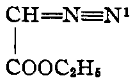
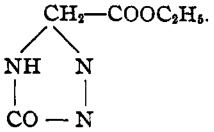


$$\begin{array}{l} CH{=}N{\equiv}N^{1} \\ | \\ COOC_2H_5 \end{array}$$

the substance,



However, we were unable to bring about a reaction here with either cyanic acid or phenyl isocyanate. Furthermore, unsuccessful attempts were made to effect a crisscross addition of phenyl isocyanate on oxalic ester, as the latter substance contains the conjugate system, $O = C — C = O$. At 220–230° the phenyl isocyanate was changed to triphenyl isocyanuric acid. The product, purified by recrystallization from glacial acetic acid, which we find preferable to alcohol, melted at 281°, whereas Wislicenus found the melting point to be 275°.[2]

Calc. for $C_{21}H_{15}O_3N_3$: N, 11.77. Found: N, 11.89.

Finally cyanogen, which contains the conjugate system, $N{\equiv}C — C{\equiv}N$, was passed into boiling phenyl isocyanate without the substances reacting.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

THE MASS ACTION OF WATER ON DYES.

BY WILLIAN M. DEHN.

Received February 27, 1917.

If solutions of the common indicators and other dyes, contained in beakers, are treated with running tap-water, the colors of some of these are changed at certain dilutions. If the original solution was acidic and its color was changed by dilution, more acid will restore the first color. If the original solution was alkaline and its color was changed by dilution, more alkali will restore the first color. Some dyes tolerate only a trace of acids or alkalies in order that they may yield colored solutions which are transformed by dilution; other dyes require much acid or much alkali to yield colored solutions which are transformed by dilution.

Chromoisomerism Produced by Water.

In Weakly Acidic Solution.—If methyl orange, reddened by a trace of acid, is treated with running tap-water, the color gradually changes to a pure yellow; if acid is now added to this dilute yellow solution, some tint of red is restored. However, if methyl orange solutions originally

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[1] Cf. Thiele, *Ber.*, 44, 2522, 3336 (1911).

[2] *Ann.*, 308, 236 (1899).

yellow are diluted, no tint of red can be developed. In other words, the mass action of water changes red helianthine to yellow helianthine, but has no effect on helianthine if it is already in solution in the yellow form.

In Weakly Alkaline Solution.—A red, weakly alkaline solution of cochineal yields by dilution with water a blue color; with more alkali, this blue reverts to the red. If the original cochineal solution was blue no tint of red can be developed by mere dilution—only different shades of blue are obtained.

In Strongly Acidic Solution.—Many of the triphenyl methane dyes as, for example, gentian, crystal or Hofmann violets, etc., require large quantities of acid to yield solutions that are transformed by dilution with water. The alkaline solutions of these dyes are unaffected by dilution.

In Strongly Alkaline Solution.—Picric acid made alkaline with strong alkali easily changes from red to yellow by the addition of water, and back to red by the addition of strong alkali. With dilution all yellow solutions of picric acid remain yellow, even to the limits of visibility.

These experiments and others indicated in the table make evident that some dyes[1] undergo hydrolytic color transformation[2] in acid solution and others in alkaline solution.

From a study of the table, and from other observations made while obtaining the data of this table, it became evident that:

(1) Hydrolytic color transformation is a phenomena common[3] to many dyes. Other dyes[4] not listed in the table were studied in the same manner, but revealed no changes of color when diluted.

(2) Most of the dyes studied, giving positive results, were hydrolyzed in acidic solutions (Table I); some were hydrolyzed in alkaline solutions (Table II); none were hydrolyzed in both acidic and alkaline solutions.

(3) Different dyes were hydrolyzed from varied concentrations of acids or alkalies, that is, different strengths of acids or alkalies were necessary to form solutions which would undergo the color transformations.

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[1] Of course, it is obvious that bicolored dyes and such of these as are easily hydrolyzed are of less value for dyeing, than others not so affected.

