# THE TWO PHTHALOXIMES: A STUDY OF THEIR ABSORPTION SPECTRA AND CONSTITUTION

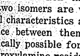
By D. S. Pratt and H. D. Gibbs[1]

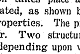
(*From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.*)

Two plates and 6 text figures

Phthaloxime was first described by Lassar-Cohn,[2] who made it by the action of phthalyl chloride on hydroxylamine. The same compound was later made by Lach,[3] who employed phthalic anhydride and hydroxylamine. Orndorff and Pratt[4] have shown that the course of this reaction depends upon the temperature.

A colorless phthaloxime is formed at 60°, and a lemon yellow isomer results when the same reaction takes place at 100°. These two isomers are very closely related, as shown by their physical characteristics and chemical properties. The principal difference between them is their color. Two structures are theoretically possible for phthaloxime, depending upon whether the hydroxylamine residue is in the symmetrical (1), or unsymmetrical (2), position in respect to the benzene ring.


1.


2.

The symmetrical formula (1) has been generally assigned to colorless oximes of this type regardless of the color of their salts. Both the white and the yellow phthaloxime give alkali salts of a brilliant red and of almost identical color in both cases. It has not been found possible, as yet, to prove beyond question which of the above formulas should be applied to phthaloxime, although a careful study of its formation and reactions points

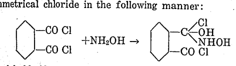
[1] Associate professor of chemistry, University of the Philippines.

[2] *Ann. d. Chem.* (Liebig) (1880), 205, 295.

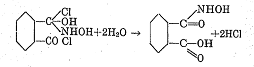
[3] *Ber. d. deutschen chem. Ges.* (1893), 16, 1781.

[4] *Am. Chem. Journ.* (1912), 47, 89.

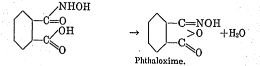
strongly to the unsymmetrical structure. The fact that phthaloxime may be made from phthalyl chloride and hydroxylamine does not distinguish between the two structures, as the reaction is not a mere elimination of hydrogen chloride with the formation of the oxime, but takes place in two steps, giving phthalhydroxamic acid as an intermediate product. Ott[5] has recently shown that the ordinary phthalyl chloride may be symmetrical, a fact indicated by its absorption spectrum according to Scheiber.[6] It is evident that an unsymmetrical oxime may result from a symmetrical chloride in the following manner:



Phthalyl chloride.



Phthalhydroxamic acid.



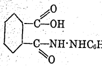
Phthaloxime.

The reactions are entirely analogous to these between phthalyl chloride and ammonia.[7] Phthalhydroxamic acid cannot be isolated from solution as it loses water to form the oxime, but its presence may be shown by the characteristic color given with ferric chloride, and its alkali salts may be obtained as colorless crystals. The reaction between phthalic anhydride and hydroxylamine follows a similar course. The anhydride combines with the free hydroxylamine giving a *clear solution* of hydroxamic acid. Since both the anhydride and the oxime are very slightly soluble in water, it is evident that the first phase of the reaction may be completed before dehydration with the result-

[5] *Ann. d. Chem.* (Liebig) (1912), 392, 245.
[6] *Ibid.* (1912), 389, 121.
[7] Scheiber, *Ber. d. deutschen chem. Ges.* (1912), 45, 2252.

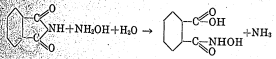
ing formation of oxime takes place. Further heating of the solution causes an abundant crystallization of phthaloxime.

When phenylhydrazine acts similarly with phthalic anhydride, the product of the first phase may be isolated. Anilidophthalamic acid is formed in this case,[8] and has a structure analogous to phthalhydroxamic acid.



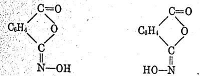
Anilidophthalamic acid.

Phthaloxime may also be made by the action of hydroxylamine on phthalimide in alkaline solution. Here again the formation of an intermediate product precludes any conclusions being drawn regarding the position of the =NOH group, although phthalimide possesses a symmetrical structure. The reaction is represented by the following equation:



Ammonia is liberated and phthalhydroxamic acid formed. This may be converted into either the white or yellow phthaloxime according to the temperature at which the solution is heated after being acidified.

The existence of two isomeric phthaloximes may be explained by means of the unsymmetrical formula in a manner similar to that employed with the benzaldoximes, and indicated graphically by the formulas IIa and IIb where the *syn* type shows the hydroxyl in closer proximity to the unsaturated carbonyl group.



IIa Syn. IIb Anti.

[8] Hötte, *Journ. f. prakt. Chem.* (1887), II, 35, 268.

A study of the absorption spectra of these and related compounds was undertaken for the purpose of obtaining an insight into their molecular arrangement and behavior and evidence regarding the production of color in their salts.

