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.

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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).

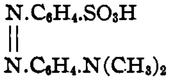
[5] For anomalous phenomena of chromate solutions see THIS JOURNAL, 36, 829 (1914).

[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.

The most commonly accepted formulas,[1] for these two substances and their salts, are as follows:

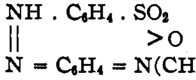
(Azoid-yellow) (Quinoid-red)

(I)



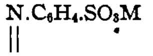
$$\begin{array}{l} N.C_6H_4.SO_3H \\ \| \\ N.C_6H_4.N(CH_3)_2 \end{array}$$

(II)



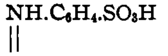
$$\begin{array}{l} NH\ .\ C_6H_4\ .\ SO_2 \\ \| \qquad\qquad\quad >O \\ N = C_6H_4 = N(CH_3)_2 \end{array}$$

(III)



$$\begin{array}{l} N.C_6H_4.SO_3M \\ \| \\ N.C_6H_4.N(CH_3)_2 \end{array}$$

(IV)



$$\begin{array}{l} NH.C_6H_4.SO_3H \\ \| \\ N = C_6H_4 = NCl(CH_3)_2 \end{array}$$

In connection with his chromophoric theory of indicators,[2] Stieglitz was the first to use all of these formulas. He showed, however, that the formulas were adaptations of the azoid and quinoid formulas of hydroxyazobenzene used by Hantzsch,[3] who in turn showed that his formulas for this compound were previously used by Goldschmidt.[4] Goldschmidt traced his formulas back to his own previous studies of nitrosophenol,[5] which he concluded is the oxime of quinone. Thus it is seen that azoid and quinoid formulas for chromoisomeric substances may be traced back to 1884.

In this same year Zincke and Bindewald[6] first used the lactoid structure for chromoisomeric substances, applying it to α-naphthoquinonephenylhydrazone. Stieglitz[7] was the first to apply it to the helianthines.

Of course, the bicolored nature of methyl orange was recognized by Griess[8] at the time of its discovery in 1876. However, from this year to the publication of Stieglitz's chromoisomerism[9] theory of indicators in 1903, two main causes of retarded development of knowledge of methyl orange were operative, *viz.*, (1) the universal acceptance of Ostwald's ionic theory of indicators, and (2) the division of chemists as to *which of two* was the true structure of bicolored substances.

The chromoisomerism of methyl orange was not definitely recognized

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[1] The evidence that the red form is the quinoid and that the yellow form is the azoid, is not presented in this paper—references on this subject must be made to the papers of Hantzsch and others.

[2] THIS JOURNAL, 25, 1117 (1903).

[3] *Ber.*, 32, 590, 3089 (1899); 41, 1189 (1908). Though Hantzsch has advocated the above simple formulas for the helianthines, his recent studies have led him to the adoption of more complicated formulas (*Vide infra*).

[4] *Ibid.*, 23, 487 (1890); 24, 2300 (1891).

[5] *Ibid.*, 17, 213 (1884).

[6] *Ibid.*, 17, 3028 (1884).

[7] All of Stieglitz's formulas have been used by Hantzsch who acknowledges them. *Ber.*, 41, 1187 (1908); 46, 1537 (1913); Hewitt, however, claims them as his own. *Analyst*, 33, 87 (1908); *Ber.*, 41, 1986 (1908). See also Tizard, *J. Chem. Soc.*, 97, 2478 (1910). For Hantzsch's present formulas, see *Ber.*, 46, 1537 (1913); 48, 167 (1915).

[8] *Ibid.*, 10, 528 (1884).

[9] Hantzsch was the first to employ the word *chromoisomer* to tautomeric dyes. *Z. angew. Chem.*, 20, 1889 (1907).

before the paper of Stieglitz[1] appeared. Since this time Hantzsch has experimentally demonstrated[2] its tautomeric nature.

As pointed out by Hantzsch,[3] pure yellow methyl orange of Formula I has never been isolated,[4] though it probably exists in certain solutions. "The change of color from red to yellow is not caused,[5] as is commonly believed, by a change from an acid solution to an alkaline solution, for the reason that not only alkaline and neutral, but also certain (*e. g.*, acetic) acid-containing solutions of helianthine are yellow. Red helianthine, the acid-stable form, varies with the concentration of hydrogen ions in the equilibrium

$$\text{yellow helianthine} \rightleftarrows \text{red helianthine}.$$

The solid red helianthine is dissolved to yellow solutions, not only by alkalies but also by indifferent solvents. Red helianthine solutions are formed *only* by hydrogen ions. Yellow helianthine solutions exist in the absence of hydrogen ions, not necessarily only in the presence of hydroxyl ions."

If the italicized word is omitted all that Hantzsch states is in accord with our conclusions. However, our experiments lead to the more extended conclusions: *The yellow form, either pure or in equilibria with the red form, exists in dilute solutions; the red form, either pure or in equilibria with the yellow form, exists in concentrated solutions. In other words, most solutions of helianthine, whether acid, neutral or alkaline, represent chromoisomeric equilibria of the two forms.*

Since these statements, if superficially considered, appear paradoxical, we give at once a résumé of evidences for their support.

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[1] Three days after the contribution of Stieglitz's paper, Thiele's paper demonstrating the chromoisomerism of aminoazobenzene hydrochloride was in the hands of the editor. *Ber.*, 36, 3965 (1903). Apparently other isomeric salts of aminoazobenzene were previously reported by investigators, but were not recognized to be chromoisomeric forms. See especially Martius and Griess, *Z. Chem.*, 1866, 132; Berju, *Ber.*, 17, 1402 (1884); Vorländer, *Ibid.*, 36, 1487 (1903). Recently many bicolored isomers and even tricolored isomers have been reported. *Ber.*, 46, 1552 (1913); 48, 158, 167 (1915).

[2] *Ber.*, 41, 1171, 1189 (1908); 46, 1537 (1913).

[3] *Ibid.*, 41, 1191 (1908); 46, 1537 (1913).

[4] *Ibid.*, 46, 1551 (1913); 48, 167 (1915). Hantzsch obtained a yellow form containing only 0.1 mol. of the sodium salt. Easy isomerization of helianthine by heat or by traces of water evidently is the cause of the difficulty of preparing yellow helianthine. Hantzsch found that his yellow helianthine was incompletely soluble in water and gave a brown-yellow solution. Difference of solubility of the yellow helianthine and its sodium salt could account for this property of solubility; isomerization to the red form through the action of water could account for the darkness of the aqueous solutions.

[5] *Ber.*, 46, 1538, 1555 (1913).

Evidences that Solutions of Methyl Orange and of Helianthine Are Mixtures of Chromophoric Isomers.

(1) Molecular absorption phenomena *very progressively* from strong alkaline solutions containing a preponderance of yellow methyl orange molecules to strong acid solutions containing large quantities of red helianthine molecules.

(2) Molecular extinction phenomena vary in the same manner.

(3) All aqueous solutions of methyl orange or of helianthine, whether strongly acidic or strongly alkaline, are red in the higher concentrations and are yellow, or at least contain some of the yellow isomer, in the lower or lowest concentrations.

(4) Many of such solutions, whether red or yellow, are *reddened* or are made more deeply red by a strong increase of temperature.

(5) All such solutions, whether red or yellow, are progressively *reddened* by increasing quantities of strong acids and are progressively rendered more yellow by increasing quantities of strong alkalies.

(6) Silk, wool and cotton are colored *yellow* either from yellow alkaline solutions or from red moderately acidic solutions of methyl orange or of helianthine. However, these fibers are colored *red*, by solutions containing greater concentrations of hydrogen ions than 0.025 N HCl. In water these red-dyed fabrics quickly become yellow, through hydrolysis. Therefore, at least in acid solutions more dilute than those containing the hydrogen ionic equivalent of 0.025 N HCl, equilibria exist of the two chromophoric isomers.

(7) Aqueous solutions of salts of methyl orange, compounded, respectively, of bases of varied alkalinities, though of a red-yellow color, differ in color for equal concentrations. Aqueous solutions of salts of helianthine, compounded respectively of acids of varied acidity, differ in color for equal concentration. Therefore, both types of salts in aqueous solutions represent equilibria of chromophoric isomers.

(8) Colorimetric studies of helianthine in aqueous solutions, with absolute phenol and absolute pyridine solutions of helianthine, used as standards of colors, showed that such aqueous solutions, whether strongly alkaline or strongly acidic, are composed of *70–99% of azoid molecules.*

(9) Other evidences[1] co-lateral to these, but previously not so interpreted by investigators, are: (*a*) the anomalous electrical conductivities: (*b*) ionic migrations: (*c*) radiometric measurements, etc.

[1] Other evidences than the above are given following. Experiments of this group are recommended to be performed by those who have little time to repeat experiments of this paper. Especially to those who are dogmatically committed to an ionic explanation of color changes of methyl orange solutions, are the following experiments recommended:

(1) To pyridine and water, respectively, add excesses of methyl orange; shake or let stand until saturation at ordinary temperature results. Filter and observe

that the aqueous solution is red and that the pyridine solution is yellow. To 1 cc. of each in 1 liter volumetric flasks gradually add water and it will be observed that soon the solutions possess identical colors. Now add more water or *equal quantities* of dil. HCl and it will be observed that the pyridine solution becomes the more deeply colored. It must be evident that the original pyridine solution contains mostly yellow azoid helianthine molecules; the aqueous solution contains a large concentration of red quinoid helianthine molecules. Methyl orange being more soluble in pyridine than in water yields finally a more deeply red aqueous solution.

(2) Helianthine in cold acetic anhydride is amber-yellow. On heating this solution, it becomes a light yellow; on adding a trace of water, it becomes red; on heating the red solution, it becomes light yellow. Here, owing to heat and hydration of the acetic anhydride, chromoisomerization is very evident to the eye. It may be observed that some aqueous acetic acid solutions of helianthine become lighter in color when heated; some aqueous hydrochloric acid solutions of helianthine become darker in color when heated.

(3) When in contact with both water and ether, helianthine gives a red aqueous solution and a yellow or nearly colorless ether solution. Its presence in the ether may be showed by adding to the isolated ether solution a little strong hydrochloric acid. The new aqueous layer becomes *red*, indicating that the original ether had extracted yellow helianthine from the original red helianthine, or that the ether had effected the chromoisomerization.

(4) Not only yellow but red ether solutions of helianthine can be prepared: the former, from helianthine itself; the latter, from helianthine in the presence of hydrogen chloride. When treated with water, the red ether solution gives a yellow ether solution and a *more intensely red* aqueous solution. Therefore, the original red ether solution must have contained, not only red quinoid molecules, but also a large percentage of yellow azoid molecules.

(5) Colloidon films containing helianthine as a pigment are somewhat yellow by reflected light but violet by transmitted light. Apparently this is a direct proof of the chromoisomeric nature of helianthine, when present as a solid.

(6) Under title of "a chemical paradox," de Vries describes a deep red-purple solution of methyl orange in a saturated aqueous solution of zinc chloride. *Weekblad,* 12, 1000 (1915). With dilute hydrochloric acid it gives a yellow solution; with an excess of acid it gives a red color. We have found that pure helianthine dissolve in saturated solutions of zinc chloride in water or in alcohol, and that such solutions behave in the manner described by de Vries.

In view of the experiments of this paper, there is nothing paradoxical in the behavior of this helianthine salt. It gives with water or with very dilute acid, a yellow solution because, like all salts of helianthine, it is hydrolyzed and when hydrolyzed in dilute solutions, it isomerizes to the yellow azoid form. Addition of more acid reverses both the isomerization and the hydrolysis, yielding the red form.

de Vries states that the yellow color formed in dilute solution of hydrochloric acid is caused by the diminution of H^+, this diminution being caused by the presence of the zinc chloride. Koltoff, who also has studied this "chemical paradox," advances the explanation that in water a basic salt is formed, which in water or in dilute hydrochloric acid gives off OH^- and consequently the yellow color is formed. *Ibid.*, 13, 1016 (1916). In view of the findings of this paper it is evident that both of these explanations are incorrect.

This zinc salt is of great interest in connection with the experiments of this paper because it uniquely illustrates that *the intensity of color of helianthine solutions is conditioned, not by the presence of hydrogen and hydroxyl ions, but by the formation of molecular compounds.*

Expanded Discussion of these Evidences.

(1) Hartley[1] obtained the first absorption spectra of free helianthine.[2] He used 0.0001 molar concentrations[3] and observed two absorption bands, one at 1/λ 1810–2880 in 10 mm. thickness of solution and the other at 1/λ 3320–4330 in 5 mm. thickness. Formaneck[4] and Vaillant[5] also made absorption studies of methyl orange.