[2] It is suggested that typical examples, as methyl orange or magenta in acid solutions and cochineal or logwood in alkaline solution, be tried out by readers who have little time to confirm the experimental observations of this paper.

[3] It is a noteworthy fact that the seven food colors, chosen with such care by the U. S. Government (Food Inspection Decision 76, July 13, 1907) gave negative results except in cases of orange I and indigo disulfonic acid.

Some dyes difficult to characterize by the dilution method may be mixtures of dyes of opposite kind.

[4] Most of the dyes tested were supplied by Badische Anilin- und Sodafabrik. At least one hundred other dyes gave negative results.

TABLE I.—DILUTION EXPERIMENTS.

Name. Dye.	Colors restored by acids. Original color in acidic solutions. I.	Colors restored by acids. Colors in dilute aqueous solutions. II.	Colors restored by acids. Colors restored by acids. III.	In $H_4P_2O_7$. Oily solution. IV.	In $H_4P_2O_7$. Diluted with water. V.
Alizarine	orange-yellow	red, pink	yellow	orange	colorless
Alizarine-SO_3Na	yellow	red	yellow	yellow	yellow
Acid violet ClOB	green	blue	green	red-brown	indigo
Acid violet CBB	green	blue, indigo, violet	green	orange	violet
Aniline blue	green	blue	green	brown-red	blue-violet
Aniline blue, methylene	green	blue, indigo	green	green-black	blue
Aniline brown	orange	yellow	orange	carmine-red	yellow
Aniline green	yellow	green	yellow	orange-red	green
Azolitmin	purple	blue	pink	cobalt red	pink
Chrysoidine RL	red	orange, yellow	orange	carmine-red	orange-yellow
Chrysoidine BTM	red	yellow	orange	carmine-red	orange-yellow
Congo red	blue	red	blue	blue	pink
Cotton red 4B	black	red	black	indigo-blue	colorless
Crystal violet	orange	green, blue, violet	orange-green	orange	violet
Cyananthol gray G	red	blue-black	red	red-brown	bluish
Cyananthol fast green G	green	blue	green	red-brown	green
Cyananthol RT	purple-red	blue	pink	deep purple	blue
Diamine green	orange	yellow, green	yellow	violet	yellow
Diamond green B	orange	green, blue	yellow	red	green
Dimethylaminoazobenzene	red	yellow	pink	brown	red
Eosine	orange	yellow, red	yellow	yellow	red
Ethyl blue B	violet	indigo, blue, green	pink	blood red	indigo

Euchrysine 3RX	brown-red	orange, yellow	orange	brown-red	orange
Fluorescene	colorless	green	colorless	red	yellow
Gentian violet	yellow	green, blue, indigo, violet	yellow	orange-red	violet
Haemotoxylin	orange	red, pink	yellow	red	pink
Hoffmann violet	green	blue, violet	green	brown	violet
Iodine green	green	blue	green	red-brown	green
Light green SF	yellow	green	yellow	orange-red	green
Litmus	purple	blue	pink	blue	purple
Litmus (paper)	red	purple	red	red	red
Magenta	yellow	red, pink	yellow	brown	red
Malachite green	orange	green, blue	colorless	brown-red	green
Marine blue BBT	red	purple, violet	pink	purple	violet
Methyl green	orange	green, blue, violet	green	....	....
Methyl orange	red	orange, yellow	red	blood red	red, yellow
Methyl violet B	green-orange	green, blue, indigo, violet	green	red-brown	violet
Neptune blue RB	green	blue	green	orange	indigo, violet
Neptune blue BG	green	blue	green	yellow	green
Neptune marine blue BBT	brown	purple, blue	colorless	red	blue
Palatine chrome blue 2B	green	blue, indigo	green	brown-black	blue
Pyramine yellow G	red	orange, yellow	red	purple	yellow
Pyramine yellow G extra	black	red, yellow	pink	....	....
Rhodamine B extra	orange	red, pink	colorless	blood red	red
Rosolic acid	orange	pink	yellow	orange	pink
Safranine TR	purple	red	violet	green	red
Tropaeolin OO	orange	yellow-red	yellow	purple	orange-red
Vesuvin	orange	yellow	orange	carmine-red	yellow
Vesuvin BPX	brown	red, orange, yellow	yellow	purple	orange

TABLE II.