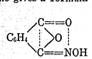
If the isomerism between the white and yellow phthaloximes is correctly indicated by the above formulas, IIa and IIb, it is evident that their absorption spectra must be very closely related. Macbeth, Stewart, and Wright[9] have studied the action of light on unsaturated centers in a molecule, and state that no great change takes place in the general absorptive power of a molecule when such a center is shifted in space with respect to a saturated radical. The carbonyl group in phthaloxime represents the point of maximum unsaturation, while the hydroxyl can hardly be looked upon as the center of much residual affinity. Any relative change in space between carbonyl and hydroxyl should produce a slight modification in the absorption spectrum, but the type would remain the same. Hartley[10] has shown that the stereoisomeric benzaldoximes have the same absorption spectra which show a broad band in the benzene region.

Hantzsch[11] has examined several isomeric oximes and states that the absorption spectra of $\alpha$ and $\gamma$ benzyl oximes, the two para nitrobenzaldoximes, and of the chlortoluquinonoximes show great similarity in each case between the two isomers. The *syn* series absorbs somewhat more strongly than the *anti*, as might be expected from the greater proximity and consequent mutual influence of the two radicals. Wilson and Heilbron[12] have recently prepared two semicarbazones of mesityl oxide, and find corresponding differences due to nitrogen stereoisomerism. Since these characteristics are manifested in the case under discussion, it thus appears that the yellow phthaloxime should be designated as *syn*-phthaloxime and the white isomer as *anti*-phthaloxime as represented by formulas IIa and IIb.

Prior workers have pointed out that absorption bands are not to be attributed to any definite molecular structure, but rather to the existence of dynamic compounds which are not necessarily capable of isolation. The presence of an absorption band is due to intramolecular change from one modification to another, and is expressed by an actual change of linking, or is due to the po-

[9] *Journ. Chem. Soc. London* (1912), 101, 599.
[10] *Ibid.* (1900), 77, 509.
[11] *Ber. d. deutschen chem. Ges.* (1910), 43, 1651.
[12] *Journ. Chem. Soc. London* (1913), 103, 377.

tential possibility of such a change. The oscillation or free period in connection with the reversible transformation of one tautomeric form into another is synchronous with the oscillation of the light waves absorbed. This transformation must be understood to include changes that cannot be graphically represented by fixed structural formulas. These peculiar cases are best indicated according to the partial valency theory developed by Thiele.[13] This assumes that all the affinity of two atoms connected by a double bond is not used in holding the atoms together, but that there is a slight excess present in each atom. Thiele designates this excess affinity by dotted lines. Application of this idea to phthaloxime gives a formula that may be expressed thus:



The two sets of partial valencies may be assumed more completely to neutralize each other during one phase of the benzene vibration when the atoms are in closer proximity to each other than during the succeeding phase when they are more widely separated. This varying adjustment of forces in connection with the disturbing influence of the hydroxyl group may be thought of as causing the ultra-violet absorption band of phthaloxime. The equilibrium is essentially the same in phthalic acid, the esters of phthalic acid, and very similar in phthalimide. All of these compounds may be expressed by analogous formulas. Moreover, they all give absorption spectra showing similar ultra-violet absorption bands. This must be considered as evidence of corresponding structure. The influence of the benzene ring is essential in these cases.

The application of the partial valency theory to explain the activity of carbonyl groups removes the indefiniteness inherent in the method employed by Stewart and Baly[14] to represent this condition. These authors suggest that nascent carbonyl groups be indicated by printing the oxygen in heavy-faced type, thus $\underset{\mathbf{O}}{\underset{\|}{-C-}}$, and that this condition is essentially dynamic in nature and cannot be successfully represented by structural formulas which

[13] *Ann. d. Chem.* (Liebig) (1899), **306**, 87.
[14] *Journ. Chem. Soc. London* (1906), **89**, 497.

are static in their meaning. The term *isorropesis* was proposed to designate the interrelation between groups of this type. The activity of a carbonyl radical is not inherent in the group itself, but is produced by the action of neighboring atoms that render the group nascent.[15] The causes underlying this action are more easily understood by means of the partial valency theory. The amount of affinity in excess of that utilized in holding the doubly bound atoms together will depend upon the presence of free affinity exerted by neighboring atoms. In the absence of such forces, the energy of the two atoms will be mutually neutralized and in equilibrium.

When phthaloxime is converted into its salts, a marked alteration in molecular vibration is manifested to the eye by the change from a colorless compound to a colored one. The new vibration may be due either to a different equilibrium of the same molecule induced by the presence of a positive metal atom, or to an actual alteration in molecular structure.

