the concentration of water in the solvent be approximately the same in each case, as shown by nearly equal values of T in Table II.[16] Secondly, one must find a concentration value, $\Sigma(\Delta m)$, at which the effects of incomplete ionization of water and solvation of the solute are canceled. For carboxylic acids, this concentration appears to be about 0.1 molal.[17] Furthermore, there appears to be little tendency for the i values to increase significantly above the theoretical value ($i = 2$) at higher concentrations, at least in the case of benzoic acid[4b,7] and potassium sulfate.[4a] That one is justified in extending these conclusions to the amino acids may be seen by examining the results obtained for ϵ-amino-*n*-caproic acid. Here the theoretical value, 3.00, is obtained at $\Sigma(\Delta m) = 0.1$. Therefore, in deriving the values of the van't Hoff i-factor for the amino acids listed in Table III, extra weight has been given to those values obtained at $\Sigma(\Delta m) \geq 0.1$. The initial value of a series is always low and has been excluded; therefore the values given in Table III are *not* averages of all the i-factors obtained in a given series. Since the rounded values are probably accurate to ± 0.05, differences of 0.1 unit in the i-factor are of questionable significance.

(16) That the i-factor of an amino acid is not independent of the water concentration may be concluded from the results with glycine, where the values observed appear to increase slightly as the water concentration decreases, as shown by a higher value of T. In the last series of measurements with this solute the self-dissociation of nearly anhydrous sulfuric acid was suppressed by the addition of potassium sulfate instead of water. Recently, R. J. Gillespie, *J. Chem. Soc.*, 2997 (1950), has employed sulfuric acid of maximum freezing point (pure H_2SO_4) instead of the slightly aqueous acid used here, by previous workers[4,7] and in his own earlier papers.[10] With the anhydrous solvent, correction for the repression of the autoprotolysis can easily be made by using the autoprotolysis constant (R. J. Gillespie, *ibid.*, 2516 (1950)

$$K = [H_3SO_4^+][HSO_4^-] = 0.00017$$

The accuracy of Gillespie's results indicates that there is no longer any justification for the use of slightly aqueous sulfuric acid for cryoscopic measurements.

(17) Treffers and Hammett[4b] report an i-factor of 1.98 for benzoic acid at this concentration; we find a value of 1.99 (*cf.* Table II).

TABLE III

Solute	i-Factor
$KHSO_4$	2.0
$Ba(HSO_4)_2$	3.0
Benzoic acid	2.0
Glycine	2.2
L-Leucine	2.3
β-Alanine	2.7
γ-Amino-*n*-butyric acid	2.9
ϵ-Amino-*n*-caproic acid	3.0
Anthranilic acid	2.3
m-Aminobenzoic acid	2.7
p-Aminobenzoic acid	2.8

PASADENA 4, CALIFORNIA RECEIVED APRIL 5, 1951

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Relation Between the Absorption Spectra and the Chemical Constitution of Dyes. XXIV. Absorption Spectra of Some Thioindigo Dyes in Sulfuric Acid

BY WALLACE R. BRODE AND GEORGE M. WYMAN

The absorption spectra of nine thioindigo dyes, containing mostly methyl and ethoxyl groups or halogens as substituents, in concentrated sulfuric acid solution were determined over the wave length range 210–800 mμ. It was observed that in this medium, most of these dyes undergo a slow, irreversible change in their absorption spectra, probably due to sulfonation and/or decomposition. Thioindigo dyes containing substituents in the 4- or 6-position were found to be particularly unstable, especially when irradiated with blue or red light; whereas the spectra of dyes having substituents in the 5- and 7-positions showed little or no change under these conditions. A comparison of the absorption spectra of most of these dyes in sulfuric acid with their spectra in organic solvents reveals an extensive shift of the absorption to lower frequencies and an increase in the separation between the first (long-wave) absorption band and the absorption peak in the near ultraviolet (300–340 mμ) region. This was attributed to the formation of two hydrogen-bonded rings (similar to what had been postulated for indigo) by the addition of two protons by the sulfuric acid. The introduction of methyl groups or halogens into the thioindigo nucleus shows a normal bathochromic effect; the absorption curve undergoes a complete change, however, when ethoxy groups are introduced in the 6,6′-positions or, in the case of bis-4,5-benzothioindigo.