Name. Dye.	Colors restored by alkalies.			In $H_4P_2O_7$.	
	Original color in alkaline solutions. I.	Colors in dilute aqueous solutions. II.	Colors restored by alkalies. III.	Oily solution. IV.	Diluted with water. V.
Cochineal	red	blue	red	carmine red	pink
Coralline	red	colorless	pink	yellow	yellow
Indigo-SO_3Na	amber	green, blue	amber	indigo	indigo
Logwood	red	colorless	pink	....	....
Methyl blue	red	purple-blue	violet	green-black	blue
Methylene blue	green	blue	colorless	chrome green	green
Orange I	red	yellow-orange	red	purple	orange
Orange II	red	orange, yellow	red	carmine red	orange
Oxamine blue 3BN	purple	blue	purple	indigo	purple
Oxamine blue BX	red	rose	red	....	....
Phenolphthalein	red	colorless	pink	orange	colorless
Picric acid	red	orange, yellow	orange	white cryst. colorless	yellow
Tumeric	orange	colorless	yellow	orange	colorless
o-Nitrophenol	red	yellow	orange	brown	orange

(4) Certain dyes, such as methyl green, methyl violet, ethyl blue, etc., pass through a number of colors before yielding the final hydrolyzed color. Since the changes of color in these cases are always in the order of the spectrum, it may be assumed[1] that the intermediate colors are varied mixtures of the original and the final colors.

(5) From acidic solutions (Table I) the change of color with different dyes may be either toward or from the more refrangible end of the spectrum. For instance, congo red and ethyl blue B change toward the less refrangible end of the spectrum; most of the other dyes change in the opposite direction.

(6) From alkaline solutions (Table II) the variations of color resulting from dilution are usually toward the more refrangible end of the spectrum. Some yield colorless solutions.

(7) The common indicators suffer changes in color by dilution only in the presence of small quantities of acids or alkalies. The less serviceable indicators tolerate larger quantities of free acids or alkalies. In other words, that indicator is the most serviceable that is stable toward water in the presence of the smallest "concentration of OH or H^+ ions," or that indicator is the most serviceable that is least easily hydrolyzed.

(8) The colors produced by dilution are not caused by a mere *thinning out of the dye*, because with the respective diluted dyes, either an acid or an alkali will restore the original color, or at least a shade of the same.

(9) The colors produced by dilution are not caused by the increase of ions of the water, because OH^- and H^+ are thus equally increased and these ions have opposite influences on the solutes.

(10) The colors produced by dilution are not caused by the ions or molecules of such impurities in the water as ammonia, carbonic acid, etc., because not only does pure water produce the respective changes of color, but, as indicated in the tables, the same tap-water with different dyes will produce opposite changes, that is, the water will hydrolyze the respective dyes either in acidic or alkaline solutions.

(11) From the foregoing it may be concluded that the colors produced by dilutions are caused not by ionization but by the *mass action of water*, that is, the changes are produced by hydrolysis or hydration, with consequent molecular dissociation or isomerization.

The Color Transformations are Independent of Ionization.

When a *simple* dye, like red sodium picrate, is acted upon by water so as to yield the yellow solution, at least three chemical effects may be imagined—the dye may be more or less (1) ionized, (2) hydrolyzed, or (3) isomerized. For instance

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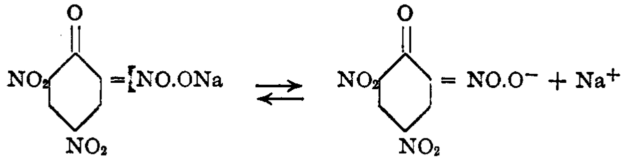
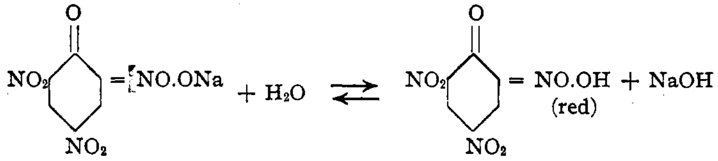
[1] Of course this conclusion is based on the assumption that the cause of color is conditioned by chemical structure. However, various dynamic explanations of these phenomena are suggested.