### COLOR, DUE TO CHANGE IN EQUILIBRIUM BETWEEN PARTIAL VALENCIES

If the production of color in the formation of salts of phthaloxime is due to a change in the vibration of the molecule unaccompanied by atomic tautomerism, it must be dependent upon a new equilibrium between the partial valencies of the unsaturated groups. The change of equilibrium is not to be attributed to the increased weight of the molecule and consequent reduction in the period of vibration. The replacement of the acidic hydrogen by groups with high molecular weight, as in the case of the benzoate, causes a change in the activity of the molecule shown by a reduction in the persistence of the characteristic absorption band in the spectrum. However, the type of spectrum remains the same. Therefore, the activity of the hydrogen is not greatly different from that of various organic radicals, and the compound retains its true oxime condition in every case. It is to be noted that an aqueous solution of oxime shows a slightly more pronounced yellow tint than a corresponding alcohol solution and that the color in both cases is decreased by a trace of mineral acid. The ethers and esters of the oxime do not behave in an analogous manner, but always give solutions of equal color intensity that are unchanged by traces of acid. The acidic hydrogen, therefore, influences the equilibrium to a

[15] Baly and Schaefer, *ibid.* (1908), 93, 1814.

slight extent depending upon the solvent, although the activity is not sufficient to cause any indication of a color band in the absorption spectrum. The stronger general absorption of the oxime as compared with the benzoate shows a tendency toward the production of a band, as might be expected.

The replacement of hydrogen by a metal atom introduces a strong positive sphere of influence that must have a greater disturbing effect on the negative latent valencies. The more positive the metal or group introduced, the greater will be the resulting change produced. The following table of optical properties of phthaloxime and various derivatives shows that the character of light transmitted by the crystals may be arranged in a graded scale corresponding with the increasing basicity of the substituting atom or radical.

TABLE I.[a]—*Optical properties of phthaloxime and derivatives.*

| Compound. | Character of light rays transmitted through crystals. | Degree of pleochroism. |
|---|---|---|
| White oxime | White | Absent. |
| Ethyl ether of yellow oxime | White and faint greenish yellow | Faint. |
| Yellow oxime | White and yellow | Do. |
| Acid sodium salt of white oxime | Pale yellow and orange | Marked. |
| Ammonium salt of white oxime | Straw yellow and reddish orange | Strong. |
| Sodium salt of white oxime | Pale purple and deeper purple | Rather marked. |

[a] Determinations made by Professor Gill, mineralogical department, Cornell University; see Orndorff and Pratt, *loc. cit.*

The potassium salt forms very small crystals that are difficult to examine, but in bulk the color appears darker than the corresponding sodium salt. The differences existing among the above salts in crystalline condition are very distinct, but cannot be accurately shown spectroscopically. Alcohol solutions of the ammonium, lithium, barium, sodium, and potassium salts were photographed. All of these solutions in hundredth molar concentration showed a well-marked color absorption band increasing in width and persistence in the order named. This was partly due to the different dissociation constants of the various alkalies, but this factor could not be eliminated in as much as the addition of an excess great enough to compensate for the dissociation always resulted in the formation of hydroxamic acid and destruction of the oxime.

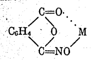
A very weak base such as pyridine dissolves phthaloxime with slight change of color, and the solution gives an absorption spectrum showing no band in the visible region. This indicates that if a salt is formed it must have the true oxime structure. The addition of increasing amounts of water to the pyridine solution causes a progressive deepening of color and gradual production of a color band until the characteristic red of the alkali salts is obtained. This effect is explained by the increased basicity of the pyridine hydrate formed upon the addition of water. The salt is unstable, and could not be isolated from solution without the entire loss of pyridine.

The silver salt of phthaloxime is insoluble in the ordinary solvents, and its true absorption spectrum could not be obtained. It dissolves readily in pyridine with a purplish red color, probably due to the formation of an addition product containing the strongly positive silver dipyridine. A similar product was isolated in the case of ammonia where one molecule of crystalline silver salt was combined with one molecule of ammonia. These addition products are deeply colored as might be expected from the strength of the double base. That the absorption band of their spectra heads at a different place than that characteristic of the alkali oxime salts is probably due to the presence of additional latent valencies in the unsaturated nitrogen atom of the pyridine-silver or ammonia-silver groups.

It is evident that the introduction of various positive atoms or radicals into the phthaloxime molecule may cause different changes in its optical activity. It may be assumed that the previous condition of equilibrium existing between the unsaturated =CO and =NOH groups is completely changed, and that the latent valencies of these groups no longer mutually neutralize each other, but that a negative portion swings to the positive metal. The equilibrium will be slightly different in various salts depending upon the electropositiveness of the substituting atom or group, but will always be of the same type unless further complicated by the introduction of other unsaturated atoms. The result of the new equilibrium between the positive group or atom and the negative partial valency of an unsaturated atom is shown by the disappearance to a greater or less extent of the absorption spectrum characteristic of the original type and the production of a new band in the spectrum.