Introduction

Two earlier papers in this series[1,2] discussed the absorption spectra of some purified thioindigo dyes in benzene and chloroform solutions. It was observed that the absorption spectra were a reversible and reproducible function of the wave-length range of the illumination to which the solutions had been exposed prior to the measurement. This phenomenon was attributed to the existence of a dynamic equilibrium between the *cis* and *trans* isomers in each dye solution. In support of this explanation the pairs of isomers of two of these dyes (thioindigo and 5,5′-dichloro-4,4′,7,7′-tetramethylthioindigo) were separated chromatographically.

The measurement of the absorption spectra of dyes of this type[3] in sulfuric acid solution, as a sequel to the earlier work on solutions in organic solvents, was considered to be of interest because of both theoretical and practical considerations. From a theoretical standpoint, a comparison of the spectra in this and other solvents was likely to provide some indication concerning the chemical species actually present in sulfuric acid solutions of these dyestuffs. In addition, it is of great practical importance to determine the solubility and stability of these dyes in concentrated sulfuric acid and, if soluble and stable, measure their absorption spectra in this medium, because of the widespread use of this acid as a solvent in the dyestuff industry.

Experimental

(a) Preparation of Solutions.—Approximately 0.01 g. of each dye was weighed accurately and dissolved in 500–600

(1) G. M. Wyman and W. R. Brode, THIS JOURNAL, **73**, 1487 (1951).

(2) W. R. Brode and G. M. Wyman, *J. Research, Natl. Bur. Standards*, in press.

(3) The dyes studied in this investigation are listed in Figs. 1–3.

ml. of concentrated sulfuric acid (C.P.) by stirring vigorously in a stoppered 1-liter, 3-neck flask for one-half hour at room temperature, or below, when the lack of stability of the dye made it necessary. The solution was then diluted to 1 liter in a volumetric flask.

(b) **Measurement of Absorption Spectra.**—The absorption spectra were determined at room temperature (unless otherwise specified) by means of a Cary Recording Quartz Spectrophotometer (Model 12) using 2.00-cm. fused quartz absorption cells over the entire (ultraviolet and visible) wave length range.

(c) **Reproducibility.**—In order to test the stability of the solutions, two measurements were made, one immediately after diluting the solution and another one an hour later. Duplicate experiments were carried out to ensure reproducibility.

(d) **Purity.**—Purity of the dyes used was 99–100% (as determined spectrophotometrically, using chromatographically purified dyes for comparison[1,2]) with one exception: 95% pure 5,5-dichloro-4,4′,7,7′-tetramethylthioindigo had to be used, because further purification of this dye yielded a crystalline modification which was exceedingly insoluble in concentrated sulfuric acid at room temperature.

(e) **Effect of Irradiation.**—A number of the solutions contained in the absorption cells were exposed to filtered light of a 100-watt Spencer Microfilm Projector for 30 minutes in order to establish if they exhibited a phototropic behavior.

Discussion of Results

The spectral absorption curves of nine thioindigo dyes in sulfuric acid solution are given in Figs. 1–3. It was observed that although these curves were reproducible under the conditions specified, they underwent a slow and irreversible change on prolonged standing, probably due to sulfonation of the dyes. Thioindigo dyes in which the 5- and 7-positions were unoccupied were found to be particularly unstable and showed an appreciable change in their absorption spectra on standing for a few hours at room temperature. For this reason, it was necessary to make up the solutions of bis-4,5-benzothioindigo and of Vat Scarlet G at 0–5°. and measure them within 15–20 minutes thereafter.