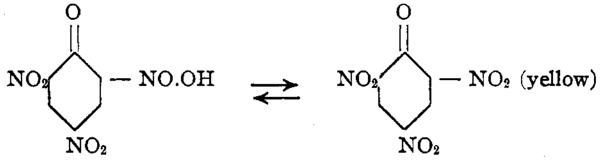
(1)



(2)



(3)



As indicated above and following,[1] the theory of ionization throws no light on the above described phenomena. On the other hand, on the basis of the quinoid theory of color, it is easy to understand with certain dyes how *hydrolysis or hydration followed by isomerization may yield the chromoisomers.*

(1) If all dyes are ionized by water, and most of them are either salts or amphoteric compounds, they should not differ widely in degrees of ionization, consequently the color of all dyes should be progressively, or at least partially, modified by increasing masses of water. However, the color of all dyes are not so modified; though many are so modified, *most dyes studied are unaffected.* Hence, it is probable that ionization of the dye itself is not the cause of change of its color.

(2) On the one hand, much alkali is necessary to yield red solutions of picric acid and these solutions are readily changed to yellow solutions by dilution. On the other hand, orange II, a "weaker" acid than picric acid, when in faintly alkaline solution, requires much water to give the yellow color. Now, since these two dyes, in large and equal "concentrations of OH^- ions," derived from the free alkali present, reveal widely different susceptibilities to color transformation, it is seen that such color transformations are largely or completely independent of the OH^- ion concentrations.

(3) Since picric acid is a stronger acid than orange II, it must be considered less easily hydrolyzed. However, it gives its hydrolyzed isomer more readily than orange II. Therefore, there must result some secondary phenomena, as, for instance, isomerization. Now, since, owing to intrinsic molecular properties, different tautomeric forms exhibit different tenden-

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[1] For a discussion of ionization and color changes see papers following.

cies to isomerize, it may be understood that the simultaneous equilibria of hydrolysis or hydration and isomerization may yield phenomena that cannot be accounted for on the basis of disturbance of one equilibrium alone.

(4) Since no dyes were found that were isomerized *in both acidic and alkaline solution, and these are both subject to ionization,* it is evident that mere ionization cannot be the chief cause of chromoisomerization.

(5) For other evidences that chromoisomerization is independent of the equilibrium of ionization, see the two following papers.

Dyes Dissolved in Anhydrous Solvents.

The most commonly used anhydrous[1] solvent for testing dyes is concentrated sulfuric acid. Since many dyes are sulfonated and otherwise modified by this acid, thus yielding molecular forms other than the original dye, it was judged more advantageous to use an inert anhydrous acid as phosphoric acid. For this purpose the oily portion of a sample of pyrophosphoric acid was used with excellent results. (See the last two columns of Tables I and II.) The following important observations were made:

(1) All dyes tested dissolved in this medium to give characteristically colored solutions.

(2) The colors of dyes in anhydrous phosphoric acid differ from the colors obtained in concentrated aqueous solutions, as may be seen by a comparison of Cols. I and II. Of the 48 dyes studied in Table I, 32 gave some shades of red, but less than one-half of this number gave shades of red in concentrated aqueous solutions. From these data it may be concluded that *basic dyes are prevailingly red in anhydrous phosphoric acid.*

(3) In Table I it will be observed that the colors of Col. I occupy positions on the spectrum intermediate to the respective colors of Cols. IV and II. In other words, a dye giving a certain color in an anhydrous medium, if modified by the addition of water, is *progressively modified in color in the order of the spectrum.* Now since these spectrum-color progressions are directly proportional to the masses of water used, it may be concluded, provided the theory of ionization is inapplicable, that hydrolysis is the cause of these color transformations.