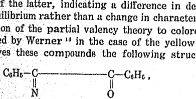
The position of the new band and consequent color, in the broad sense, of the salt given by any compound undergoing changes of this general type will depend upon the resulting configuration of the molecule. The presence of the benzene ring or its equivalent in the molecule is probably essential whenever the absorption band of the salt falls in the characteristic quinone position.

The molecular equilibrium of phthaloxime salts may be represented by the formula:



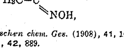
This indicates merely the partial valency equilibrium between negative carbonyl and positive metal, and shows a ring formation resembling the quinoid configuration. It is to be noted that neither phthalic acid nor phthalimide can give analogous salts, although the compounds themselves present a condition similar to that of the oxime. The addition of alkali to solutions of these substances causes no radical change in the position of their absorption bands, but causes a marked increase in the width of the original band of the latter, indicating a difference in degree of the existing equilibrium rather than a change in character.

The application of the partial valency theory to colored salts has been utilized by Werner [16] in the case of the yellow benzil-oxime. He gives these compounds the following structure:



but makes no mention of the equilibrium that must exist between the unsaturated groups before the entrance of the metal atom. Hantzsch has also used similar conceptions in much of his later work, and has applied partial valency structures to many compounds in which it is otherwise very difficult to explain the absorption spectra.

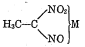
Lassar-Cohn calls attention to the resemblance between phthaloxime and the nitrolic acids, and Hantzsch and Kanasirski [17] have studied the absorption spectrum of the latter. They find that ethyl nitrolic acid,



[16] *Ber. d. deutschen chem. Ges.* (1908), 41, 1062.
[17] *Ibid.* (1909), 42, 889.

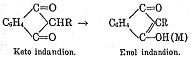
shows only general absorption, while its red potassium salt gives a broad absorption band heading at $\frac{1}{\lambda}=3050$.

In this case there is no possibility for quinoid formation in a ring in connection with conjugated linking between unsaturated groups, and the colored salts do not give absorption spectra showing a band in the quinone region. There is, however, a marked difference between the spectra of the salts and free acid. Hantzsch represents the equilibrium of the former by the formula:



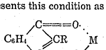
This explains the change in optical properties that takes place when the acid is converted into its salts, and corresponds to our oxime structure.

Certain diketones represented by the type of indandions are colorless or very faintly yellow, but dissolve in alkaline solutions giving highly colored salts. In this case the salt formation has been shown to take place with a tautomeric change from the keto to the enol form as represented by the formulas:



Keto indandion. Enol indandion.

The alkali salt exists in the conjugated form according to Hantzsch [18] who represents this condition as



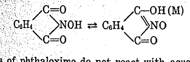
Conjugated enol salt of indandion.

This class of compounds is evidently more nearly related to the phthaloximes than are the nitrolic acids. There are several important points of difference, however, that serve to throw light

[18] *Ann. d. Chem.* (Liebig) (1912), 392, 286.

upon the structure of the oximes. The absorption spectra of the indandions have been carefully studied by Hantzsch, and found to vary in a marked degree with change of solvent. Phenyl indandion was shown to give only general absorption in ether solution, but selective absorption in methyl alcohol with 1 well-developed band and 2 step-offs. In the presence of alkali these develop into 3 well-marked absorption bands. The equilibrium of the enol-keto tautomerism in ether solution differs from that in methyl alcohol, and causes a corresponding difference in the absorption spectra.[19]

The application of Hantzsch's work to our problem gives additional evidence concerning the structure of phthaloxime. If the oxime were correctly represented by the symmetrical formula, it might be expected to resemble the indandions both chemically and spectroscopically, and undergo enol-keto tautomerism. The absorption spectra would show this equilibrium, and the approximate amount of the enol form in solution could be determined by titration with bromine.[20] Molecular rearrangement of this type would result in the following equilibrium:



Solutions of phthaloxime do not react with aqueous bromine, however, and no chemical or optical indications of enol-keto tautomerism could be observed. Moreover, the absorption spectra of the oximes in various neutral solvents are practically identical, do not show evidences of an enol-keto band, and are of an entirely different type from those given by the indandions. The other alternative for salt formation with a symmetrical oxime would be direct replacement of hydrogen by a metal atom, giving salts analogous in many respects to the salts of phthalimide. Since neither of the above conditions is characteristic of phthaloxime, it seems very probable from spectroscopic evidence alone that only the unsymmetrical structure will explain the facts.

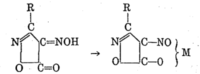
Oximido-oxazolone is colorless or faintly yellow, and also forms highly colored salts with colorless metals. Hantzsch[21]

[19] Hantzsch, *loc. cit.*

[20] Meyer, *Ann. d. Chem.* (Liebig) (1911), 380, 212.

