ON THE THEORY OF INDICATORS AND THE REACTIONS OF PHTHALEINS AND THEIR SALTS.

DISSERTATION

Published @ 2017 Trieste Publishing Pty Ltd

ISBN 9780649190546

On the theory of indicators and the reactions of phthaleins and their salts. Dissertation by Edgar Apple Slagle

Edited by Trieste Publishing Pty Ltd.
Cover @ 2017

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ACKNOWLEDGMENT.

The author takes pleasure in expressing his gratitude to President Remsen, Professor Morse, Professor Jones, Professor Ames, Professor Renouf, Associate Professor Acree and Dr. Gilpin, for instruction in the class room and laboratory.

Especially does he wish to express his sincere gratitude and thanks to Associate Professor Acree, under whose personal direction this investigation has been pursued.

On the Theory of Indicators and the Reactions of Phthaleins and Their Salts

The rapid advance in our knowledge of the constitution and reactions of colored compounds of the aromatic series has made it clear that we must seek the cause of the manifestation of color in some deep-seated change in the molecule itself. The view formerly held that the color of these particular benzene derivatives is a function only of the increase in the molecular weight, or depends upon the introduction of certain elements or groups which tend to produce color, has long been abandoned.

The first important attempt to formulate a theory of color is seen in the hypothesis of O. N. Witt,[1] brought out in 1876, in which he assumed in all colored compounds the presence of certain specific groups (nitro, azo, cyan, etc.) which were thought to be responsible for the color. Witt called these groups *chromophores*. He recognized in some cases the additional influence of certain salt-forming groups (hydroxyl, amino, etc.) which intensify the color of the chromophore

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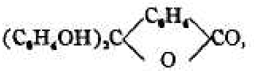
[1] Ber. d. chem. Ges., 9, 522.

and give to the compound the properties necessary in making the dye practically useful. These latter groups were called *auxochromes*.

The quinone theory was first advanced by E. and O. Fischer to explain the colors of the dyestuffs of the rosaniline series and is really an extension of Witt's, which gives a more definite meaning to the term *chromophore*.

In 1889 Nietzki[1] extended the quinone theory, using, however, the modern formula of quinone, to the indamine and azine series. This conception was shortly after extended by Armstrong to include all colored compounds of the aromatic group.

In 1893 Friedländer[2] assigned a corresponding quinone structure to phenolphthalein salts. He accepted Baeyer's formula for phenolphthalein in the free condition,



$$(C_6H_4OH)_2C\left\langle\begin{matrix}C_6H_4\\O\end{matrix}\right\rangle CO,$$

but assumed that an intramolecular change takes place in the molecule in the presence of alkalies which results in the formation of the colored quinone salt,

$$NaOOCC_6H_4C(:C_6H_4:O)(C_6H_4ONa),$$

which he assumed to be analogous to the salts of aurin,

$$(NaOC_6H_4)_2C:C_6H_4:O,$$

and of rosolic acid,

$$(NaOC_6H_4)(O:C_6H_4:)C[C_6H_3(CH_3)ONa].$$

As a proof of the existence of the quinone structure in the salt

$$(KOOCC_6H_4)C(:C_6H_4:O)(C_6H_4OK),$$

he prepared an oxime by treating an alkaline solution of phenolphthalein with hydroxylamine. Friedländer also suggested that phenolphthalein is a dibasic acid and that the salts are dibasic salts, but it remained for Meyer and Spengler[3] to prove

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[1] Organische Farbstoffe, 1st Edition, p. 2.

[2] Ber. d. chem. Ges., 26, 172.

[3] *Ibid.*, 28, 1318.

this by isolating and analyzing the salt $C_{20}H_{12}O_4Na_2$. At about the same time Bernsthen[1] came to similar conclusions in his researches on rhodamine 6 G and suggested that fluorescein exists in the free condition as the lactone compound but has the quinone structure in its salts.