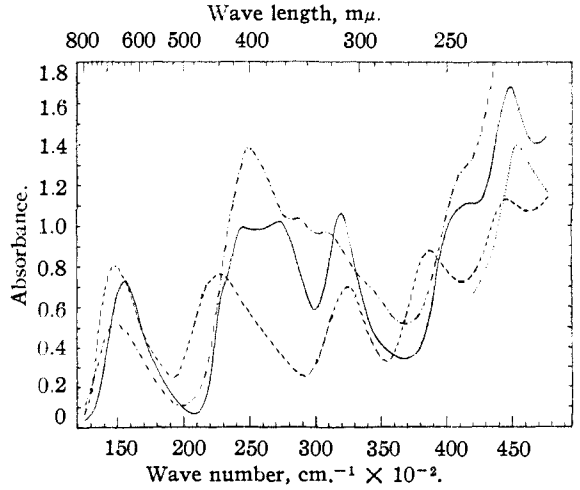
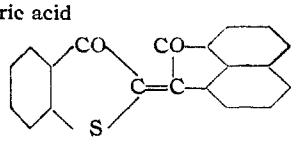


Fig. 1.—Absorption spectra of (a) thioindigo (——); (b) 4,4′-dimethyl-6,6′-dichlorothioindigo (- - - -); and (c) Vat Scarlet G (-·-·-) in sulfuric acid

(Vat Scarlet G/ Colour index #1228)



(Dotted curve (. . . . .) refers to a concentration of 0.0050 g./l.) Concentration: 0.0100 g./l.; cell length: 2.00 cm.

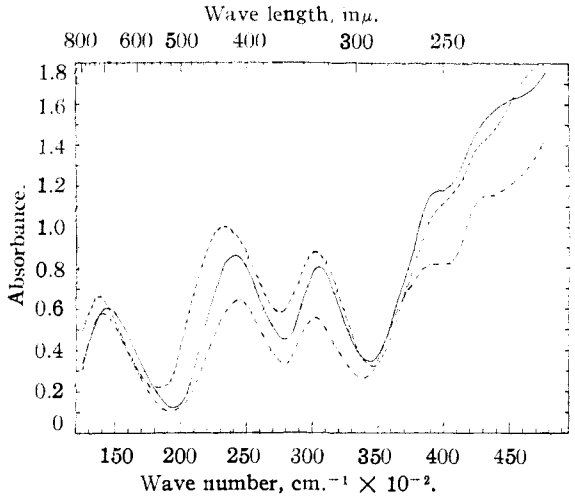


Fig. 2.—Absorption spectra of (a) 5,5′,7,7′-tetramethylthioindigo (- - - -); (b) 5,5′-dichloro-7,7′-dimethylthioindigo (——) and (c) 5,5′-dichloro-4,4′,7,7′-tetramethylthioindigo (-·-·-) in sulfuric acid. Concentration: 0.0125 g./l.; cell length: 2.00 cm.

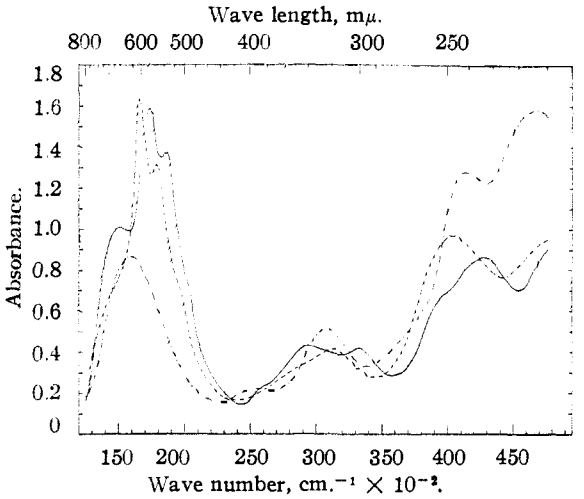


Fig. 3.—Absorption spectra of (a) 6,6′-diethoxythioindigo (concentration: 0.0080 g./l.) (——); (b) 5,5′-dibromo-6,6′-diethoxythioindigo (concentration: 0.0100 g./l.) (- - - -) and (c) bis-4,5-benzothioindigo (-·-·-) in sulfuric acid. Cell length: 2.00 cm.