[21] *Ber. d. deutschen Chem. Ges.* (1909), 42, 1007; (1910), 43, 68.

represents the chromophoric development in this case by the formulas:



Oximido-oxazolone. (Colorless.) Oximido-oxazolone salts. (Colored.)

He has found that this oxime shows only general absorption in its spectrum, while solutions of its salts are strongly selective with a well-marked band in the color region. It is evident that conditions in compounds of this type are similar to those in phthaloxime as far as the production of color upon salt formation is concerned. There is no possibility for quinoid configuration of a ring in the oximido-oxazolones, yet the change in their absorption spectra upon the addition of alkali closely resembles that shown by phthaloxime. It does not seem essential, therefore, to assume an actual quinoid structure in the latter case, but merely that the two rings act similarly toward the conjugated partial valencies in both classes of compounds, and that the general effect of a positive metal atom in the molecule is analogous.

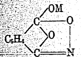
### COLOR DUE TO MOLECULAR REARRANGEMENT

There are several factors which render it improbable that the salts of phthaloxime possess a different molecular structure from that of the oxime. The red silver salt reacts easily and at low temperatures with alkyl iodides giving ethers that undoubtedly possess the true oxime structure. These ethers are colorless in the case of the colorless isomer, and faintly yellow when derived from the yellow oxime. They are broken down by solutions of the caustic alkalies into substituted hydroxylamines, and give absorption spectra closely resembling the parent oximes. No ethers have thus far been made that show the color characteristic of the salts, and if formed as the first phase of the reaction between silver salt and alkyl iodide they must be very unstable.

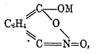
Since the two phthaloximes have been shown to retain their identity when converted into salts,[22] any formula representing a different arrangement of the molecule to explain color must include the doubly bound nitrogen upon which the isomerism

[22] Orndorff and Pratt, *loc. cit.*

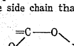
depends. Two possible formulas representing the oxime salts may be expressed as:



and



the second of which would explain color formation as depending upon the quinoid condition of the benzene ring and might be considered as in equilibrium with the first. The theory of partial valency may also be applied to the second formula giving a conjugated linking in the side chain that may be represented by the formula:



The salts would then belong to the enol-nitroso type.

No method is available to decide definitely between these two explanations of the very marked change that takes place when phthaloxime is converted into its highly colored salts. The partial valency theory explaining color as dependent upon a changed condition of equilibrium brought about by a positive metal atom without actual molecular rearrangement has much to recommend it, and seems to be in better accord with our present ideas of chromophoric chemistry.

## ABSORPTION SPECTRA OF THE PHTHALOXIMES, THEIR METHYL ETHERS, ACETATES, AND BENZOATES

The complete curves of the absorption spectra of the two phthaloximes are shown in fig. 1. Solutions in absolute alcohol were employed when not otherwise stated, and the spectra photographed with a Hilger spectrograph [23] using a nickel arc as the source of light.

The curves are plotted with logarithms of thickness of layer in millimeters of ten thousandth molar concentration as ordinates, and oscillation frequencies of the limits of transmission as abscissa.

[23] The purchase of this instrument was made possible through the generosity of Mr. Enrique Zobel, Mr. Antonio Roxas, Mr. Manuel Earnshaw, Dr. Ariston Bautista y Lim, the San Miguel Brewery, and the Germinal Tobacco Factory.

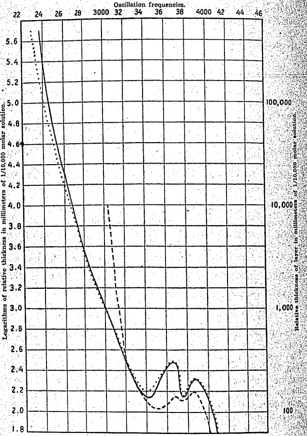



Fig. 1. Full curve=white phthaloxime.
Dot curve=yellow phthaloxime.
Dash curve=benzoate of white phthaloxime.

*Description of fig. 1.*—The region of greatest difference between the two curves is found in the total absorption at high concentrations. The upper limit of these curves from log. 5.8 to 5.7 represents higher concentrations than can be conveniently handled with alcohol alone as a solvent. A mixture of equal parts of alcohol and acetone proved satisfactory for this region. The yellow isomer shows greater total absorption in the visible spectrum. With decreasing concentration the curves approach until they are practically identical, but separate again as they reach the absorption band at $\frac{1}{\lambda} = 3400$ where the white isomer shows slightly greater persistence. The benzene bands, numbers 1, 2, 4, and 6, are clearly defined in neutral or acid solution although not separately plotted in fig. 1.

