone-phenolate salt, — $C(:C_6H_4:O)(C_6H_4OK)$, may also be intensely colored, but its concentration is small in dilute solutions.

6. The intense and very sharp color changes in the sulfonphthalein series are far more satisfactory than in the phenolphthalein series because the monobasic salts of the sulfonphthaleins are changed practically quantitatively into the deeply colored quinone-phenolate ion, whereas phenolphthalein gives only about 50% of such deeply colored dibasic ion, the other 50% going over into the colorless lactoidal dibasic ion. The tetrachloro-, tetrabromo-, and tetraiodo-phenolphthalein give only about 1% of the colored, dibasic quinone-phenolate ion, the remainder forming colorless dibasic salts. These facts make the phenolsulfonphthalein series of indicators the best yet discovered. The derivatives described by us, and by Lubs and Clark and one of us, have a wide range of useful *P*H values, show very little of the fading characteristic of the phenolphthaleins and their colors are not greatly disturbed by the "salt effects" which we are studying by the spectrophotometric methods.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE PURDUE EXPERIMENT STATION.]

SOFT CORN—ITS CHEMICAL COMPOSITION AND NITROGEN DISTRIBUTION.

BY GEORGE SPITZER, R. H. CARR AND W. F. EPPLE.

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Introduction.

The large amount of corn (maize) produced in this country makes one of our greatest and most valuable sources of food, and hence the success or failure of the crop in any year is a matter of great economic importance. The failure of considerable of the corn to mature properly during 1918 led to much speculation as to the feeding value of soft corn, or to state it another way, the question "What is soft corn?" was often asked. One publication[1] has answered the question in part by stating that very soft corn contains 65% of water (rare) and ranges down to 25%, which is low enough to allow the corn to be stored in cribs. whereas old corn usually contains about 12% of moisture. It might be inferred from this that soft corn differs from mature (corn) only in the amount of moisture it contains, but the present writers have found characteristic differences in the carbohydrates, proteins and mineral constituents. The idea is prevalent in some localities that soft corn is worthless for feeding purposes, whereas others have succeeded in feeding the wet and therefore often moldy corn to cattle and hogs with profitable returns, no cases of poisoning from the mold having been reported to our knowledge. Thus, evidently, soft corn has a feeding value that, although not to be considered equal to that

[1] Iowa Expt. Sta., *Circ.* 40 (1917).