In 1908 Hantzsch[6] made some preliminary absorption studies of helianthine in water, in water containing 1 mol. of NaOH, and in water containing 12 mols. of HCl. In 1913 he obtained absorption spectra of helianthine at 0.00305% concentration[7] in water, in water containing 500–10000 mols. of HCl, in water containing 10,000 mols. of NaOH, and in absolute alcohol containing 1 mol. of $NaOC_2H_5$.

From inspection of Hantzsch's curves, it is evident that variations from strong alkaline solutions of helianthine to strong acid solutions of the same, produce progressive displacement of the absorption bands towards the red region of the spectrum. From inspection of Vaillant's data, it is evident that variations[8] from dilute acid solutions of helianthine to concentrated acid solutions of the same produce similar progressive variations. These results are in exact agreement with our colorimetric studies.

That Hantzsch's curves, whether of acid or of alkaline solutions, showed remarkable similarities, can be explained on the basis that all of his solutions contained *more than 80% of azoid molecules.*[9]

(2) Molecular extinction experiments of helianthine made by Hantzsch, respectively in 0.00305 to 0.01525% aqueous concentrations, in the same with 1 mol. of NaOH, and in the same with 10 mols. of NaOH, showed nearly identical effects. In 0.00305% concentration with 2, 3,

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[1] *J. Chem. Soc.*, 51, 192 (1887).

[2] See Hartley's curve on Plate VII and compare it with Hantzsch's curve on Plate I, *Ber.*, 46, 1540 (1913).

[3] Correspondnig to 0.00305% concentration of our studies (q. v.).

[4] *Spectral Anal. Nach. kenst. org. Farbstoffe*, 42, 168; Plate 54.

[5] *Compt. rend.*, 137, 849 (1903).

[6] *Ber.*, 41, 1190 (1908).

[7] Observe that the concentrations used by Hantzsch were nearly identical with our 0.003% solutions.

[8] For certain observations on absorption bands produced by solutions of equal and varied concentrations, see THIS JOURNAL, 38, 14 (1916).

[9] *Vide infra.* Largely for the reason that his curves presented abnormalities, Hantzsch was led to use new and more complicated formulas for the helianthines than those given above. He was further led to this advocacy for the reason that certain helianthines (no dimethyl helianthines, however) apparently exist in a third, graphite-like, chromoisomeric form. However, it may be stated that all recorded observations of this paper, together with all non-recorded observations incident to this development, presented no phenomena that cannot be explained on the basis of two chromoisomers, for all of its solutions.

and 12 mols. of HCl, progressive diminutions were observed. In other words, the coefficients of molecular extinction varied progressively from solutions in strong alkalies to solutions in strong acids. These facts, as pointed out by Hantzsch,[1] indicate progressive disturbances of the azoid-quinoid equilibria.

(3) The most important observation of this paper is that practically all solutions of helianthine, whether neutral or strongly acidic or strongly alkaline, *are red in the higher concentrations and are yellow in the lower or lowest concentrations.* The simple and inevitable conclusion is that many red quinoid molecules exist in the higher concentrations and a preponderance of yellow azoid molecules exist in the lower concentrations. In fact, it has been found that water as well as certain organic solvents, when present in relatively large quantities (dilute solutions) tend to yield hydrolytically the yellow azoid form and conversely, in concentrated solutions, tend to yield the red quinoid form. Therefore we have the equilibria

$$\left.\begin{array}{l}\text{1. Acids}\\ \text{2. Concentration}\end{array}\right\} \begin{array}{l}\text{red}\\ \text{helianthine}\end{array} \rightleftarrows \begin{array}{l}\text{yellow}\\ \text{helianthine}\end{array} \left\{\begin{array}{l}\text{1. alkalies}\\ \text{2. dilution.}\end{array}\right.$$

(4) At constant concentrations of helianthine it was found that progressive "increase of hydrogen ions" yielded redder solutions and progressive "increase of hydroxyl ions" yielded purer yellow solutions. That this is true only within certain limits is proven by the following experiments: The most intensely red series of solutions are prepared in absolute phenol and the most intensely yellow series of solutions are prepared in absolute pyridine. All aqueous solutions containing equal concentrations of helianthine and the respective organic and inorganic acids, are less red than the corresponding phenol solutions; all aqueous solutions, containing the respective organic and inorganic bases, are less yellow than the corresponding pyridine solutions. In other words, *the presence of water itself is an important factor in the determination of the color of helianthine solutions.*[2] Since the absolute pyridine solutions *do not contain hydroxyl ions* and the absolute phenol solutions contain relatively few, if any, *hydrogen ions*, it is evident that the widely varying colored solutions of helianthine are primarily independent of the presence of free ions.[3]

(5) Increase of temperature from the ordinary to that of the water bath produced changes of color. Usually concentrated solutions showed

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[1] *Ber.*, 41, 1190, 1192 (1908).

[2] In a paper preceding and in the pages following, the effect of water is discussed in detail.

[3] This will be discussed below. Since Hantzsch obtained more persistent azoid solutions of helianthine in an alcoholic solution of sodium ethylate, than in aqueous solutions of sodium hydroxide, he concluded that the formation of yellow azoid helianthine is independent of the presence of hydroxide ions. *Ber.*, 46, 1540 (1913).

increase of color and diluted solutions showed decrease of color. Now if aqueous solutions possess helianthine molecules in equilibria of the two isomers,[1] it is evident that the deepening of color resulted from a change of yellow azoid molecules to red quinoid molecules and the lightening of color resulted from a change of red quinoid molecules to yellow azoid molecules.

Conversely considered, hot solutions of helianthine give by cooling either less intense reds or redder yellows. These reverse changes of color indicate progressive disturbances of the azoid-quinoid equilibria. Since intense cold reveals further color changes, it must be evident that solutions of helianthine, at least at ordinary temperatures, are equilibria mixtures of the chromoisomers.

From consideration of the observations thus far given it may be concluded that:

$$\left.\begin{array}{l}1.\ \text{Acids}\\ 2.\ \text{Concentration}\\ 3.\ \text{Rise of Temperature}\end{array}\right\} \begin{array}{l}\text{red}\\ \text{helianthine}\end{array} \rightleftarrows \begin{array}{l}\text{yellow}\\ \text{helianthine}\end{array} \left\{\begin{array}{l}1.\ \text{Alkalies}\\ 2.\ \text{Dilution}\\ 3.\ \text{Fall of temperature}\end{array}\right.$$

(6) Since vegetable and animal fibers are colored yellow by red solutions of helianthine,[2] it follows that such red quinoid solutions must also contain yellow azoid molecules, unless it is assumed that the fiber itself chemically transforms red molecules to yellow molecules. However this latter is improbable, since very concentrated acid solutions color the fibers *red* and since the red-dyed fibers are made yellow by water alone. Therefore it must be concluded that moderately acid solutions of helianthine contain both chromoisomers in equilibrium.

(7) It will be shown that the presence of water in solutions of helianthine has a most important influence on its isomerization, tending to yield a preponderance of azoid molecules. Since all salts of helianthine,[3] whether compounded of bases on the one hand, or of acids on the other hand, are thus hydrolyzed, it is evident that different equilibria will be

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[1] Since, as shown below, all aqueous solutions of helianthine contain more than 70% of azoid molecules, it is easy to understand how it is possible that changes of temperature easily disturb these azoid-quinoid equilibria.

[2] See experiments following, also see such text-books on dyes as Nietzki, "Chemistry of Organic Dyestuffs," 1892, 32; Fay's "Coal-Tar Dyes," p. 160.

[3] Whether helianthine is an acid or a base has led to varied opinions. Most investigators agree with Ostwald that it (methyl orange) is a weak acid. Waddell (*Chem. News*, 107, 206 (1913)), Jones (THIS JOURNAL, 37, 788 (1915)), and others, believe that it is a weak base. Stieglitz, Noyes and Hantzsch, and others believe that it is both a weak acid and a weak base. The observations of this paper are in agreement with the last opinion. Since all aqueous solutions of helianthine contain more than 70% of the azoid form (Formula I) it is evident that the acid properties of helianthine predominate. This is corroborated by the observation that helianthine forms salts more readily with bases than with acids. Even weak bases yield such salts, but some strong acids do not.

represented by equimolecular aqueous solutions of such salts. Veley's experiments,[1] directed toward the determination of the affinity constants[2] of acids and bases, involved color changes of methyl orange solutions. His calculations, not involving the factor of a large concentration of azoid molecules, led to anomalous conclusions.

(8) This will be discussed in connection with the experimental work.

(9) If all salts of helianthine are largely hydrolyzed to the azoid form, as indicated by the experiments of this paper, it is evident that the "ionic dissociation constants"[3] as determined by various investigators, are really the composite "constants" resulting from simultaneous hydrolysis, tautomerism and ionization. That such data were found by investigators[4] to be discordant, obviously was the result of varied conditions influencing these co-existing equilibria.

If Az, Az_2, etc., and Q, Q_2, etc., represent the ions containing respectively azoid and quinoid structures, we may assume: that Formulas I and II yield Az^-, H^+ and M^+; that Formula IV yields Q^- and H^+, Q_2^+ and Cl^-; that Formula II yields Q_3^- and H^+; that a hydrated form of Formula I yields Az_2^- and H^+, Az_3^+ and OH^-; and that a hydrated form of Formula II yields Q_4^- and H^+. Thus the different solutions of helianthine yield Az^-, Az_2^-, Az_3^-, Q^-, Q_2^+, Q_3^-, Q_4^-, M^+, H^+, OH^-, and Cl^-. Theoretically, methyl orange itself yields all of these ions except Q_2^+ and Cl^-.[5]

It is evident from these possibilities, when applied to methyl orange, that calculations of electrical conductivities, etc., to terms of H^+ concentrations must involve errors. Certainly, as shown by this paper, if changes of color of helianthine solutions are not caused primarily by hydrogen and hydroxyl ions, then the voluminous mathematical deductions of

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[1] *Proc. Chem. Soc.*, 23, 284; 24, 50; *Z. physik. Chem.*, 57, 147 (1906); 61, 464 (1907); *J. Chem. Soc.*, 93, 652, 2122 (1909); *Chem. News*, 104, 115 (1911).

[2] Various salts of helianthine were prepared and will be reported later. Parallels between known affinity constants of acids and bases, and their ease of salt formation or the stability of such salts toward water, could not be discovered.

[3] Friedenthal, *Z. Electrochem.*, 10, 114 (1910); Salessky, *Ibid.*, 10, 204; Fels, *Ibid.*, 10, 208; Salm, *Ibid.*, 10, 341; 12, 99 (1912); *Z. physik. Chem.*, 57, 494 (1910); 63, 83 (1908); Noyes, THIS JOURNAL, 32, 824 (1910); Tizard, *J. Chem. Soc.*, 97, 2483 (1910); Jones, THIS JOURNAL, 37, 776 (1915).

[4] Friedenthal gives the H^+ concentration of helianthine as 10^{-5} for the orange; Salessky, $10^{-2.8}$ for the red and $10^{-5.15}$ for the yellow; Fels, $10^{-3.3}$ for the red, $10^{-4.67}$ for the orange and $10^{-5.23}$ for the yellow; Salm, 10^{-5} for the orange; Noyes, 10^{-6} for the "sensitive point;" Tizard, 10^{-7} for the "neutral point." Jones gives the ionization of methyl orange as a base, 2.1×10^{-11}.

[5] For a discussion of the anomalous ionization of methyl orange see Tizard (*loc. cit.*). For inaccuracies of ionization constants of indicators as determined by various investigators, see Jones (*loc. cit.*).

Noyes,[1] of Jones,[2] and of others,[3] based on such H^+ and OH^- assumptions, must involve extensive errors.

That the change of color of helianthine solutions is independent of the ionization of the helianthine itself was first recognized almost simultaneously by Stieglitz[4] and Vaillant.[5] Previous to this, difficulty in interpreting these color changes on the basis of Ostwald's theory[6] had been met with by Küster,[7] Waddell,[8] and others.[9]

The Change of Color of Helianthine Solutions is Independent of Free Hydroxyl Ions and of Free Hydrogen Ions.—Hantzsch was the first to recognize that the changes of color from the red quinoid form to the yellow azoid form is independent of the presence of hydroxyl ions. Our experiments show this same independence and, on the other hand, the independence of the presence of hydrogen ions. Evidences for these conclusions are given herewith.

Its Independence of Hydroxyl Ions.

(1) Most *indifferent* solvents yield *yellow* helianthine solutions. (Absence of both OH^- and H^+.)