The absorption curve of the benzoate of white phthaloxime is also shown in fig. 1. The spectra of the methyl ethers and acetates were also studied, but are not plotted as the curves fall between the oximes and the benzoates. All of these curves are very similar. The absorption bands extend to about the same dilution for each compound, but the intervening transmitted portion is very different in each case. The transmission band at $\frac{1}{\lambda} = 3676$ decreases from about 2.5 in the oximes and methyl ethers to 2.4 in the acetates and 2.15 in the benzoates. The transmission bands bounding the other benzene absorption bands show about the same decrease; that is, the transmission band heading at $\frac{1}{\lambda} = 3870$ persists to about log. 2.32 in the oximes, 2.25 in the acetates, and 2.20 in the benzoates.

### THE METHYL ETHERS OF THE TWO PHTHALOXIMES

The methyl ethers of the two oximes were made by treating the respective silver salts suspended in ether with methyl iodide. The reaction proceeds rapidly at room temperature with the separation of silver iodide. The ethers were extracted from the residue and recrystallized from alcohol in the form of long needles, that of the white oxime being colorless while the corresponding derivative of the yellow oxime is faintly yellow. Both ethers melt at 133° uncorrected.

### THE BENZOATES OF THE TWO PHTHALOXIMES

The two benzoates were similarly made from the silver salts and benzoyl chloride. They crystallize from alcohol in columns, one colorless and the other faintly yellow. Both melt at 171°.5 uncorrected. The benzoates may conveniently be prepared also from benzoyl chloride and an alkali salt of the oxime dissolved in water.

THE ALKALI SALTS OF THE TWO PHTHALOXIMES

The profound changes that take place in phthaloxime on the addition of alkali are manifested in the absorption spectra by the appearance of a broad absorption band extending from about $\frac{1}{\lambda}=1800$ to 2860, and heading at $\frac{1}{\lambda}=2300$. The absorption band of the oximes heading at $\frac{1}{\lambda}=3400$ decreases regularly with increasing concentrations of alkali, and practically disappears when the amount of alkali is sufficiently great to effect the complete transformation into the red salt. These differences with various concentrations of alkali are shown in fig. 2.

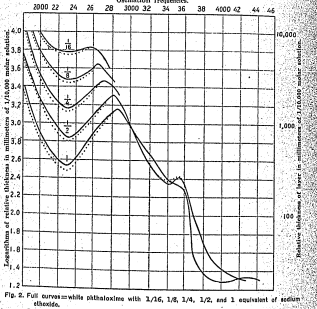



Fig. 2. Full curves = white phthaloxime with 1/16, 1/8, 1/4, 1/2, and 1 equivalent of sodium ethoxide.
Dot curves = yellow phthaloxime with corresponding alkali.

*Description of fig. 2.*—In order to avoid confusion arising from the large number of lines, the curves with one-sixteenth, one-eighth, and one-quarter molecular equivalents of alkali are not drawn throughout the entire regions measured. It is sufficient to state that they lie between the curve of the oxime itself and that formed with one-half equivalent of alkali.

These curves are plotted from photographs made through absolute alcohol solutions wherever possible. Since the desired concentration could not always be obtained with this solvent, 90 per cent alcohol was used when 1 equivalent and one-half equivalent of alkali were employed in the 1/100 molar solutions, and 99 per cent alcohol for the 1/1000 molar solutions. Ninety-five per cent alcohol solutions were used for the other 1/100 molar concentrations. These small amounts of water have no appreciable effect upon the curves.

The difference between the yellow and the white modification of the oxime is here manifested in the color absorption band. This has a greater persistence in the yellow than in the white, and shows that the salts of the former are somewhat more deeply colored than the corresponding salts of the latter.

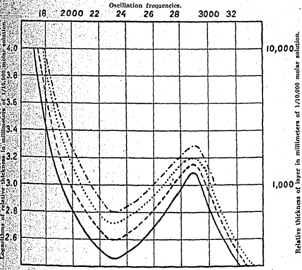



Fig. 3. Salts of white phthaloxime in 90 per cent alcohol.
Full curve = potassium salt.
Dash curve = sodium salt.
Dot curve = barium salt.
Dash and dot curve = ammonium salt.

### THE ABSORPTION SPECTRA OF PHTHALOXIME SALTS IN 90 PER CENT ALCOHOL

Weighed quantities of the pure salts were dissolved in the requisite volume of water and absolute alcohol added at once to make a 90 per cent alcohol solvent. In this manner exactly 1 equivalent of alkali to 1 of oxime was easily obtained. Photographs were made on Cramer's spectrum plates to cover as much of the color absorption band as possible, and the curves in fig. 3 plotted from these.