(4) Since the colors of Col. I differ from the colors of Col. IV, it may be concluded that equilibria of products of certain dyes, such as their chromoisomers, are represented in all of their aqueous solutions. In other words, *some dyes when dissolved in water exhibit not their true[2] colors but mixtures of colored hydrolytic products.*

[1] For the action of alcohol, ether, etc., on picric acid, see paper following.

[2] Of course it is a well-known fact that some solid dyes differ in color from solutions of the same and from fabrics dyed by the same. Since many solid dyes and colored salts do not differ essentially in color from their aqueous solutions, it may be concluded that such dyes as are changed by the action of water are hydrolytically transformed.

(5) That the diluted solutions of phosphoric acid are less hydrolyzed than very dilute aqueous solutions (see Cols. V and II) is owing to the comparatively large concentrations of phosphoric acid present in the former. In other words, secondary constituents such as acids[1] exert inhibiting effects[2] on the hydrolysis of dyes.

The Mechanism of Color Changes in Aqueous Solutions.

As indicated in equations above, it might easily be concluded that the color changes of certain solutions, if not the effects of ionization, may be explained on the basis of hydrolysis followed by isomerization. This simple hypothesis, involving no new assumptions of chemistry, seems to be applicable to certain quinoid dyes forming true solutions, such as methyl orange and picric acid. However, certain dyes, as for example the triphenylmethane dyes, have not been shown to possess chromoisomeric forms and these very dyes exhibit the greatest variety of colors in aqueous solutions. That the latter colors may be blended mixtures of two or more chromoisomers presents itself as a possible partial explanation, but the second chromoisomers of dyes like crystal violet, Hoffmann violet, etc., though possible, have not been proven. On the other hand, it must not necessarily be concluded that all dyes are correlated on the same basis. For instance, if the azo dyes were proven to exist as azoid and quinoid isomers, such chromoisomerism can afford no explanation of the yellow varieties of mercury oxide and other bicolored substances. Other explanations must, therefore, be sought.

Different classes of dyes in solution may exist in states of aggregation such as:

(1) Colloidal forms.[3]

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[1] Here an ionic explanation presents itself. However, see counter arguments given above, also let it be remembered that, whereas acids inhibit the color transformations, water alone promotes them.

[2] That heat also has effects on the color of dye solutions is well known. See the effects of heat on methyl orange and picric acid in the papers following. For the effects of heat on chromate solutions, see THIS JOURNAL, **36**, 845 (1914); see also Rohland, *Chem. Ztg.*, **30**, 375 (1906); and expecially Kurbatoff, *Ibid.*, **31**, 1169 (1907).

[3] For the colloidal, semicolloidal and crystalloidal nature of dyes, see especially the following: W. Ostwald, *Z. Chem. Ind. Kolloide*, **10**, 132 (1912); Höber and Chassin, *Ibid.*, **3**, 76 (1909); Vorländer, *Z. physik. Chem.*, **85**, 701 (1913); Hantzsch, *Kolloide-Z.*, **15**, 79 (1914); Vignon, *Compt. rend.*, **150**, 619, 923 (1910); Baylis, *Proc. Roy. Soc. London*, **81B**, 269 (1910); Taylor, "The Chemistry of Colloids," **1915**, 271; Knecht and Bayley; Sheppard, *J. Soc. Chem. Ind.*, **28**, 697 (1909).

Ostwald found that 28 of 50 common dyes are colloids and holds that colloidal phenomena play an important part in the color changes of organic dyes. Hantzsch shows that methyl orange, contrary to the conclusion of Ostwald, is not a colloid. Vignon states that soluble dyes form true solutions; dyes exhibiting the phenomena of electrical transport, form colloidal solutions. He holds that congo red is a colloid but Baylis shows that it consists of single molecules and only its free acid form is colloidal.