(2) Many helianthine solutions, *though acid to litmus*, are yellow in the lower concentrations. (Yellow in the presence of H^+.)

(3) Pure helianthine in pure water is red in the higher concentrations and is yellow when the solutions are more dilute than 0.001%. (In the practical absence of OH^- and H^+, it is either red or yellow.)

(4) Mere cooling changes quinoid molecules to azoid molecules. (No corresponding increase of OH^- ions.)

(5) *Acid* solutions of helianthine color fibers *yellow*. (Such yellow formation not hindered by the presence of H^+.)

(6) Absolute pyridine solutions are more persistently yellow than all corresponding *aqueous-alkaline* solutions. (Pyridine solutions contain no OH^-; solutions containing OH^- are less yellow.)

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[1] THIS JOURNAL, 32, 815 (1910).

[2] *Ibid.*, 37, 776 (1915).

[3] Stieglitz, THIS JOURNAL, 35, 1120 (1903); Acree, *Am. Chem. J.*, 38, 19 (1907).

[4] THIS JOURNAL, 25, 1114–1115 (1903).

[5] *Compt. rend.*, 137, 849 (1903). Vaillant's experiments showed that the molecular absorption of aqueous solutions remained practically constant at all dilutions in spite of varying ionic dissociations. Hantzsch's experiments showed varying absorptions of different acid and alkaline solutions at constant concentration, though these are not parallel with the respective ionic concentrations (*Ber.*, 46, 1540 (1913)).

[6] "Anal. Chem.," 105. "Methyl orange is a moderately strong acid, whose ion is yellow and whose undissociated molecule is red."

[7] *Z. anorg. Chem.*, 13, 136 (1897). See here Küster, "hybrid ion."

[8] *J. Phys. Chem.*, 2, 176 (1898). "The undissociated substance is yellow and the ion, whatever it may be, is red. This is a flat contradiction of Ostwald's view."

[9] Winkelblech, *Z. physik. Chem.*, 36, 569 (1901); Wagner, *Ibid.*, 27, 138 (1901); Bredig, *Z. Electrochem.*, 6, 35 (1901); Kremann, *Z. anorg. Chem.*, 33, 87 (1902); 35, 48 (1902); Bredig, *Ibid.*, 34, 202 (1902); Veley (*loc. cit.*).

(7) Hantzsch's absorption curves[1] are positive evidence.

Its Independence of Hydrogen Ions.

(1) Some indifferent solvents yield red helianthine solutions. (Absence of both OH^- and H^+.)

(2) Many helianthine solutions, *though alkaline to litmus,* are red in their higher concentrations. (Red in the presence of OH^-.)

(3) Same as (3) above.

(4) Heating certain concentrated solutions changes yellow azoid molecules to red quinoid molecules. (No corresponding increase of H^+.)

(5) Very acidic solutions of helianthine color fibers *red* while less acidic solutions color fibers *yellow.* (The color is not primarily determined by the mere presence of H^+.)

(6) Anhydrous phenol solutions[2] are more intensely red than are corresponding aqueous solutions containing strong acids. (Such phenol solutions contain few, if any, hydrogen ions; such aqueous acid solutions contain the maximum concentrations of hydrogen ions.)

Its Independence of Both OH^- and H^+.

In addition to the reasons given above may be added the following observations:

(1) Vaillant[3] found that the molecular absorption of aqueous solutions of methyl orange remains constant at all dilutions in spite of varying dissociation.

(2) "In pure aqueous solution,[4] both methyl orange and helianthine, notwithstanding the neutral reaction of the former and the acid reaction of the latter, are optically identical and are of the azoid form."

Methods of Colorimetric Study.

The methods of study employed below are largely the same as previously described.[5] A great variety of aqueous solutions of helianthine in percentage concentrations were prepared in 30 cc., square, clear glass bottles of 27 mm. diameter. The respective colors were then studied in contrast with standard solutions of helianthine contained in:

(*a*) Absolute phenol.

(*b*) Absolute pyridine.

(*c*) Formic acid (90%).

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[1] *Ber.*, 46, 1540 (1913); see also *Ibid.*, 48, 167 (1915). The other evidences presented by Hantzsch are, respectively, (1) and (2).

[2] That the quinhydrone theory is applicable to these intensely red-colored phenol solutions is rendered improbable not only by the observations of this paper but also by Hantzsch's molecular-weight determinations of certain helianthines in phenol. All of these salts are of intense violet color, are slightly dissociated and are *monomolecular*. *Ber.*, 42, 2129 (1909).

[3] *Compt. rend.*, 137, 849 (1903).

[4] Hantzsch, *Ber.*, 41, 1191 (1908).

[5] THIS JOURNAL, 36, 837 (1914).

(*d*) Normal hydrochloric acid.

(*e*) Water, with or without acids or alkalies.

If we assume that all solutions of helianthine represent equilibria of the two chromoisomers, it is easy to understand that almost an infinite variety of tints of color may be obtained, for we are dealing with two variables in a constant volume. Consider, by way of an example, that we can distinguish ten pure shades of red and ten pure shades of yellow. Now when these are mixed it is possible to obtain 100 different tints, for each shade of red can be blended with the respective ten shades of yellow. As a matter of fact, more than ten pure shades of red and yellow, respectively, can be distinguished, hence hundreds of tints of helianthine are obtainable and indeed were observed.

It may be stated here that though difficulty was met with, finally all the shades of helianthine were duplicated by the standards used, either singly or *in tandem*.

For the purpose of estimating quantitatively the components of such mixtures, experiments were undertaken to obtain pure yellow standard solutions and pure red standard solutions. Since the presence of water must rigorously be excluded and since the solvents must be, respectively, an alkali and an acid, the search quickly narrowed to pyridine[1] for the former and phenol[2] for the latter.

(*a*) **The Monochromatic Red Helianthine Standards.**—To 0.025 g. of pure helianthine contained in a 250 cc. volumetric flask was added pure anhydrous melted phenol. When filled to the mark, the flask contained 0.01% of helianthine. From this solution, various decimal solutions down to 0.00001% concentration were prepared by adding pure melted phenol. The bottles were then tightly stoppered so as to exclude atmospheric moisture. Of course, the contents of the bottles solidified[3]

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[1] On account of its greater alkaline properties and little tendency to turn yellow on standing, piperidine probably is a better solvent than pyridine for the yellow standards. Its greater expense, however, made its use prohibitive.

[2] Since phenol melts at 42–45° and *m*-cresol at 40°, the latter, if readily available, is better than the former for the red standard solutions.

[3] The undercooled phenol solutions crystallized on momentarily removing the corks.

Phenol containing varied quantities of water and the same quantities of helianthine (0.001%) were analyzed colorimetrically at 43°.

	Azoid.
90% Phenol was matched by 0.0008% phenol standard....	20%
80% Phenol was matched by 0.0007% phenol standard....	30%
70% Phenol was matched by 0.0004% phenol standard....	60%
60% Phenol was matched by 0.001% helianthine sol.......	100% cir.

The aqueous portion of the phenol-water mixtures, containing more than 40% of water, possessed no helianthine, This was showed by treatment of such aqueous portions with *N* HCl. On the other hand, the lower phenol layers contained all of the helianthine. Therefore, phenol can be used to extract helianthine from aqueous solutions.

Of course, Thompson's observation that phenol solutions are neutral toward methyl orange, is valid only in respect to aqueous solutions. *Chem. News*, **49**, 32, 38, 119 (1884).

on standing, but most often undercooling to the room temperature was possible without solidification. However, since heat tends to promote the formation of red helianthine and the phenol solutions were desired to be as red as possible, no disadvantage was imagined in using these phenol solutions when heated some degrees above 43°.

These phenol solutions were assumed to contain 100% of red helianthine molecules, for the reasons: (1) Their color was a deep *purple-red,* many times more intensely colored than corresponding aqueous helianthine solutions containing strong acids; (2) many anhydrous phenol, cresol and other phenolic solutions of helianthine of the same concentration were found to be identical in color; (3) heat does not appreciably intensify the color of such phenolic solutions; (4) solutions so dilute as to approach the limit of visibility were still pink in color.

That the solutions did contain traces of water and strictly did not contain 100% of red helianthine molecules was evidenced[1] by the fact that phenol solutions,[2] in concentrations lower than 0.00005%, were less intensely red colored than corresponding (90%) formic acid solutions.

(*b*) **The Monochromatic Yellow Helianthine Standards.**—A 0.01% solution of pure helianthine in pure anhydrous pyridine was prepared. By diluting this with pure pyridine any desired lower concentration of helianthine was obtained. A decimal series of such solutions, contained in the square 27 mm. bottles, gave a series of standard concentrations of yellow helianthine molecules. That few red helianthine molecules were contained in such solutions was indicated (1) by the persistently yellow color in all concentrations lower than 0.01%; (2) by such solutions being a purer yellow[3] than any prepared series of aqueous-alkaline solutions; (3) by special colorimetric studies.[4]

[1] *Vide infra.*

[2] When exposed for days to direct sunlight, some of the higher phenol standards became purple or blue; concentrations lower than 0.00006% became colorless. Evidently sunlight promotes deep-seated chemical changes that destroy the chromophor of helianthine. Perhaps the sulfonic group of helianthine, like various well-known reagents, oxidizes the phenol to colored products.

[3] The pyridine salt of helianthine has a solubility of 7.5 g. per 1000 cc. of pyridine. It is probable that between this concentration and the 0.01% concentration, many red molecules exist, because these pyridine solutions, like all other concentrated helianthine solutions, are either orange or nearly pure red. The higher pyridine solutions, however, were found to be convenient for matching certain solutions studied. The very dilute solutions of helianthine in pyridine were found to be of little value for pyridine itself is somewhat yellow.

[4] Two pyridine solutions placed *in tandem,* beside another pyridine solution whose concentration equalled the sum of the other two concentrations, were found to be equal in color. Here equal quantities of helianthine contained, respectively, in one and two volumes of pyridine possessed identical colors, hence, no disturbances of the tautomeric equilibria of helianthine resulted from increased concentration, as observed in aqueous alkaline solutions.

That the pyridine solutions contained some red molecules was evidenced by heating the respective bottles. Concentrations lower than 0.01% gave purer yellow shades.

(*c*) **The Formic Acid Series.**—Each of the bottles of this series contained 90% of formic acid and the decimal concentrations of helianthine. The advantage of this series was stability towards sunlight—one series remained practically unchanged for a year. The colors too were found to be redder than most hydrochloric acid series.

(*d*) **The Normal Hydrochloric Acid Series.**—Each bottle of this series contained *N* HCl and the decimal concentrations of helianthine. The solutions were easily prepared, were persistently red, and were more stable toward sunlight than more concentrated hydrochloric acid solutions.

(*e*) **The Aqueous Helianthine Solutions.**—These bottles contained the decimal concentrations of the helianthine and water alone or with known concentrations of acids or alkalies. These series were convenient for estimating the chromoisomerisms of solutions containing low concentrations of acids or alkalies.

The Method of Estimating Colors of Chromoisomeric Mixtures.—The solutions studied were of known concentration and were contained in square 27 mm. bottles similar to the ones containing the red and yellow standards. One red standard and one yellow standard, whose concentrations together equalled the concentration of the solution studied, were placed *in tandem* beside this solution. If the two viewed fields of color were found to be identical, the components of the chromoisomeric mixtures were assumed[1] to be equal, respectively, to the concentration of the red and of the yellow standards used. For example, if a 0.09% solution of methyl orange required a 0.008% solution of the yellow and a 0.001% solution of the red standards to give identical colors, then such methyl orange solution was assumed to contain 88.8% of yellow and 11.2% of red helianthine molecules.

As indicated by the tables following, solutions were more easily matched by one set of standards than by another. Frequently a number of trials were made before an exact duplication of color was obtained. Within certain limits[2] of concentration, it was found to be possible to obtain the exact tints and depths of all colors. These experiments were surprizingly satisfactory because they not only revealed at once the qualitative and the quantitative composition of helianthine solutions but proved conclusively that only two[3] chromoisomeric forms are involved in such solutions.

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[1] Of course, since the helianthine molecules are contained in two bottles in the one case and in one bottle in the other case, slight errors of optical distribution and disturbed equilibria are involved.

[2] Between 0.01 and 0.00005%.

[3] *Vide infra.*

Furthermore, these experiments gave convincing evidence that the *cause*[1] of the varied colors of helianthine solutions must be assigned to chromoisomeric groups and not to purely dynamic phenomena.