*Description of fig. 3.*—The curves show that the ammonium, barium, sodium, and potassium salts give absorption bands heading at $\frac{1}{\lambda} = 2300$ in each case, but appearing at increasing dilutions. The original ultra-violet oxime band heading at $\frac{1}{\lambda} = 3400$ was most pronounced in the ammonium salt and least in the potassium. The barium and sodium salts give intermediate curves. The residual oxime band gives an indication of the relative dissociation of the different salts, and corresponds in persistence inversely with the strength of the base. The silver salt of phthaloxime in crystalline form shows a deeper red than the corresponding potassium salt, but could not be included in the series because of its insolubility.

### THE ABSORPTION SPECTRA OF PHTHALOXIME AND ITS SALTS IN PYRIDINE

Pyridine is the only suitable solvent for the silver salt, and gives a deep purplish red solution containing an addition product of salt and base.

*Description of fig. 4.*—The absorption band appears at greater dilution, and heads at $\frac{1}{\lambda} = 2140$. It is of the same general type as the corresponding band given by the alkali salts, but shows by its position farther toward the red that a slightly different molecular equilibrium is represented in the compound. The curve given by oxime in pyridine shows general absorption extending into the visible spectrum, but retaining the oxime type. It is probable that no true salt is formed since a weighed amount of oxime did not gain in weight when dry pyridine vapor was passed over it. The dash curve represents oxime dissolved in a mixture containing equal volumes of water and pyridine. The color of this solution is deep red, and the absorption spectrum clearly shows the presence of a true salt.

## THE ABSORPTION SPECTRA OF PHTHALOXIME SALTS IN AQUEOUS PYRIDINE

The absorption spectra of the ammonium, sodium, potassium, and silver salts of the white oxime in pyridine solution containing 14 per cent water are plotted in fig. 5. The addition of water is necessary to dissolve the alkali salts, as their solubility in pyridine is slight.

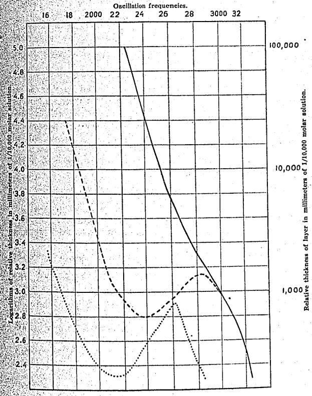



FIG. 4. Full curve=white phthaloxime in pyridine.
Dash curve=white phthaloxime in 50 per cent pyridine and 50 per cent water.
Dot curve=Silver salt of white phthaloxime in pyridine.

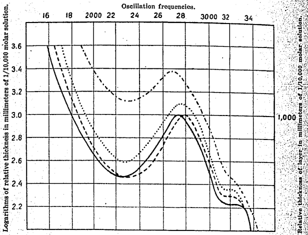



Fig. 5. Salts of white phthaloxime in pyridine containing 14 per cent water.
Full curve=silver salt.
Dash curve=potassium salt.
Dot curve=sodium salt.
Dash and dot curve=ammonium salt.

*Description of fig. 5.*—These curves bring out the difference in persistence and width of the color band and the corresponding residues of the ultra-violet oxime band. Since there is very little difference in the persistence of the latter in each case, it is reasonable to assume that the hydrolysis of the salts does not vary greatly in this solvent. The width of the color band and the dilution at which it appears are very different, especially with the weak ammonia base. These curves bring out the effect of different substituents and the relation between color and positive affinity better than any other series we have obtained. The addition product of silver salt and pyridine has been largely destroyed, and the absorption curve now heads at approximately the same point as that of the normal salts.

A solution of silver salt in alcoholic ammonia was prepared and photographed. The curve of its absorption spectrum falls between that of silver salt in pyridine and silver salt in pyridine containing 14 per cent water. This solution is unstable, and rapidly loses its red color with the formation of metallic silver. The addition product may be obtained by passing dry ammonia over a weighed amount of silver salt in a porcelain boat. Decomposition occurs with gradual loss of weight in a few hours. The results of one experiment are as follows:

| Substance (gram). | Gain (gram). | Gain (per cent). |
|---|---|---|
| 0.2133 | 0.0153 | 6.81 |
| | .0145 | 6.80 |
| | .0123 | 5.76 |
| | .0118 | 5.58 |
| Calculated for $C_8H_4O_2NAg{\cdot}NH_3$ | | 6.30 |

The boat and contents were then heated at 100° with a loss of weight corresponding approximately to the ammonia previously absorbed. The color remained a brownish gray, indicating no recovery of the original silver salt.