The spectra of 5,7-substituted thioindigo dyes, on the other hand, showed little or no change even when allowed to stand overnight at room temperature.[4] Similarly, thioindigo dyes containing substituents in the 4- or 6-positions exhibited drastic changes in their absorption spectra after being irradiated with blue or red light. This phototropic effect, however, was not reversible nor reproducible as in the case of benzene or chloroform solutions of these dyes[1,2] and, for this reason, it was attributed to secondary reactions, (possibly sulfonation and/or cleavage) and not to *cis–trans* isomerism. This was considered to be all the more likely, because thioindigo dyes containing substituents in the 5-

(4) Except for 5,5′-dichloro-4,4′,7,7′-tetramethylthioindigo which underwent some change on standing. No change in its spectrum was observed, however, when the solution was made up by stirring for 6 hours at 0–5°.

and 7-positions, showed no change in their absorption spectra when exposed to blue ($\lambda < 495$ mμ) or red ($\lambda > 599$ mμ) light for one-half hour. It seems probable that the 5- and 7-positions in the thioindigo nucleus are susceptible to sulfonation and, when these are occupied by substituents, the dye is relatively stable in sulfuric acid solution.

The spectral absorption curves illustrated in Figs. 1–3 fall into two principal types. The absorption curves of thioindigo and its methyl and/or chlorine substituted derivatives are similar in shape (Type I). The introduction of these substituents into the thioindigo molecule shows the expected bathochromic effect, substituents in the 4- and 6-positions causing a smaller shift than substituents in the 5- and 7-positions; methyl groups in the 5- and 7-positions have the strongest effect. The two dyes containing ethoxy groups in the 6,6′-positions have totally different spectra from the other dyes (Type II); the spectrum of the brominated compound is displaced toward lower frequencies, thus exhibiting the normal bathochromic shift due to the introduction of the halogen atoms. The spectral absorption curves of the other two dyes, bis-4,5-benzothioindigo and of Vat Scarlet G show little similarity to each other or to any of the other dyes investigated. It is of interest to note that the same dyes are grouped together here on the basis of similarities in their absorption spectra in sulfuric acid solution as in the case of their solutions in organic solvents.[1,2]

Because of the absence of any evidence for a dynamic equilibrium between two geometrical isomers (as had been observed in benzene and chloroform solutions of these dyes), it was concluded that these dyes exist in only one form in sulfuric acid. A comparison of the absorption spectra of the dyes of Type I in sulfuric acid solution with their spectra in organic solvents[1,2] reveals two effects. In each case the absorption bands have been shifted considerably toward lower frequencies and the ratio of the frequency of the band in the near ultraviolet to that of the first visible absorption band has been appreciably increased. This is illustrated by the data in Table I.

TABLE I

FREQUENCY RATIOS OF MAIN ABSORPTION BANDS

	In chloroform (*trans*-form)			In H_2SO_4		
	$\nu_1' \times 10^{-3}$	$\nu_2' \times 10^{-3}$	ν_2'/ν_1'	$\nu_1' \times 10^{-3}$	$\nu_2' \times 10^{-3}$	ν_2'/ν_1'
Thioindigo	183	359	1.96	156	320	2.05
5,5′-Dichloro-7,7′-dimethylthioindigo	177	343	1.93	144	305	2.12
5,5′-Dichloro-4,4′,7,7′-tetramethylthioindigo	174	339	1.94	141	302	2.14
5,5′,7,7′-Tetramethylthioindigo	176	343	1.95	137	301	2.20
4,4′-Dimethyl-6,6′-dichlorothioindigo	185	354	1.89	149	325	2.18
Indigo	166	350	2.10	[a]		

[a] Unstable.

These effects are similar to those observed when the spectra of the *trans*-forms of thioindigo dyes in organic solvents are compared with indigo (*cf.* Table I) (which is known to exist in the *trans*-form in solution[5]) as shown in Fig. 4. This shift of the first absorption band toward the red and the increased separation between the two absorption bands in the case of indigo have been attributed to the existence of hydrogen bonding (as shown in structure I) in indigo.[6] Since the formation of this chelate ring is possible in the *trans*-form exclusively, it will explain why the *trans*-isomer of indigo is so much more stable than the *cis*-isomer.[7] On the basis of these observations it seems reasonable to conclude that thioindigo and its methyl and/or halogenated derivatives (*i.e.*, thioindigo dyes of Type I) add two protons in concentrated sulfuric acid solution and exist in the chelated structure (II) in a *trans*-configuration similar to structure (I) for indigo in organic solvents.