The upper ranges of concentrations were more or less inaccurately resolved colorimetrically into their respective azoid and quinoid components. At least three causes contributed to this inaccuracy: (1) all solutions of helianthine, whether acidic or neutral or alkaline, are red in their upper concentrations; (2) the operation of Weber's law of sensation, as applied to the sense of sight, involves large errors in reading; (3) helianthine in concentrated acid solution, as for example in hydrochloric acid, apparently lose color after standing, through deep-seated chemical reaction.[2]

Very dilute solutions also were estimated inaccurately or with difficulty for the reasons: (1) they approach the limit of visibility; (2) they are sensitive to traces of water, ammonia, carbon dioxide, etc., derived from the air; (3) they are faded by sunlight or are absorbed by the glass.[3]

The Chromoisomerism of Formic Acid (90%) Solutions of Helianthine.

Solutions of helianthine in formic acid (sp. gr. 1.20) in concentrations of 0.01% to 0.00001% were prepared. These solutions, though more intensely red than most hydrochloric acid solutions, were found to contain about $^2/_3$ of the helianthine in the azoid form, therefore it may be concluded that all aqueous solutions, whether acidic, neutral or alkaline, contain the greater[4] part of the helianthine in the yellow azoid form.

It will be observed here that: (1) the lower phenolic solutions contain some azoid molecules of helianthine, since such solutions are less colored than the corresponding concentrations in 90% formic acid. The presence of such azoid molecules evidently is caused by traces of water in the phenol; in the presence of water, being a stronger acid than phenol, formic acid maintains the helianthine more largely in the quinoid form. (2) Between 0.0001% and 0.01% concentrations in the formic acid, the colors could be matched quite easily; above these concentrations, owing to the operation of Weber's law, thick layers could not be analyzed and thin layers could be analyzed only approximately.

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[1] *Vide infra.*

[2] For the action of dilute nitric acid on helianthine, see Fox, *Ber.*, 41, 1989 (1908). For the action of nitrous acid, Lunge, *Z. angew. Chem.*, 16, 509 (1903). For the action of phenol, see above. For the effects of oxidation and hydrolysis on dyes, see Gebhard, *Ibid.*, 22, 2484 (1911).

[3] Reinitzer observes that ordinary glass may contain dissolved alkalies, etc., *Ibid.*, 7, 547, 574 (1894).

[4] From molecular extinction experiments Hantzsch came to the conclusion that only a small percentage of red quinoid molecules exist in aqueous solutions of helianthine. *Ber.*, 41, 1192 (1908). As showed above our experiments lead to the same conclusion.

TABLE I.

Formic Acid (Sp. Gr. 1.20).

Concentrations of solutions of				
	Matched by solutions of		Percentages of	
Formic acid (90%).	Phenol.	Pyridine.	Azoid.	Quinoid.
0.00001	0.00002	...	....	....
0.000015	0.00003	...	....	....
0.00002	0.00005	...	....	....
0.00005	0.00005	...	....	....
0.00007	0.00007	...	....	....
0.0001	0.00027	0.00063	63.0	37.0
0.0002	0.00015	0.0001	50.0	50.0
0.00024	0.00018	0.00012	50.0	50.0
0.0005	0.00021	0.00029	57.5	42.5
0.001	0.00027	0.00063	63.0	37.0
0.0012	0.0004	0.0008	66.6	33.4
0.0015	0.0005	0.0001	66.6	40.0
0.003	0.0006	0.0024	80.0	20.0
0.004	0.0006	0.003	75.0	25.0
0.005	0.0009	0.0041	82.0	18.0
0.015	0.0012	0.0138	92.0	8.0
0.018	0.0015	0.0165	92.0	8.0
0.019	0.001	0.018	94.7	5.3
0.025	0.0018	0.023	92.0	8.0
		Average,	73.2	26.8

The Chromoisomerism of Normal Hydrochloric Acid Solutions of Helianthine.

These solutions were studied by duplicating the colors with pyridine and formic acid solutions viewed *in tandem*. Whereas the sum of the two latter concentrations ought always to equal the concentrations of the *N* HCl solutions, it was found that moderate variations from the true concentrations of the pyridine solutions made no observable effect on the duplications of color. Therefore the matching of colors[1] was made by using either the exact or the approximate shade of yellow, with the exact shade of red. The formic acid reading was subtracted from the *N* HCl concentration to give the calculated pyridine concentration. This difference divided by the *N* HCl concentration gave the *apparent azoid* concentration. Assuming that the azoid concentration of the 90% formic acid[2] solutions to be 70%, the *true azoid* concentrations can be calculated.

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[1] Since artificial light tends to obscure the yellow of helianthine solutions, readings to determine the percentages of the red may advantageously be made by such light. This phenomenon was also observed by Tizard, *J. Chem. Soc.*, **97**, 2481 (1910).

[2] Though the average value obtained was 73.2%, the lower value of 70% was used in the following calculations for the reasons: (1) calculations were thereby simplified; (2) no claim of great experimental accuracy can be made for the 73.2%, owing to the great color density of the phenol solutions.

The N HCl solutions[1] were red-to-pink throughout and were found to contain about an average of 87% concentration of yellow azoid molecules. This discovery was surprizing since it indirectly demonstrated that *all aqueous solutions of strong acids are capable of transforming only a small percentage of helianthine molecules to the red quinoid form.*[2]

TABLE II.

Normal Hydrochloric Acid Solutions of Helianthine.

Concentration of solutions in			Percentages of chromoisomers.		
	Matched by solutions of				
N HCl.	Pyridine (calc.).	Formic acid (90%).	Azoid (apparent).	Azoid (calc.).	Quinoid.
$0.0_{4}15$	$0.0_{5}5$	$0.0_{4}1$	33.3	80.0	20.0
$0.0_{4}2$	$0.0_{5}5$	$0.0_{4}15$	25.0	77.5	22.5
$0.0_{4}3$	$0.0_{4}1$	$0.0_{4}2$	33.3	80.0	20.0
$0.0_{4}4$	$0.0_{4}2$	$0.0_{4}2$	50.0	85.0	15.0
$0.0_{4}5$	$0.0_{4}25$	$0.0_{4}25$	50.0	85.0	15.0
$0.0_{4}6$	$0.0_{4}3$	$0.0_{4}3$	50.0	85.0	15.0
$0.0_{4}7$	$0.0_{4}35$	$0.0_{4}35$	50.0	85.0	15.0
$0.0_{4}8$	$0.0_{4}4$	$0.0_{4}4$	50.0	85.0	15.0
$0.0_{4}9$	$0.0_{4}45$	$0.0_{4}45$	50.0	85.0	15.0
$0.0_{3}1$	$0.0_{3}5$	$0.0_{4}5$	50.0	85.0	15.0
$0.0_{3}15$	$0.0_{3}7$	$0.0_{4}8$	46.6	84.0	16.0
$0.0_{3}2$	$0.0_{3}1$	$0.0_{3}1$	50.0	85.0	15.0
$0.0_{3}3$	$0.0_{3}15$	$0.0_{3}15$	50.0	85.0	15.0
$0.0_{3}4$	$0.0_{3}2$	$0.0_{3}2$	50.0	85.0	15.0
$0.0_{3}5$	$0.0_{3}25$	$0.0_{3}25$	50.0	85.0	15.0
$0.0_{3}6$	$0.0_{3}3$	$0.0_{3}3$	50.0	85.0	15.0
$0.0_{3}7$	$0.0_{3}3$	$0.0_{3}4$	42.5	82.7	17.3
$0.0_{3}8$	$0.0_{3}4$	$0.0_{3}4$	50.0	85.0	15.0
$0.0_{3}9$	$0.0_{3}45$	$0.0_{3}45$	50.0	85.0	15.0
$0.0_{2}1$	$0.0_{3}5$	$0.0_{3}5$	50.0	85.0	15.0
$0.0_{2}15$	$0.0_{3}7$	$0.0_{3}8$	46.6	84.0	16.0
$0.0_{2}2$	$0.0_{2}12$	$0.0_{3}8$	60.0	88.0	12.0
$0.0_{2}3$	$0.0_{2}21$	$0.0_{3}9$	70.0	91.0	9.0
$0.0_{2}4$	$0.0_{2}3$	$0.0_{3}9$	77.5	93.2	6.8
$0.0_{2}5$	$0.0_{2}4$	$0.0_{2}1$	80.0	94.0	6.0
$0.0_{2}6$	$0.0_{2}45$	$0.0_{2}15$	75.0	92.1	7.9
$0.0_{2}7$	$0.0_{2}55$	$0.0_{2}15$	78.5	93.5	6.5
$0.0_{2}8$	$0.0_{2}65$	$0.0_{2}15$	81.3	94.4	5.6
$0.0_{2}9$	$0.0_{2}75$	$0.0_{2}15$	83.3	95.0	5.0
0.01	$0.0_{2}85$	$0.0_{2}15$	85.0	95.5	4.5
		Average,	50.28	86.66	13.34

Alkaline Solutions of Helianthine.

Pure helianthine was prepared according to the method of Hantzsch.[3]

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[1] Whereas the hydrochloric acid solutions were normal, the formic acid solutions were $23.5/N$.

[2] The end point of methyl orange titrations will be discussed later.

[3] *Ber.*, 46, 1538 (1913).

It was also prepared by treating methyl orange with an excess of acetic acid, filtering, and then boiling for some time with a large volume of water. On cooling and filtering pure helianthine was obtained. It may be washed first with alcohol then with ether, if rapid drying is necessary.

TABLE III.

Alkaline Solutions of Helianthine Matched against *N* HCl Solutions of Helianthine.