(2) Polymerized forms.[1]
(3) Quinhydrone forms.[2]
(4) Hydrated forms.[3]
(5) Tautomeric forms.[4]

It is not purposed at this time to enter into a detailed discussion of the mechanics of hydrolysis of dyes. It can only be indicated here that different dyes, possessing almost endless varieties of chemical structures, may exhibit as solids and as solutes different degrees of molecular aggregation

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[1] Hantzsch, *Ber.*, **42**, 68, 2129 (1909); Willstätter, *Ibid.*, **42**, 4135 (1909); Moir, *S. African J. Sci.*, **10**, 163 (1915).

[2] Wöhler, *Ann.*, **51**, 153 (1844); Städeler, *Ibid.*, **69**, 300 (1849); Graebe, *Ibid.*, 146, 36 (1868); Wichelhaus, *Ber.*, **5**, 844 (1872); **12**, 1500 (1897); Liebermann, *Ber.*, 10, 1614 (1875); Nietzki, *Ibid.*, 10, 2003 (1875); *Ann.*, **215**, 125 (1882); Hesse, *Ibid.*, **200**, 232 (1880); Klinger and Standke, *Ber.*, **24**, 1341 (1889); Clark, *Am. Chem. J.*, **14**, 574 (1892); Ling and Baker, *J. Chem. Soc.*, **63**, 1314 (1893); Jackson, *Am. Chem. J.*, **17**, 588 (1895); **18**, 1 (1896); **34**, 441 (1905); **35**, 173 (1906); Liebmann, *Z. Electrotech. Electrochem.*, **1896**, 497; Valeur, *Ann. chim. phys.*, [7] **21**, 470 (1900); Posner, *Ann.*, **336**, 85 (1904); Duregger, *Monatsh.*, **26**, 823 (1905); Torrey and Hardenbergh, *Am. Chem. J.*, **33**, 167 (1905); Baeyer, *Ann.*, **354**, 162 (1907); Stieglitz, *Am. Chem. J.*, **39**, 431, 651 (1908); Acree, *Ibid.*, **39**, 529, 649 (1908); Willstätter, *Ber.*, **37**, 1494, 3761, 4605 (1904); **38**, 2244 (1905); **39**, 3482 (1906); **41**, 1458 (1908); **42**, 1902 (1909); **44**, 2171 (1911); Urban, *Monatsh.*, **28**, 299 (1907); Hartley and Leonard, *J. Chem. Soc.*, **95**, 34 (1909); Siegmund, *Monatsh.*, **29**, 1087 (1908); *J. prakt. Chem.*, **83**, 553 (1908); Schlenk, *Ann.*, **368**, 277 (1910); Haakh, *Ber.*, **42**, 4594 (1909); Knorr, *Ber.*, **43**, 798 (1910); **44**, 1503 (1911); Richter, *Ibid.*, **43**, 3603 (1910); **44**, 3466 (1911); Luther and Leubner, *J. prakt. Chem.*, **85**, 314 (1912); Hantzsch, *Ber.*, **39**, 1089, 1095, 3076, 3080 (1906); **40**, 333, 1527 (1907); **46**, 682, 1925 (1913); Pfeiffer, *Ann.*, **404**, 1 (1914); Pummer and Frankforter, *Ber.*, **47**, 1472 (1914).

[3] Sheppard, *Proc. Roy. Soc. London*, **82A**, 256 (1909); des Bancels and Siegrist, *Rev. gen. mat. color*, **14**, 249 (1911); Blitz and Hegesach, *Z. physik. Chem.*, **73**, 481 (1910). Sheppard holds that solutions of dyes are combined processes of disaggregation of the solute accompanied by progressive combination with the solvent. Languier des Bancels and Siegrist state that certain dyes are capable of different degrees of hydration. Blitz and Hagesach state that molecules of dyes exist in water solutions together with products of their hydrolytic and electrolytic dissociation and that increasing the concentration of the dye in general is favorable to increasing the degree of association, as shown by osmotic pressures and the ultramicroscope. See also Gebhard, *Z. angew. Chem.*, **22**, 2484 (1909); W. Ostwald, *Kolloid-chem. Beiheft*, **1911**, 12.