A few years ago another conception of the cause of color was advanced by Baeyer[2] and called by him *halochromy*. He assumed the existence, in colored bodies of the triphenylmethane series, of a peculiar form of valence represented by a wavy bond, $C \sim\sim Cl$, which Baeyer and Villiger called the *carbonium valence*. In this condition carbon was assumed to act as a strongly basic element which brings about the manifestation of color. This theory has recently been given up by Baeyer.

In 1890 Ostwald[3] proposed an explanation of color changes based on the theory of electrolytic dissociation. He assumed phenolphthalein to be an extremely weak acid and consequently but little dissociated; on the addition of an alkali a salt is formed which is largely dissociated, and the red color was thought to be due to the anion. The work on the physical constants of phenolphthalein has shown that a close quantitative relationship exists between Ostwald's theory and color change, yet many facts make it evident that this theory is in itself not able to account for all of the known phenomena. While it is true that the negative ions are colored, the change in color is due to a change in constitution of the compound, the ions having a structure different from that of the mother substance.

In 1903 Stieglitz[4] published a valuable article on the theory of indicators. By the use of (*a*) the evidence on the quinone theory furnished by Friedländer and Nietzki, (*b*) Hantzsch's ideas and equations concerning pseudoacids, and (*c*) Ostwald's conception of the quantitative relationships in the indicator work, Stieglitz came to the conclusion, in con-

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[1] Chem. Ztg., **1892**, 1956.

[2] Ber. d. chem. Ges., **35**, 570, 1156.

[3] Lehrbuch der allgemeinen Chemie, **1891**, p. 462; Scientific Foundations of Analytical Chemistry, 1890.

[4] J. Am. Chem. Soc., **25**, 1112.

sidering phenolphthalein, that (p. 1115) "its red salts are the salts of a carboxylic acid, *not a phenol*, and have the constitution

$$(MOOCC_6H_4)(HOC_6H_4)C : C_6H_4 : O.$$

The strongly chromophoric quinoid complex ($: C_6H_4 : O$) *gives us an explanation of the production of intense color, which is entirely adequate* in view of the laws governing color in organic compounds." After developing the equation

$$C_Q \times C_H = K'' \times C_{LH}$$

for the affinity constant of the phenolphthalein he stated (p. 1122) that "its tendency to produce *the red color* (*the red salt*)[1] is measured by the same constant K''." Hantzsch[2] points out that he too had proposed this theory.

In 1905 Meyer and Spengler[3] published a very important article in which they showed that the colored salts of phenolphthalein are dibasic salts, but they discarded the quinone hypothesis and accepted Baeyer's theory of halochromy.

In May, 1906, Acree and Brunel[4] began an investigation on indicators as a part of their work on tautomerism. It was seen by them that previous theories did not account fully for either the color phenomena or the alkylation reactions of aurin, phenolphthalein, fluorescein, etc., and they began work on these substances from the point of view that the tautomeric mono- and dibasic phenol and carboxyl salts are concerned in the alkylation reactions and in the color phenomena. It was seen, for instance, as had already been surmised by Friedländer,[5] that *the chief source of color in the salts of aurin, phenolphthalein, etc., is not the quinone group* assumed by practically all of the other workers, but *a quinone-phenolate group*,

$—C(: C_6H_4 : O)(C_6H_4ONa);$

$$(KOOCC_6H_4)C(: C_6H_4 : O)(C_6H_4OK);$$

$$(KOC_6H_4)C(: C_6H_4 : O)(C_6H_4OK).$$

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[1] All the italics and words in parentheses are mine for emphasis.

[2] Ber. d. chem. Ges., **39**, 1090. Rohland: *Ibid.*, **40**, 2172.

[3] *Ibid.*, **38**, 1318.

[4] Amer. Chem. J., **37**, 71. See also *Ibid.*, **27**, 118; **31**, 185; **32**, 606; **37**, 361; **38**, 1; **39**, 124, 226; Ber. d. chem. Ges., **35**, 553; **36**, 3139; **37**, 184, 618; **41**, 3199.

[5] Ber. d. chem. Ges., **26**, 172.