Concentrations of solutions tested.	Free helianthine.			Methyl orange.			Helianthine + 10 mols. NaOH.			Helianthine + 100 mols. NaOH.		
	Pyridine.	*N* HCl.	Azoid, %.	Pyridine.	*N* HCl.	Azoid, %.	Pyridine.	*N* HCl.	Azoid, %.	Pyridine.	*N* HCl.	Azoid, %.
$0.0_{3}1$	$0.0_{3}1$	...	....	...	...	....	$0.0_{4}9$	$0.0_{4}1$	90.0	$0.0_{4}8$	$0.0_{4}15$	85.0
$0.0_{3}15$	$0.0_{3}1$	$0.0_{4}2$	86.6	...	...	....	$0.0_{3}1$	$0.0_{4}15$	90.0	$0.0_{3}1$	$0.0_{4}2$	86.6
$0.0_{3}2$	$0.0_{3}2$	$0.0_{4}25$	87.5	...	...	....	$0.0_{3}2$	$0.0_{4}2$	90.0	$0.0_{3}2$	$0.0_{4}2$	90.0
$0.0_{3}3$	$0.0_{3}3$	$0.0_{4}4$	86.6	$0.0_{3}3$	$0.0_{4}3$	90.0	$0.0_{3}3$	$0.0_{4}3$	90.0	$0.0_{3}3$	$0.0_{4}3$	90.0
$0.0_{3}4$	$0.0_{3}3$	$0.0_{4}6$	85.0	$0.0_{3}3$	$0.0_{4}5$	92.5	$0.0_{3}3$	$0.0_{4}4$	90.0	$0.0_{3}3$	$0.0_{4}5$	87.5
$0.0_{3}5$	$0.0_{3}4$	$0.0_{4}7$	86.0	$0.0_{3}4$	$0.0_{4}7$	86.0	$0.0_{3}4$	$0.0_{4}8$	84.0	$0.0_{6}4$	$0.0_{4}6$	88.0
$0.0_{3}6$	$0.0_{3}5$	$0.0_{4}8$	86.6	$0.0_{3}5$	$0.0_{4}9$	85.0	$0.0_{3}5$	$0.0_{4}9$	85.0	$0.0_{3}5$	$0.0_{4}7$	88.3
$0.0_{3}7$	$0.0_{3}6$	$0.0_{3}1$	85.5	$0.0_{3}6$	$0.0_{3}1$	85.7	$0.0_{3}6$	$0.0_{3}1$	85.7	$0.0_{3}6$	$0.0_{4}8$	88.2
$0.0_{3}8$	$0.0_{3}7$	$0.0_{3}1$	87.5	$0.0_{3}6$	$0.0_{3}15$	81.2	$0.0_{3}7$	$0.0_{3}12$	85.0	$0.0_{3}7$	$0.0_{4}9$	90.0
$0.0_{3}9$	$0.0_{3}8$	$0.0_{3}12$	86.6	$0.0_{3}7$	$0.0_{3}15$	83.6	$0.0_{3}7$	$0.0_{3}13$	86.6	$0.0_{3}8$	$0.0_{3}1$	88.8
$0.0_{2}1$	$0.0_{3}9$	$0.0_{3}15$	85.0	$0.0_{3}8$	$0.0_{3}15$	85.0	$0.0_{3}8$	$0.0_{3}15$	85.0	$0.0_{3}9$	$0.0_{3}15$	85.0
$0.0_{2}15$	$0.0_{2}1$	$0.0_{3}2$	86.6	$0.0_{2}1$	$0.0_{3}2$	86.5	$0.0_{2}1$	$0.0_{3}15$	90.0	$0.0_{2}1$	$0.0_{3}15$	90.0
$0.0_{2}2$	$0.0_{2}2$	$0.0_{3}25$	87.5	$0.0_{2}2$	$0.0_{3}25$	87.5	$0.0_{2}2$	$0.0_{3}2$	90.0	$0.0_{2}15$	$0.0_{3}2$	90.0
$0.0_{2}3$	$0.0_{2}3$	$0.0_{3}4$	86.6	$0.0_{2}3$	$0.0_{3}3$	90.0	$0.0_{2}3$	$0.0_{3}3$	90.0	$0.0_{2}3$	$0.0_{3}2$	93.3
$0.0_{2}4$	$0.0_{2}4$	$0.0_{3}6$	85.0	$0.0_{2}4$	$0.0_{3}3$	92.5	$0.0_{2}4$	$0.0_{3}3$	92.5	$0.0_{2}4$	$0.0_{3}4$	90.0
$0.0_{2}5$	$0.0_{2}5$	$0.0_{2}15$	70.0	$0.0_{2}25$	$0.0_{3}4$	92.0	$0.0_{2}5$	$0.0_{3}4$	92.0	$0.0_{2}4$	$0.0_{3}4$	92.0
$0.0_{2}6$	$0.0_{2}5$	$0.0_{2}15$	75.0	$0.0_{2}6$	$0.0_{3}5$	91.6	$0.0_{2}6$	$0.0_{3}5$	91.7	$0.0_{2}5$	$0.0_{3}4$	90.0
$0.0_{2}7$	$0.0_{2}5$	$0.0_{2}2$	71.4	$0.0_{2}7$	$0.0_{3}5$	83.0	$0.0_{2}6$	$0.0_{2}5$	93.0	$0.0_{2}6$	$0.0_{3}5$	83.0
$0.0_{2}8$	$0.0_{2}6$	$0.0_{2}2$	75.0	$0.0_{2}7$	$0.0_{3}6$	92.5	$0.0_{2}7$	$0.0_{2}6$	92.5	$0.0_{2}7$	$0.0_{3}5$	94.0
$0.0_{2}9$	$0.0_{2}7$	$0.0_{2}2$	77.7	$0.0_{2}8$	$0.0_{2}1$	88.8	$0.0_{2}8$	$0.0_{2}6$	92.2	$0.0_{2}8$	$0.0_{3}5$	94.5
0.01	$0.0_{2}8$	$0.0_{2}2$	80.0	...	...	....	$0.0_{2}9$	$0.0_{3}6$	94.0	$0.0_{2}9$	$0.0_{3}6$	94.0
0.015	...	...	....	...	...	....	0.01	$0.0_{3}9$	94.0	0.01	$0.0_{3}9$	94.0
0.02	...	...	....	...	...	....	0.02	$0.0_{2}15$	92.5	0.02	$0.0_{2}15$	92.5
0.03	...	...	....	...	...	....	0.03	$0.0_{2}2$	90.0	0.03	$0.0_{2}2$	93.3
0.04	...	...	....	...	...	....	0.03	$0.0_{2}6$	85.0	0.04	$0.0_{2}2$	95.0
0.05	...	...	....	...	...	....	0.04	$0.0_{2}7$	86.0	...	...	....
Apparent average,			82.8	Average,		87.2	Average,		89.5	Average,		90.1
Calculated average,			97.70	Average,		98.28	Average,		98.59	Average,		98.67

Here it is observed that:

(1) Helianthine itself averages 97.70% of azoid[1] molecules when dissolved in water.

(2) In the presence of 1, 10 and 100 molecules of sodium hydroxide, when dissolved in water, helianthine gives, respectively, 98.28%, 98.59%

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[1] Assuming the *N* HCl to be 13.34% quinoid (see Table II), we have 82.8 × 13.34 = 11.04; this added to the 86.66 azoid gives 97.70% azoid for the pure helianthine.

and 98.67% azoid concentrations. These data show that *even much strong alkali does not yield pure yellow solutions.* Other direct proofs[1] of this statement are: (*a*) heating these solutions gives purer yellows; (*b*) comparing these solutions with pyridine solutions reveal their *redder* color.

TABLE IV.

Alkaline Solutions Compared with Pure Pyridine Solutions.

Pyridine.	Methyl orange. I.	10 NaOH. II.	100 NaOH. III.	1000 NaOH. IV.	10000 NaOH. V.	Color ratios. I.	II.	III.	IV.	V.
0.0_23	...	...	...	0.0_37	...	....	....	....	4.3	....
0.0_24	...	...	...	...	0.0_36	....	....	....	....	6.6
0.0_25	...	...	0.0_36	...	0.0_37	....	....	8.3	....	7.1
0.0_26	...	0.0_36	0.0_37	...	0.0_38*	....	10.0	8.5	....	7.7
0.0_27	0.0_37	0.0_37	0.0_38	0.0_38	...	....	10.0	11.2	11.2	....
0.0_28	0.0_38	0.0_38	0.0_39*	0.0_39*	...	8.8	8.8	8.8	8.8	....
0.0_29	0.0_39*	0.0_39*	...	...	...	10.0	10.0	....	....	....
0.01	0.0_21	0.0_21	0.0_21	0.0_21	0.0_39	10.0	10.0	10.0	10.0	11.1
0.015	...	...	0.0_215	0.0_215	0.0_21	....	....	10.0	10.0	15.0
0.02	0.0_215	0.0_22	0.0_22	0.0_22	$\underline{0.0_22}$	13.3	10.0	10.0	10.0	10.0
0.03	0.0_22	0.0_22	...	...	...	....	....	....	....	....
0.04	...	0.0_23	0.0_23	0.0_23	0.0_23	....	13.3	13.3	13.3	13.3
0.05	0.0_23	0.0_24	0.0_24	0.0_24	...	16.6	12.5	12.5	12.5	....
0.06	0.0_24	0.0_24	...	...	...	15.0	15.0	....	....	....
0.07	0.0_25	0.0_25	0.0_25	0.0_25	...	14.0	14.0	14.0	14.0	....
0.08	0.0_25	0.0_26	0.0_26	0.0_26	...	16.0	13.3	13.3	13.3	....
0.09	0.0_26	0.0_27	0.0_27	0.0_27	...	15.0	12.9	12.9	12.9	....
0.1	0.0_28	0.0_28	0.0_28	$\underline{0.0_28}$	...	12.5	12.5	12.5	12.5	....
0.2	0.01	0.01	$\underline{0.01}$	0.01	...	20.0	20.0	20.0	20.0	....
0.3	0.02	$\underline{0.02}$	0.02	...	...	15.0	15.0	15.0	....	....
0.4	...	...	...	...	...	....	....	....	....	....
0.5	$\underline{0.03}$	0.03	0.03	...	...	16.7	16.7	16.7	....	....
0.6	...	0.04	...	...	...	....	15.0	....	....	....
$\underline{0.7}$	...	...	...	...	...	....	....	....	....	....
					Average,	14.1	13.5	12.3	11.7	10.1

Here it is observed that aqueous alkaline solutions of helianthine are many times "redder" than pyridine solutions and indeed that all aqueous solutions of helianthine contain red quinoid molecules.

The data of these tables show:

(1) Below 0.0_81% concentration of helianthine all alkaline and some acid solutions possess identical shades of color; at higher concentrations of helianthine, varied alkaline and acid solutions possess different shades of color.

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[1] See tables following.

* Above this sign, colors do not match the pyridine solutions, the latter being nearly pure yellow and the aqueous solutions being tinged with red. The horizontal line marks the limits of solubility.

TABLE V.

Solutions Compared with a Strong Alkaline Solution.

8.3 KOH taken as standard.	2.7 KOH. I.	0.1 KOH. II.	0.1 HCl. III.	1.7 HCl. IV.	3.3 HCl. V.	193 HCl. VI.	Color ratios.					
							I.	II.	III.	IV.	V.	VI.
0.0_32	0.0_32	0.0_32	0.0_32	0.0_32	0.0_32	...	1.0	1.0	1.0	1.0	1.0	....
0.0_33	0.0_33	0.0_33	0.0_33-	0.0_33-	...	...	1.0	1.0	1+	1+	....	....
0.0_34	0.0_34	0.0_34	0.0_34-	0.0_34-	...	...	1.0	1.0	1+	1+	....	....
0.0_35	0.0_35	0.0_35	0.0_35-	0.0_35-	...	...	1.0	1.0	1+	1+	....	....
0.0_36	0.0_36	0.0_36	0.0_36-	0.0_36-	0.0_36-	...	1.0	1.0	1+	1+	1+	....
0.0_37	0.0_37	0.0_37	0.0_36	0.0_36	...	...	1.0	1.0	1.16	1.16	....	....
0.0_38	0.0_38	0.0_38	0.0_37	0.0_37	...	0.0_37	1.0	1.0	1.14	1.14	....	1.14
0.0_39	0.0_39	0.0_39	0.0_38	0.0_38	0.0_38	...	1.0	1.0	1.13	1.13	1.13	....
0.0_21	0.0_21	0.0_21	0.0_39-	0.0_39-	...	...	1.0	1.0	1.11	1.11	....	....
0.0_22	0.0_22	0.0_22	0.0_22-	0.0_22-	...	0.0_21+	1.0	1.0	1+	1+	....	2−
0.0_23	0.0_23	0.0_23	0.0_22+	0.0_22	...	...	1.0	1.0	1.50	1.50	....	....
0.0_24	0.0_24	0.0_24	0.0_23+	0.0_23	0.0_22+	...	1.0	1.0	1.33−	1.33−	2−	....
0.0_25	0.0_25	0.0_25	0.0_24	0.0_24-	...	...	1.0	1.0	1.25	1.25−	....	....
0.0_26	0.0_26	0.0_26	0.0_25-	0.0_24	...	...	1.0	1.0	1.20	1.50	....	....
0.0_27	0.0_27	0.0_27	0.0_25	0.0_24+	...	...	1.0	1.0	1.40	1.75−	....	....
0.0_28	0.0_28	0.0_28	0.0_26	0.0_26	...	...	1.0	1.0	1.33	1.33	....	....
0.0_29	0.0_29	0.0_29	0.0_27	0.0_26	...	0.0_22	1.0	1.0	1.30	1.50	....	4.5
0.01	0.01	0.01	0.0_28	0.0_26	...	0.0_22+	1.0	1.0	1.25	1.66	....	5.0−
0.02	0.02	0.02	0.01+	0.0_28	0.0_23-	0.0_22	1.0	1.0	2.0 −	2.50	6.6+	10.0
0.03	0.03	0.03	0.015	0.0_29	0.0_23	...	1.0	1.0	2.00	3.33	10.0	....
						Average,	1.0	1.0	1.25	1.41	3.62	4.53

TABLE VI.

Solution Compared with a Very Strong Alkaline Solution.

10000 mol. NaOH. Standard.	1000 mol. NaOH. I.	100 mol. NaOH. II.	10 mol. NaOH. III.	1 mol. NaOH. IV.	Color ratios.			
					I.	II.	III.	IV.
0.0_31	0.0_31	0.0_31	0.0_31	0.0_31	1.0	1.0	1.0	1.0
0.0_315	0.0_315-	0.0_315-	0.0_31	0.0_31	1+	1.1+	1.5	1.5
0.0_32	0.0_32-	0.0_32-	0.0_32-	0.0_32-	1+	1+	1+	1+
0.0_33	0.0_33-	0.0_33-	0.0_33-	0.0_33-	1+	1+	1+	1+
0.0_34	0.0_34-	0.0_34-	0.0_34-	0.0_34-	1+	1+	1+	1+
0.0_35	0.0_35-	0.0_35-	0.0_35-	0.0_35-	1+	1+	1+	1+
0.0_36	0.0_36-	0.0_36-	0.0_35	0.0_35	1+	1+	1.2	1.2
0.0_37	0.0_37-	0.0_37-	0.0_36	0.0_36	1+	1+	1.14	1.14
0.0_38	0.0_38-	0.0_38-	0.0_37	0.0_37	1+	1+	1.14	1.14
0.0_39	0.0_39-	0.0_39-	0.0_38	0.0_38	1+	1+	1.13	1.13
0.0_21	0.0_21-	0.0_21-	0.0_39	0.0_39	1+	1+	1.11	1.11
0.0_22	0.0_22-	0.0_22-	0.0_215	0.0_215	1+	1+	1.33	1.33
0.0_23	0.0_23-	0.0_23-	0.0_22	0.0_22-	1+	1+	1.50	1.50+
				Average,	1+	1+	1.15+	1.16+

(2) Alkaline solutions of helianthine differ from one another less widely than do acid solutions of the same. As showed above, this is be-

cause all alkaline and certain aqueous acidic solutions of helianthine are largely possessed of yellow azoid molecules.