[4] Of course, the tautomeric, bicolored nature of some dyes, particularly indicators, have been recognized for a long time. See especially, Stieglitz, THIS JOURNAL, **25**, 1112 (1903) and the bibliography in following paper on methyl orange. Hantzsch was the first to apply the word *chromoisomerism* to tautomeric dyes. Hantzsch, *Z. angew. Chem.*, **20**, 1889 (1907); *Ber.*, **43**, 2512 (1910); **44**, 1783, 2001 (1911); **46**, 1537 (1913); **48**, 785, 797 (1910); 1332, 1338 (1915); **49**, 213, 234, 1511 (1916); *Ann.*, **392**, 286 (1913); Dimroth and Dienstbach, *Ber.*, **41**, 4055 (1908); Piutti and De Conno, *Mem. accad. Lincei*, **8**, 793 (1911); Darapsky, *Chem. Ztg.*, **35**, 707 (1912); Jones and Oesper, THIS JOURNAL, **36**, 2208 (1914); Vecchiotti, *Atti. accad. Lincei*, II, **22**, 75 (1913); Kehrmann and Danecki, *Ber.*, **47**, 279 (1914); Mendola and Hollely, *J. Chem. Soc.*, **105**, 977 (1914). For the color and ionization of crystal violet, see THIS JOURNAL, **36**, 1452 (1914).

and dissociation; and, whereas the color changes of some dyes may, for example, be explained quite satisfactorily on the basis of the quinhydrone or the chromoisomerism theories, other dyes may not fall under these categories. Evidently much knowledge is lacking to arrive at definite conclusions concerning the nature of color changes of some dyes, especially dyes of the triphenylmethane type.

However, this is certain that the qualitative color changes exhibited by dyes in water solutions, as shown above, and the quantitative studies of methyl orange and picric acid discussed in papers following demonstrate that water itself has a very important influence on the molecular state of the dye. Now since this influence generally has not been taken into consideration, many discordant experiments with colored solutes are found in the literature. Chief among these are variations from the laws of Weber,[1] Beer,[2] Ostwald,[3] and Kundt,[4] and faulty determinations made with diluted indicators and with dilution colorimeters.

Certain fallacies of colorimetry are discussed in a paper following; other errors resulting from the use of colored solutions[5] will be made.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

STUDIES OF THE CHROMOISOMERISM OF METHYL ORANGE.

BY WILLIAM M. DEHN AND LOIS MCBRIDE.

Received February 27, 1917.

Both on account of their comparatively simple structures and on account of their great usefulness as indicators, the chromoisomers, methyl orange and helianthine,[6] have been favorite substances to illustrate chromoisomerism, various theories of color, and various theories of indicators.

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[1] From the foregoing it may easily be understood why color variations of bicolored and polychromic solutes do not follow the logarithmic function conditioned by Weber's law.

[2] *Ann. chim. phys.*, 86, 78 (1872).

[3] *Z. physik. Chem.*, 2, 270 (1888).

[4] *Ann. Physik*, 1871–1872; Vogel, *Monatsch. Ber. Akad.*, 1878, 427; Pulfrich, *Ann. Physik*, [3] 14, 177 (1881); Stenger, *Ibid.*, 33, 577 (1888); Wiedemann, *Ibid.*, 37, 177 (1889); Katz, *Inaug. Dissert.*, Erlangen, 1898; Sheppard, *J. Chem. Soc.*, 95, 15 (1909). Also see discussion of absorption spectra in the following paper on methyl orange. Hantzsch, *Ann.*, 384, 135 (1915); Piccard, *Ibid.*, 381, 347 (1911).

[5] For anomalous phenomena of chromate solutions see THIS JOURNAL, 36, 829 (1914).

[6] *Ber.*, 41, 1187 (1908); 46, 1537 (1913); 48, 167 (1915). Hantzsch has used the name *helianthine* for both isomers, distinguishing them as the *red quinoid* helianthine and the *yellow azoid* helianthine. This nomenclature is convenient and is largely employed in this paper.