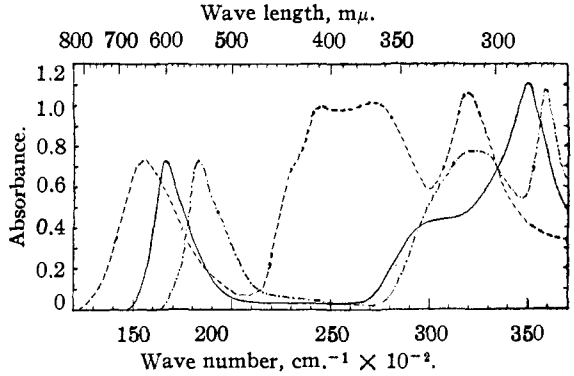
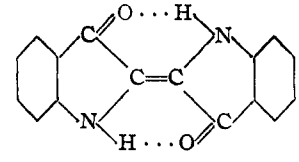
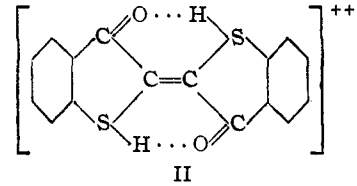


Fig. 4.—Absorption spectra of (a) thioindigo in sulfuric acid (– – – –); (b) *trans*-thioindigo in chloroform (–·–·–) and (c) indigo in chloroform (——); at arbitrary concentrations.



I



II

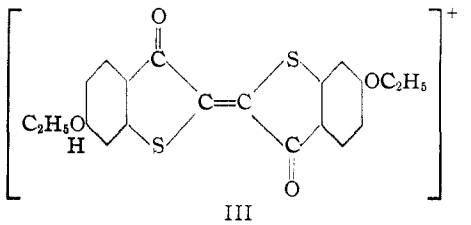
The completely different absorption spectrum of 6,6′-diethoxythioindigo and of its dibromo derivative (Type II) suggests that dyes of this type in sulfuric acid solutions should be represented by an entirely different structure.[8] It is possible that addition of the proton (or protons) takes place on the ethoxy groups, resulting in structures III and/or IV. It seems somewhat difficult to reconcile the bathochromic shifts observed in the case of these dyes

(5) T. Posner, *Ber.*, **59B**, 1799 (1926).

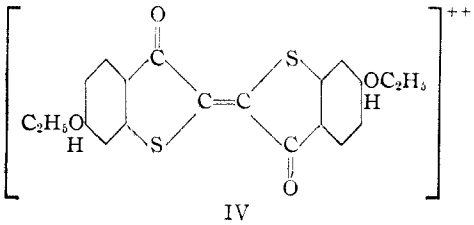
(6) N. Dokunikhin and E. Levin, *Compt. rend. acad. sci., U. S. S. R.*, **35**, 110 (1942).

(7) G. Heller, *Ber.*, **72**, 1858 (1939).

(8) A sample of 6,6′-diethoxythioindigo was recovered from sulfuric acid solution by pouring into a large volume of water and filtering. After drying at 60–65°, this was found to give quantitatively the same spectrum in benzene as the original dye, thus establishing that no irreversible decomposition had taken place.



III



IV

when going from solutions in organic solvents to solutions in sulfuric acid, since no additional chelate rings are formed as in the case of structure II above. It is possible, as an alternative, that the strong resonance effect[9] of the ethoxy group in the 6,6′-positions changes the relative basicities of the carbonyl oxygen and the sulfur atoms to such an extent that the structure of these dyes in sulfuric acid solution differs from the dyes of Type I (structure II, above) mainly in the distribution of the electron cloud and, possibly, in the interatomic distances in the chelate rings. This hypothesis is consistent with the observed bathochromic shift and the absence of *cis*- and *trans*-isomers, but it is questionable whether structural differences of this kind will be sufficient to explain the fundamentally different absorption spectra obtained.