(3) Solutions of helianthine containing concentrated alkalies are more yellow, that is, they are less red, than are dilute alkaline solutions of the same. That even the concentrated solutions contain red molecules is easily proven by the contrasts evident when compared with anhydrous pyridine solutions—for equal concentrations of helianthine, the former are always redder.

If series of aqueous solutions in decimal concentrations of helianthine, of helianthine with 1 mol. NaOH, and of helianthine with 1 mol. HCl are aligned adjacent to one another, no great differences of color are noticeable—all of the solutions are red in the upper, and yellow in the lower concentrations. If whole series are moved along, they can be made to match one another quite closely, or if the individual concentrations of one series are carefully compared with different concentrations of another series, duplications of color can always be made. In other words, the different shades of color are found in all three series but at lower or at higher concentrations for the respective series.

TABLE VII.

Color Ratios of Alkaline and Acid Solutions of Helianthine—Compared with Aqueous Solutions of Helianthine.

			Color ratios.	
1 mol. NaOH.	Helianthine.	1 mol. HCl.		
$0.0_{3}3$	$0.0_{3}3$	$0.0_{3}3$	1.00	1.00
$0.0_{3}4$ (A)	$0.0_{3}4$	$0.0_{3}4$	1.00	1.00
$0.0_{3}5$	$0.0_{3}5$	$0.0_{3}4$	1.00	0.80
$0.0_{3}6$	$0.0_{3}6$	$0.0_{3}5$	1.00	0.83
$0.0_{3}7$	$0.0_{3}7$	$0.0_{3}6$	1.00	0.85
$0.0_{3}8$	$0.0_{3}8$ (B)	$0.0_{3}7$	1.00	0.87
$0.0_{2}1$	$0.0_{3}9$	$0.0_{3}8$	1.11	0.88
$0.0_{2}15$	$0.0_{2}1$	$0.0_{3}9$ (C)	1.50	0.90
$0.0_{2}25$	$0.0_{2}15$	$0.0_{2}1$	1.66	0.66
$0.0_{2}4$	$0.0_{2}2$	$0.0_{2}15$	2.00	0.75
$0.0_{2}9$	$0.0_{2}3$	$0.0_{2}25$	3.00	0.87
0.02 (D)	$0.0_{2}4$	$0.0_{2}3$	5.00	0.75
0.035	$0.0_{2}5$	$0.0_{2}4$	7.00	0.80
0.04 (E)	$0.0_{2}6$	$0.0_{2}4$	6.66	0.66
0.05	$0.0_{2}7$	$0.0_{2}4$	7.14	0.57
....	$0.0_{2}8$	$0.0_{2}45$	....	0.50
....	$0.0_{2}9$	$0.0_{2}5$	....	0.55
....	0.01	$0.0_{2}6$	....	0.60
			Average, 2.74	0.71

It will be observed that:

(1) Below $0.0_{3}4$% and at equal concentrations, the three series possess identical shades of color; above $0.0_{3}8$% and at *unequal* concentrations,

the three series possess identical shades of color. The horizontal lines (A) and (B) indicate the concentrations at which the colors become identical.

From this table it becomes evident that too dilute solutions of helianthine are useless for titrations, for the reason that such solutions are *equally yellow*,[1] though containing free acids or free alkalies.[2] Since, on the other hand, too concentrated solutions of helianthine are red, though unequally red for different concentrations of acids and alkalies, such concentrated[3] solutions are also useless for titrations. Hence it must be evident that some intermediate concentration of helianthine is the most favorable for titrations.

(2) The horizontal line (C) indicates the concentration at which the color changes are most *abrupt*, that is, the "neutral point" obtained in titrations or the transition-concentration from "red to yellow." It is evident that while using slightly more helianthine and 1 mol. NaOH or slightly less helianthine and 1 mol. HCl, this same "end point" may be obtained, therefore, strictly speaking, it is neither an "end point" or a "neutral point." This will become more evident when the following tables are studied, for it will be showed that with certain concentrations of helianthine, of far greater concentrations than 1 mol. NaOH and 1 mol. HCl, the same "end points" may be obtained. Hence, in all accurate titrations[4] involving methyl orange as the indicator, it must be evident that *the concentration of the indicator*[5] *in the final volume of titrated solution must be constant.* This, as revealed in the table, is 1–1.5 parts of helianthine in 10,000 of water.

(3) The horizontal lines (D) and (E) mark the limits of solubility at room temperatures. Heating the solutions so as to obtain supersaturated solutions at room temperatures enables one to compare the colors to higher limits.

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[1] Also see tables following.

[2] As proven: (*a*) by litmus paper; (*b*) by the known addition of acids and alkalies; and (*c*) by the colorimetric experiments of this paper.

[3] Owing to the operation of Weber's law, as applied to color impressions, increasing or high concentrations of colored solutions are of less value in titrations.

[4] Since nearly all titrations are colorimetric processes, it is evident that other errors of colorimetry discussed in a following paper must be avoided.

[5] The usual stock concentration of methyl orange is 1 g. in 1000 cc. In titrations one drop of this is diluted to 100 cc., thus giving a final concentration of 0.045%. This is 20 times too dilute.

Since methyl orange is soluble only 0.4 g. per liter at room temperatures, the stock concentration should be this, or *if 0.15 g. of methyl orange is dissolved in 1000 cc. of water and 1 cc. of this is used in 100 cc. of titrated solution*, the final concentration of helianthine will be nearly equal to 0.0015%, the most favorable concentration. Of course, for final volumes passing 100 cc., other cc.'s of indicator and water should be added so that the final volume is exactly 100 times the number of cc.'s used.

TABLE VIII.

Hydrochloric Acid Solutions of Helianthine, Compared with Pyridine and Formic Acid Solutions.

Concentrations of solutions tested.	A. Helianthine.		B. Hel. + HCl.		C. Hel. + 10HCl.		D. Hel. + 20HCl.		E. Hel. + 100HCl.		F. Hel. + 200HCl.		G. Hel. + 1000HCl. Formic acid.	H. Hel. + 10000HCl. Formic acid.	I. *N* HCl. Formic acid.
	Formic.	Pyr.	Formic.	Pyr.	Formic.	Pyr.	Formic.	Pyr.	Formic.	Pyr.	Formic.	Pyr.			
$0.0_{4}2$	....	...	....	....	....	...	....	...	....	...	....	...	....	$0.0_{3}1$	$0.0_{4}9$
$0.0_{4}3$	....	...	....	....	....	...	....	...	....	...	....	...	$0.0_{4}2$	$0.0_{3}15$	$0.0_{3}15$
$0.0_{4}4$	....	...	....	....	....	...	....	...	....	...	....	...	$0.0_{4}2$	$0.0_{3}2$	$0.0_{3}3$
$0.0_{4}5$	....	...	....	....	....	...	....	...	....	...	$0.0_{4}2$	...	$0.0_{4}2$	....	....
$0.0_{4}6$	....	...	....	....	....	...	....	...	....	...	$0.0_{4}2$	...	$0.0_{4}2$	$0.0_{3}3$	....
$0.0_{4}7$	....	...	....	....	....	...	....	...	....	...	$0.0_{4}2$	...	$0.0_{4}3$	$0.0_{3}4$	$0.0_{3}4$
$0.0_{4}8$	....	...	....	....	....	...	....	...	....	...	$0.0_{4}2$	...	$0.0_{4}3$	$0.0_{3}5$	$0.0_{3}4$
$0.0_{4}9$	....	...	....	....	....	...	....	...	....	...	$0.0_{4}3$	...	$0.0_{4}3$	$0.0_{3}6$	$0.0_{3}5$
$0.0_{3}1$	....	...	....	....	$0.0_{4}2$	$0.0_{3}1$	....	...	....	...	$0.0_{4}3$	...	$0.0_{4}4$	$0.0_{3}7$	$0.0_{3}6$
$0.0_{3}15$	....	...	....	....	....	...	....	...	....	...	$0.0_{4}4$	...	$0.0_{4}6$	$0.0_{3}8$	$0.0_{3}9$
$0.0_{3}2$	....	...	....	....	$0.0_{4}3$	$0.0_{3}3$	$0.0_{4}2$	$0.0_{3}1$	....	...	$0.0_{4}7$	...	$0.0_{3}1$	$0.0_{3}9$	$0.0_{2}15$
$0.0_{3}3$	....	...	....	....	$0.0_{4}5$	$0.0_{3}3$	$0.0_{4}4$	$0.0_{3}2$	....	...	$0.0_{3}1$	...	$0.0_{3}15$	$0.0_{2}1$	$0.0_{2}15$
$0.0_{3}4$	....	...	....	....	$0.0_{3}1$	$0.0_{3}5$	$0.0_{4}6$	$0.0_{3}2$	....	...	$0.0_{3}15$	$0.0_{3}2$	$0.0_{3}2$	....	$0.0_{2}3$
$0.0_{3}5$	....	...	....	....	$0.0_{3}15$	$0.0_{3}5$	$0.0_{4}8$	$0.0_{3}2$	$0.0_{3}2$	$0.0_{3}1$	$0.0_{3}2$	$0.0_{3}2$	$0.0_{3}3$	....	$0.0_{2}3$
$0.0_{3}6$	....	...	....	....	$0.0_{3}2$	$0.0_{3}6$	$0.0_{4}9$	$0.0_{3}2$	$0.0_{3}3$	$0.0_{3}1$	$0.0_{3}3$	$0.0_{3}2$	$0.0_{3}4$	....	$0.0_{2}4$
$0.0_{3}7$	....	$0.0_{2}3$	....	....	$0.0_{3}2$	$0.0_{3}6$	$0.0_{3}11$	$0.0_{3}2$	$0.0_{3}3$	$0.0_{3}1$	$0.0_{3}3$	$0.0_{3}2$	$0.0_{3}4$	....	$0.0_{2}5$
$0.0_{3}8$	....	$0.0_{2}4$	....	$0.0_{2}5$	$0.0_{3}3$	$0.0_{3}6$	$0.0_{3}13$	$0.0_{3}2$	$0.0_{3}4$	$0.0_{3}1$	$0.0_{3}4$	$0.0_{3}2$	$0.0_{3}4$	$0.0_{2}2$	$0.0_{2}6$
$0.0_{3}9$	....	$0.0_{2}5$	....	$0.0_{2}8$	$0.0_{3}4$	$0.0_{3}6$	$0.0_{3}15$	$0.0_{3}2$	$0.0_{3}5$	$0.0_{3}1$	$0.0_{3}4$	$0.0_{3}2$	$0.0_{3}4$	$0.0_{2}3$	$0.0_{2}7$
$0.0_{2}1$	....	$0.0_{2}6$	....	$0.0_{2}15$	$0.0_{3}6$	$0.0_{3}6$	$0.0_{3}16$	$0.0_{3}2$	$0.0_{3}6$	$0.0_{3}1$	$0.0_{3}45$	$0.0_{3}2$	....	....	$0.0_{2}8$
$0.0_{2}15$	....	$0.0_{2}8$	....	$0.0_{2}3$	$0.0_{3}8$	$0.0_{3}6$	$0.0_{3}2$	$0.0_{3}2$	$0.0_{3}6$	$0.0_{3}1$	$0.0_{3}5$	$0.0_{3}2$	....	$0.0_{2}4$	....
$0.0_{2}2$	$0.0_{3}1$	0.02	$0.0_{3}15$	0.02	....	...	$0.0_{3}3$	$0.0_{3}2$	$0.0_{3}7$	$0.0_{3}1$	$0.0_{3}5$	$0.0_{3}2$	....	$0.0_{2}5$	....
$0.0_{2}3$	$0.0_{3}2$	0.03	$0.0_{3}3$	0.03	....	...	$0.0_{3}4$	$0.0_{3}2$	$0.0_{3}7$	$0.0_{3}1$	....	...	....	....	....
$0.0_{2}4$	$0.0_{3}4$	0.05	$0.0_{3}7$	0.04	....	...	$0.0_{3}5$	$0.0_{3}2$	$0.0_{3}8$	$0.0_{3}1$	....	...	....	....	....
$0.0_{2}5$	$0.0_{3}5$	0.05	$0.0_{3}8$	0.05	....	...	$0.0_{3}8$	$0.0_{3}2$	$0.0_{2}15$	...	....	...	....	....	....
$0.0_{2}6$	$0.0_{3}6$	0.06	$0.0_{3}8$	0.06	....	...	$0.0_{2}15$	$0.0_{3}2$	....	...	....	...	....	....	....
$0.0_{2}7$	$0.0_{3}7$	0.07	$0.0_{3}9$	0.07	....	...	....	...	....	...	....	...	....	....	....
$0.0_{2}8$	$0.0_{3}9$	0.07	$0.0_{3}9$	0.08	....	...	....	...	....	...	....	...	....	....	....
$0.0_{2}9$	$0.0_{2}15$	0.08	$0.0_{2}15$	0.09	....	...	....	...	....	...	....	...	....	....	....
0.01	$0.0_{2}15$	0.08	$0.0_{2}15$	0.09	....	...	....	...	....	...	....	...	....	....	....

TABLE IX.

Hydrochloric Acid Solutions of Helianthine, Compared with Pyridine, Formic Acid and *N* HCl.

Concentrations of solutions tested.	J. Hel. + 10 mols.		K. Hel. + mols.		L. Hel. + 1000 mols.		M. Hel. + 35000 mols.		Color ratios in terms of formic acid.							
	Pyridine.	*N* HCl.	Pyridine.	*N* HCl.	Formic acid.	*N* HCl.	Formic acid.	Pyridine.	D.	E.	F.	G.	H.	I.	L.	M.
0.0_42	...	...	...	...	...	0.0_43	0.0_47	...	....	...	...	...	5.0	4.5	...	3.5
0.0_43	...	...	...	...	...	0.0_43	0.0_48	...	....	...	...	0.6	5.0	5.0	...	2.6
0.0_44	...	...	...	...	...	0.0_45	0.0_31	...	....	...	...	0.5	5.0	7.5	...	2.5
0.0_45	...	...	...	...	0.0_42	0.0_46	0.0_31	...	....	...	0.4	0.4	...	...	0.4	2.0
0.0_46	...	...	...	...	0.0_42	0.0_31	0.0_31	...	....	...	0.3	0.3	5.0	...	0.3	1.6
0.0_47	...	...	...	...	0.0_43	0.0_31	0.0_31	...	....	...	0.3	0.4	5.7	5.7	0.4	1.4
0.0_48	...	...	...	...	0.0_43	0.0_31	0.0_315	...	....	...	0.3	0.4	6.2	5.0	0.4	1.9
0.0_49	...	...	0.0_41	0.0_48	0.0_43	0.0_315	0.0_315	...	....	...	0.3	0.3	6.4	5.5	0.3	1.7
0.0_31	0.0_31	0.0_44	0.0_47	0.0_49	0.0_44	0.0_32	0.0_32	...	....	...	0.3	0.4	7.0	6.5	0.3	2.0
0.0_315	0.0_31	0.0_415	0.0_47	0.0_31	0.0_46	0.0_32	0.0_34	...	....	...	0.3	0.4	7.3	6.0	0.4	1.3
0.0_32	0.0_33	0.0_315	0.0_47	0.0_315	0.0_31	0.0_34	0.0_35	...	0.10	...	0.3	0.5	4.5	7.5	0.5	2.5
0.0_33	0.0_33	0.0_32	0.0_47	0.0_32	0.0_315	0.0_35	0.0_36	...	0.13	...	0.3	0.5	3.3	5.0	0.5	2.0
0.0_34	0.0_33	0.0_33	0.0_47	0.0_33	0.0_32	0.0_36	0.0_38	...	0.15	...	0.4	0.5	...	7.5	0.5	2.0
0.0_35	0.0_34	0.0_34	0.0_47	0.0_34	0.0_33	0.0_37	0.0_39	...	0.16	0.4	0.4	0.6	...	6.0	0.6	1.8
0.0_36	0.0_35	0.0_36	0.0_47	0.0_35	0.0_34	0.0_39	0.0_39	0.0_48	0.15	0.5	0.5	0.7	...	6.6	0.6	...
0.0_37	0.0_35	0.0_37	0.0_47	0.0_36	0.0_34	0.0_21	0.0_215	0.0_31	0.15	0.4	0.4	0.6	...	7.1	0.5	...
0.0_38	0.0_35	0.0_38	0.0_47	0.0_38	0.0_34	0.0_211	0.0_22	0.0_32	0.16	0.5	0.5	0.5	2.5	7.5	0.5	...
0.0_39	0.0_36	0.0_39	...	0.0_39	0.0_35	0.0_212	0.0_225	0.0_32	0.16	0.5	0.4	0.5	3.3	7.7	0.5	...
0.0_21	0.0_36	0.0_21	...	0.0_21	0.0_36	0.0_213	0.0_23	0.0_32	0.16	0.6	0.5	...	...	8.0	0.6	...
0.0_215	0.0_36	0.0_21	...	0.0_215	0.0_38	0.0_215	...	...	0.13	0.4	0.3	...	2.6	...	0.5	...
0.0_22	0.0_36	0.0_22	...	0.0_215	0.0_39	0.0_218	...	...	0.15	0.4	0.3	...	2.5	...	0.5	...
0.0_23	0.0_37	0.0_23	...	0.0_22	0.0_215	0.0_220	...	...	0.13	0.4	...	...	...	...	0.5	...
0.0_24	0.0_38	0.0_24	...	0.0_22	...	...	...	...	0.12	0.2	...	...	...	...	...	...
0.0_25	0.0_38	0.0_24	...	0.0_24	...	...	...	...	0.16	0.3	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	0.25	...	...	...	...	...	...	...
								Average,	0.15	0.42	0.36	0.47	4.8	6.4	0.46	2.1
									95.89	88.75	90.35	87.40			87.67	43.72

(4) The color ratios of helianthine, as compared with methyl orange, averages 2.74, that is, the former is 2.74 times as *red* as the latter. It is furthermore seen to be only 0.71 times as red as helianthine influenced by the presence of 1 mol. HCl. These data may otherwise be interpreted—(*a*) 1 mol. NaOH has nearly four times as much effect on the chromoisomeric equilibrium of helianthine as 1 mol. HCl has; (*b*) nearly four times as much red helianthine is made yellow by 1 mol. NaOH as yellow helianthine is made red by 1 mol. HCl; (*c*) helianthine is more of an acid than a base; (*d*) all the solutions of these three series are in chromoisomeric equilibria.

In Tables VIII and IX it will be observed:

(1) To duplicate the colors, solutions containing the least acid concentration always require much yellow pyridine solution. On the other hand, concentrated acid solutions tolerate no pyridine. It must be interpreted that the former contain large quantities of yellow azoid molecules.

TABLE X.

Pyridine Helianthate Compared with Various Solutions.

Concentration of the Pyr. Hel.	I.	II.		III.		Color ratios.		
	Pyridine.	Pyridine.	*N* HCl.	Pyridine.	Formic.	I.	II.	III.
0.0_31	....	0.0_48	0.0_415	0.0_49	0.0_41	...	0.15	0.10
0.0_315	....	0.0_46	0.0_415	0.0_315	0.0_41	...	0.10	0.07
0.0_32	....	0.0_32	0.0_415	0.0_32	0.0_415	...	0.08	0.08
0.0_33	....	0.0_325	0.0_45	0.0_43	0.0_42	...	0.17	0.07
0.0_34	....	0.0_335	0.0_45	0.0_34	0.0_43	...	0.12	0.08
0.0_35	....	0.0_34	0.0_46	0.0_35	0.0_44	...	0.12	0.08
0.0_36	....	0.0_35	0.0_48	0.0_36	0.0_44	...	0.13	0.07
0.0_37	....	0.0_36	0.0_48	0.0_37	0.0_44	...	0.11	0.06
0.0_38	....	0.0_37	0.0_31	0.0_38	0.0_45	...	0.12	0.06
0.0_39	....	0.0_38	0.0_31	0.0_38	0.0_46	...	0.11	0.06
0.0_21	0.0_25–10	0.0_39	0.0_31	0.0_39	0.0_47	10.00	0.10	0.07
0.0_215	0.015	0.0_22	0.0_315	0.0_215	0.0_48	10.00	0.10	0.05
0.0_22	0.02	0.0_22	0.0_32	0.0_22	0.0_49	10.00	0.10	0.04
0.0_23	0.04	0.0_23	0.0_32	0.0_23	0.0_31	13.33	0.07	0.03
0.0_24	0.055	0.0_24	0.0_23	0.0_24	0.0_315	13.75	0.07	0.04
0.0_25	0.07	0.0_25	0.0_34	0.0_25	0.0_315	14.00	0.08	0.03
0.0_26	0.08	0.0_26	0.0_34	0.0_26	0.0_32	13.33	0.10	0.03
0.0_27	....	0.0_26	0.0_35	0.0_27	0.0_32	...	....	....
0.0_28	0.1	0.0_27	0.0_35	....	....	12.50	0.08	....
0.0_29	....	0.0_28	0.0_36	....	....	...	0.07	....
0.01	0.2	0.0_29	0.0_36	....	....	20.00	0.06	....
0.015	0.3	....	....	....	....	20.00	....	....
0.02	0.4	0.017	0.0_23	....	....	20.00	0.15	....
0.03	0.55	0.027	0.0_23	....	....	18.33	0.10	....
0.04	0.7	....	....	....	....	17.50	....	....
					Average,	14.83	0.10	0.06

(2) All of the acid solutions, except the Hel. + 35000 mols. HCl series, are lighter red than the corresponding formic acid concentrations. Now since the latter was proven to contain 72% of azoid molecules, it must be evident that all aqueous acid solutions of helianthine contain mostly azoid molecules.

TABLE XI.

Colors of Helianthine Salts of Bases, Compared with Formic Acid Solutions.

		0.01%.		0.001%.	
Base used.	Number of mols.	Cold.	Hot.	Cold.	Hot.
Methyl orange	1	$0.0_{3}2$	....	$0.0_{4}8$	....
Aniline	1	$0.0_{3}4$*	$0.0_{3}6$*	$0.0_{4}4$*	$0.0_{4}3$*
Aniline	10	$0.0_{3}3$	$0.0_{3}4$	$0.0_{4}4$	$0.0_{4}4$
Methyl aniline	1	$0.0_{3}5$	$0.0_{3}6$	$0.0_{4}8$	$0.0_{4}5$
Methyl aniline	10	$0.0_{3}3$	$0.0_{3}4$	$0.0_{4}8$	$0.0_{4}8$
Dimethyl aniline	1	$0.0_{3}35$*	$0.0_{2}3$*	$0.0_{4}3$*	$0.0_{4}5$*
Dimethyl aniline	10	$0.0_{3}3$	$0.0_{2}3$	$0.0_{4}5$	$0.0_{4}4$
o-Toluidine	1	$0.0_{3}6$*	$0.0_{3}9$*	$0.0_{4}4$*	$0.0_{4}3$*
o-Toluidine	10	$0.0_{3}3$	$0.0_{3}4$	$0.0_{4}8$	$0.0_{4}5$
Quinoline	1	$0.0_{3}7$	$0.0_{3}8$*	$0.0_{4}8$	$0.0_{4}5$*
Quinoline	10	$0.0_{3}3$*	....	$0.0_{4}8$*	....
Ammonia	20	$0.0_{3}3$*	$0.0_{3}25$	$0.0_{4}4$*	$0.0_{4}3$
Barium hydroxide	2	$0.0_{3}2$	$0.0_{3}3$	$0.0_{4}4$	$0.0_{4}3$
Barium hydroxide	10	$0.0_{3}2$	$0.0_{3}3$	$0.0_{4}3$	$0.0_{3}6$
Sodium hydroxide	1	$0.0_{3}2$	$0.0_{3}2$	$0.0_{4}4$	$0.0_{4}4$
Sodium hydroxide	10	$0.0_{3}2$	$0.0_{3}2$	$0.0_{4}5$	$0.0_{4}5$
Potassium hydroxide	10	$0.0_{3}3$	$0.0_{2}3$	$0.0_{4}8$	$0.0_{4}8$
Phenyl hydrazine	1	$0.0_{3}15$	$0.0_{3}3$	$0.0_{4}4$	$0.0_{4}3$
Phenyl hydrazine	10	$0.0_{3}1$	$0.0_{3}15$	$0.0_{4}3$	$0.0_{4}3$

* Concentrations of the pyridine standard equal to the concentration of the tested solution was required with the formic acid standard, to obtain duplication of color.

TABLE XII.