Since Vat Scarlet G is a hemi-thioindigoid dye, its spectrum was expected to be considerably different from the other dyes investigated. Bis-4,5-benzothioindigo, however, also shows a spectral absorption curve that is not similar to any of the other thioindigo dyes and there seems to be no adequate explanation available for this observation. The first absorption band in the case of either of these dyes in sulfuric acid solution is at a considerably lower frequency than when dissolved in organic solvents, indicating complex formation with the solvent, perhaps by the formation of one chelated ring (or possibly two in the case of bis-4,5-benzothioindigo), similar to that suggested above for thioindigo.

(9) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 231.

WASHINGTON 25, D. C. RECEIVED MARCH 14, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

A Spectrophotometric Study of the Hydrolysis of Iron(III) Ion[1]

BY THOMAS H. SIDDALL, III, AND W. C. VOSBURGH

A method for the determination of the first hydrolysis constant of iron(III) ion has been devised involving measurements of the optical densities of a series of solutions of constant ionic strength, constant total iron concentration, and known variable acidity. Several series of measurements were made at temperatures from 24 to 30° from which the value of the hydrolysis constant at 25° and zero ionic strength was found to be 0.0065 ± 0.0004.

The first hydrolysis constant of the iron(III) ion, has been determined[2-6] by several methods, with results from 2.5 to 11 $\times 10^{-3}$ at 25° and similar lack of agreement at other temperatures. Bray and Hershey[7] calculated (6.0 ± 0.5) $\times 10^{-3}$ at 25° from the equilibrium measurements of Popoff, Fleharty and Hanson[8] and Noyes and Brann.[9] The two values in best agreement are those of Bray and Hershey and Olson and Simonson if the latter is extrapolated to zero ionic strength. Extrapolation by the method described below gives 5.4 $\times 10^{-3}$.

In the present investigation the value 6.5 $\times 10^{-3}$ was found by a spectrophotometric method somewhat different from that of Olson and Simonson.

Experimental

Materials and Apparatus.—Iron(III) perchlorate obtained from the G. Frederick Smith Chemical Company was used. For one series of measurements this material was recrystallized as a check on purity.

Standard perchloric acid solutions were prepared from reagent grade acid and standardized against standard sodium hydroxide solutions.

Sodium perchlorate solutions were made from standard perchloric acid and sodium hydroxide solutions. The perchloric acid and sodium perchlorate solutions gave negative tests for chloride and iron(III) ions.

The water used was redistilled from alkaline permanganate in an all-glass still. Iron(III) perchlorate solutions made from the ordinary distilled water available at the time had appreciably higher optical densities at wave length 340 mμ than solutions of the same concentration and acidity made from redistilled water. However, solutions prepared from water redistilled a second time did not differ significantly from solutions prepared from once redistilled water.

Optical density measurements were made by means of a model DU Beckman spectrophotometer. Most of the measurements were made in 10-cm. corex cells; but some were made in 1-cm. quartz cells. Both sets of cells were calibrated. It was found that the measured optical density of iron(III) perchlorate solutions was independent of the slit width in the spectral regions used. There was no provision for automatic temperature control. Considerable care was taken to bring each set of solutions to be measured to room temperature. Just previous to placing a solution in the cell for measurement its temperature was measured and adjusted if necessary to the temperature of the series. The filling of the cells and the measurement were carried out rapidly, requiring only 30 seconds. No changes were observed over an additional 30-second period, and it is believed that errors attributable to temperature differences were not significant.

(1) Thesis submitted by Thomas H. Siddall, III, in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Duke University.

(2) Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907).

(3) Brönsted and Volqvartz, *ibid.*, **134**, 97 (1928).

(4) Lamb and Jacques, THIS JOURNAL, **60**, 967, 1215 (1938).

(5) Lindstrand, *Svensk Kem. Tid.*, **56**, 251 (1944).

(6) Olson and Simonson, *J. Chem. Phys.*, **17**, 1322 (1949).

(7) Bray and Hershey, THIS JOURNAL, **56**, 1889 (1934).

(8) Popoff, Fleharty and Hanson, *ibid.*, **53**, 1643 (1931); Fleharty, *ibid.*, **55**, 2646 (1933).

(9) Noyes and Brann, *ibid.*, **34**, 1016 (1912).