Helianthine Salts Compared with Phenol Solutions.[1]

	0.01%.		0.001%.		
Helianthine and	Cold.	Hot.	Cold.	Hot.	0.0001%. *N* HCl.
Trichloroacetic	....	....	$0.0_{4}3$	$0.0_{6}2$	....
Dichloroacetic	$0.0_{3}1$	$0.0_{4}9$	$0.0_{4}4$	$0.0_{4}3$	$0.0_{3}2$
Cinnamic acid	$0.0_{3}1$	$0.0_{4}85$	$0.0_{4}25$	$0.0_{4}18$	$0.0_{4}3$
Succinic acid	$0.0_{3}1$	$0.0_{4}8$	$0.0_{4}25$	$0.0_{4}2$	$0.0_{4}3$
m-Cresol	$0.0_{4}7$	$0.0_{4}2$	$0.0_{4}6$	$0.0_{4}15$	$0.0_{4}3$
Phloroglucinol	$0.0_{4}8$	$0.0_{4}2$	$0.0_{4}7$	$0.0_{4}15$	$0.0_{4}2$
Methyl orange	$0.0_{4}75$	$0.0_{4}15$	$0.0_{4}8$	$0.0_{4}2$	....
Ammonia	$0.0_{4}4$	$0.0_{4}15$	$0.0_{4}8$	$0.0_{4}15$	$0.0_{4}2$
Potassium hydroxide	$0.0_{4}6$	$0.0_{4}3$	$0.0_{4}7$	$0.0_{4}25$	$0.0_{4}2$
Naphthylamine	$0.0_{4}8$	$0.0_{4}2$	$0.0_{4}8$	$0.0_{4}2$	$0.0_{4}3$
Picoline	$0.0_{4}4$	$0.0_{4}15$	$0.0_{4}4$	$0.0_{4}15$	$0.0_{4}2$
Nicotine	$0.0_{4}4$	$0.0_{4}25$	$0.0_{4}45$	$0.0_{4}25$	....

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[1] In tandem with the phenol solutions, pyridine solutions of equal concentration with the 0.01% and 0.001% were used in all readings.

The pyridine salt of helianthine was prepared according to the method of Hantzsch. The other salts were prepared in solution by mixing equimolecular quantities of helianthine and the respective base or the respective acid. Some of the salts were prepared in the pure dry condition but were found to give colors identical with the salts prepared by the first method, hence the former method was used almost entirely.

In Table X it will be observed that pyridine helianthate is readily hydrolyzed, since when dissolved in water, it is 14.83 times as red colored as when dissolved in anhydrous pyridine. That pyridine itself is alkaline, however, is showed by the color ratios of 0.10 and 0.06, when compared with *N* HCl and formic acid.

In Table XI a number of salts compounded of helianthine and bases are compared, both at different concentrations and at ordinary temperatures and 100°. It will be observed that most of the bases are "weaker" than sodium hydroxide at 0.01% but tend to become equal to it at 0.001%.

In Table XII, salts compounded of helianthine and acids and bases are compared. It will be observed that these oppositely constituted salts when dissolved in water differ in behavior and in color from one another only in degree and not in kind.

The Influence of Heat on Helianthine Solutions.[1]

When certain solutions of helianthine are heated on the water bath, some are darkened and others are lightened.[2] Conditions favoring the darkening of color (reddening) are concentrated and acidic solutions; conditions favoring the lightening of color, that is, a changing to a lighter red or a purer yellow, are diluted or alkaline solutions. The higher members of most series are darkened when heated, while the lower members of the same series are lightened.

When solutions of helianthine in 90% formic acid are heated on the water bath and are then compared with cold members of the same series, purer and darker shades of red are observed for all concentrations above 0.031%. Below this concentration other members of the series are either lightened or are not changed at all.

When pyridine solutions of helianthine are heated on the water bath,

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[1] For the effects of heat on chromate solutions see THIS JOURNAL, 36, 845 (1914). For other colored substances see Kurbatov, *J. Russ. Phys. Chem. Soc.*, 39, 456 (1909).

When helianthine solutions are heated it must be remembered that other conditions tending to produce color changes may be effective.

[2] Concentrated solutions containing precipitated helianthine are reddened by heat and are lightened by cooling. Examination with the microscope for crystals of helianthine will enable one to avoid this source of error. Heating from 20° to 100° causes a 4% expansion of water, thus causing a lightening of color. This may lessen, compensate, or increase the apparent chromoisomerization. Evaporation may have opposite effects. Acids, such as hydrochloric, carbolic, etc., tend to destroy the color of helianthine; this effect is increased by heat, hence, lighter colors are produced.

TABLE XIII.

Effects of Heat on Helianthine Solutions at 100°, Compared with Cold Solutions of the Same.

Concentrations of solutions heated.	Pyridine.	10000 mols. NaOH.	1000 mols. NaOH.	100 mols. NaOH.	10 mols. NaOH.	Methyl orange.	Helianthine.	10 mols. HCl.	100 mols. HCl.	200 mols. HCl.	10000 mols. HCl.	35000 mols. HCl.	90% formic acid.
0.0_46	....	....	...	0.0_42	....	....	....	....	....	...	0.0_45	0.0_45	....
0.0_47	....	....	...	...	....	....	....	....	....	0.0_41	0.0_46	0.0_46	0.0_48
0.0_48	....	....	...	0.0_47	....	....	....	....	....	...	...	0.0_47	....
0.0_49	....	....	...	0.0_48	....	....	....	....	....	0.0_45	...	0.0_48	0.0_48
0.0_31	....	....	...	...	....	....	....	....	....	...	...	...	0.0_315
0.0_315	....	....	...	...	....	0.0_49	0.0_315	....	....	...	...	0.0_31	....
0.0_32	....	....	...	...	0.0_31	0.0_315	0.0_32	....	....	0.0_47	...	...	....
0.0_33	....	....	...	0.0_33	0.0_32	....	0.0_33	....	....	...	0.0_32	...	....
0.0_34	0.0_36	....	...	0.0_34	....	....	....	....	0.0_33, 0.0_34[1]	...	0.0_33	...	0.0_36
0.0_35	....	....	...	0.0_35	0.0_34	0.0_34	0.0_34	....	....	...	0.0_34	...	...
0.0_36	....	....	...	...	0.0_35	....	....	0.0_32, 0.0_34[1]	0.0_35, 0.0_32[1]	0.0_32	0.0_37	...	0.0_38
0.0_37	0.0_36	....	...	...	0.0_35	0.0_36	0.0_35	....	....	...	...	...	...
0.0_38	0.0_37	....	...	...	0.0_36	0.0_36	....	0.0_33, 0.0_35[1]	0.0_37, 0.0_31[1]	...	0.0_38	...	...
0.0_39	0.0_38	....	...	...	0.0_37	....	0.0_38	....	....	0.0_34	0.0_38	...	...
0.0_21	0.0_39	0.0_21	...	...	0.0_38	....	0.0_39	0.0_36, 0.0_38[1]	0.0_37, 0.0_31[1]	0.0_34	...	...	...
0.0_215	0.0_21	0.0_215	...	...	....	....	....	....	....	...	0.0_23	...	0.03
0.0_22	0.0_215	0.0_22	...	...	0.0_22	0.0_215	....	0.0_212, 0.0_215[1]	....	...	0.0_25	...	...
0.0_23	0.0_215	0.0_23	0.0_23	...	0.0_23	....	0.0_22	....	....	0.0_35	...	...	...
0.0_24	0.0_22	0.0_24	0.0_25	0.0_25	0.0_24	0.0_24	0.0_23	....	....	...	...	...	...
0.0_25	0.0_22	0.0_25	0.0_26	...	0.0_27	....	0.0_24	....	....	...	...	...	...
0.0_26	0.0_23	0.0_27	0.0_28	0.0_27	0.0_28	....	....	....	....	...	...	...	...
0.0_27	0.0_24	0.0_28	0.0_29	...	0.0_29	....	....	0.0_24	....	...	...	...	...
0.0_28	0.0_25	0.0_29	0.01	0.01	0.0_21	0.0_28	....	0.0_26	....	...	...	...	...
0.0_29	0.0_25	0.01	0.015	...	0.015	....	0.0_28	0.0_28	....	...	...	...	...
0.01	0.0_27	0.02	0.015	...	....	....	0.0_29	....	....	...	...	...	...
0.02	0.01	....	0.025	...	....	....	....	....	....	...	...	...	...
0.03	0.01	....	...	...	....	....	....	....	....	...	...	...	...

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[1] Pyridine solutions.

there are obtained for all concentrations above 0.001% purer shades of yellow, which are easily matched in quality and density of color by cold lower concentrations of the same series. On heating lower concentrations than 0.001% little or no change of color is observable. These two cases are typical; many other cases are given in the table.

The data of this table are to be interpreted that the concentrations of the heated solutions, as given in the first column, are equal in color to the parallel cold concentrations given in the respective columns. For an example, a hot 0.01% solution of pyridine is equal in color to a cold 0.007% solution of pyridine.

The following observations are made:

(1) Dilute hydrochloric acid solutions of helianthine, as the 10 mols. and the 100 mols., were especially susceptible to the lightening effect of heat. Pyridine solutions also gave similar, easily observed effects.

(2) In general, conditions tending to favor the formation of the red isomer of helianthine, namely concentration and acidity, are further promoted by the action of heat; conditions tending to favor the formation of the yellow isomer are further promoted by the action of heat. In other words, heat will promote the formation of either the red isomer or the yellow isomer, depending upon the existing conditions, such as the mass action of water and the presence of acids, alkalies, and other substances.

At this point it may again be observed that the concentration of OH^- and H^+ is not the cause of change of color, for some acid solutions containing large "concentrations of hydrogen ions" are lightened by heat; others are darkened by heat. Some alkaline solutions containing large "concentrations of hydroxide ions" are lightened by heat; others are darkened by heat.

Summary.

(1) Methyl orange, or helianthine, exists in isomeric forms, one being yellow and of the azoid structure and the other being red and of the quinoid structure.

(2) Solutions of helianthine involve the two, co-existing in equilibria. Their chromoisomeric equilibria are disturbed by acids and alkalies, by heat, and by the mass influence of water and by other solvents.

(3) Perhaps no solvent contains helianthine as 100% of one of the chromoisomers. Anhydrous phenol solutions of helianthine were assumed to contain 100% of the red quinoid form and absolute pyridine solutions of helianthine were assumed to contain 100% of the yellow azoid form. Aqueous solutions were found by comparison with these standards to vary from 70% to 100% of the yellow azoid form. This was found to be true even though the respective aqueous solutions were "acid or neutral or alkaline."

(4) Since salts of helianthine, whether compounded of acids or of

alkalies, give at great aqueous dilutions identical colors which are some shade of yellow, it follows that the mass influence of water is to yield the azoid form, notwithstanding the presence of acids or of alkalies.

(5) At higher concentrations, aqueous solutions of the two types of helianthine salts differ in degree but not in kind. For high and equal concentrations of helianthine, the "acid solutions" are a deeper yellow-red while the "alkaline solutions" are a lighter red-yellow. Only in the dry condition or in some anhydrous solvents are the acid salts red and the alkaline salts yellow.

(6) Strictly speaking, there is no neutral point in titrations with methyl orange, for all aqueous solutions of helianthine, with equimolecular quantities of acids and alkalies, contain at least some of each chromoisomer. With larger quantities of acids and alkalies, color changes are more evident; at extreme concentrations only, that is at 100% concentration, are pure reds or pure yellows obtained. Since the mass influence of water on all equimolecular acid and alkaline solutions of helianthine yields the same color—the volume of water, that is, the concentrations of the methyl orange, is important with all titrations with this indicator.

(7) Since hydrolysis of its salts conditions the changes of color, the specific nature of such salts is a determining factor in the production of the varied color effects. That the color changes of these salts, however, are not directly proportional to the known affinity constants of the involved acids and bases, indicate that the affinity constants of the two helianthines and the mass influence of water produce a *leveling* effect.

(8) The changes of color of helianthine solutions are not primarily influenced by the concentrations of hydrogen or hydroxyl ions. *The simultaneous and equal influence of both ions* of an acid or of a base, either dissociated or undissociated, influence the color changes, but that the H^+ of "acid solutions" or that the OH^- of "alkaline solutions" independently affect indicators seems improbable. This and other phases of indicator theories will be discussed in a future paper.

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

COLORIMETRIC DETERMINATION OF THE SOLUBILITIES OF HELIANTHINE AND ITS SALTS.

BY WILLIAM M. DEHN.

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Pure helianthine made from the pyridine salt of helianthine, according to the method of Hantzsch,[1] was placed in small glass-stoppered bottles and was treated with sufficient quantities of the respective solvents.

[1] *Ber.*, 46, 1538 (1913).