### THE ACID SALTS OF PHTHALOXIME

When an alcoholic solution of phthaloxime is treated with alcoholic potassium acetate, an orange-colored crystalline salt is precipitated.[24] A study of the absorption spectrum of this double salt clearly showed that in solution it was identical with the original oxime in the presence of one-half an equivalent of potassium ethoxide. Sodium acetate forms a similar double salt which is more difficult to crystallize and isolate. The underlying reasons for this fact are to be found in the relative solubilities of the normal sodium and potassium salts of phthaloxime. We have found that 100 cubic centimeters of absolute alcohol at 30° will dissolve 0.0590 gram of the potassium salt and only 0.0076 gram of the corresponding sodium salt.

Since the absorption spectra of the double salts were found to be identical with those of the oximes plus one-half an equivalent of corresponding alkali, we concluded that these salts could be crystallized from alcoholic solutions with equal ease by the addition of the proper amount of the hydroxide or ethoxide of the metal. This was found to be the case, and the fact that sodium or potassium acetate dissociates in solution, giving a small excess of hydroxyl ions over hydrogen ions, explains why these double salts were originally obtained by the addition of alkali acetates, while the formation with alkali hydroxides was overlooked. The double salts may also be prepared by mixing equal molecular equivalents of alcohol solutions of oxime and the normal alkali salt and concentrating to crystallization.

[24] Orndorff and Pratt, *loc. cit.*

COLORLESS ALKALI SALTS OF PHTHALOXIME

The effect of temperature upon molecular equilibrium is little understood, but there is undoubtedly a decreased activity at low temperatures. Alcohol solutions of phthaloxime show less yellow color when cooled in a mixture of solid carbon dioxide and ether. This may be due to a decreased activity of hydrogen toward the partial valencics of the unsaturated groups, or may be caused by a change in the equilibrium of molecular rearrangement. When a cold alcohol solution of sodium ethoxide was added to the above oxime solution, crystals of sodium salt were precipitated in an almost colorless form. These showed no increase of color as long as they were kept cold in the freezing mixture, but rapidly turned red after filtering from the mother liquor, due in all probability both to the rise in temperature and the condensation of water. The colorless crystals may be taken as the true oxime type of salt, regardless of which theory be applied to explain the colored compounds.

THE ABSORPTION SPECTRA OF PHTHALHYDROXAMIC ACID

Alkaline solutions of phthaloxime salts suffer rapid transformation into salts of phthalhydroxamic acid [25] with loss of identity between the white and the yellow isomer.[26] It appears that the difference between the two forms depends upon the integrity of the double bond between carbon and nitrogen, and that this is destroyed when the hydroxamic acid forms. Moreover, the free hydroxamic acid when heated in solution gives phthaloxime, the white isomer forming at 60° and the yellow at 100°. The formation of hydroxamic acid may be due to the increased activity of molecular vibration when hydrogen is replaced by a metal atom or to the tendency of the rearranged molecule to take up the elements of water. However, phthaloxime suspended in distilled water gradually forms hydroxamic acid upon standing even in the presence of mineral acid and without passing through a colored stage, so it is not essential to assume a different molecular condition as necessary for the transformation. Alkali appears merely to accelerate the rate of reaction, without influencing the final product. This is further evidence that the oxime and its salts possess identical molecular structure.

For purposes of photographing the absorption spectrum of the hydroxamic acid, alcohol solutions of oxime were treated with an excess of alkali and allowed to stand until colorless.

[25] Lassar-Cohn, *loc. cit.*

[26] Orndorff and Pratt, *loc. cit.*

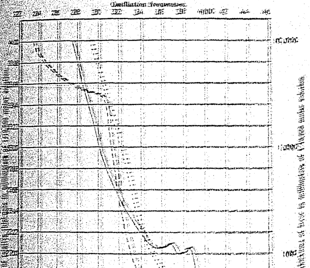
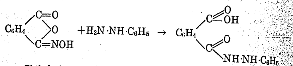



Fig. 6. Full curve = phthalhydroxamic acid.
Dash curve = phthalylhydroxylamine.
Dot curve = phthalonimic acid.

*Description of fig. 6.*—The absorption spectrum of phthalhydroxamic acid shows a small band in the ultra-violet reading at $\frac{1}{\lambda} = 3550$ and indications of benzene bands. This is evidence that the condition present in oximes, phthalic acid, phthalimide, etc., is still present, although the persistence of the characteristic band is greatly decreased in the case of the hydroxamic acid. The spectroscopic behavior of phthalhydroxamic acid, therefore, corresponds with the formula generally assigned to this compound.

ACTION OF PHENYLHYDRAZINE ON PHTHALOXIME

When an alcohol solution of either the white or yellow phthaloxime is gently warmed with phenylhydrazine, the following reaction takes place:



Phthaloxime. Anilidophthalamic acid.

The anilidophthalamic acid thus formed was recrystallized from alcohol until colorless, and found to be identical with the compound described by Hötte [27] who obtained it from phthalic anhydride and phenylhydrazine.

0.1698 gram gave 17.2 cubic centimeters nitrogen over water at 31°.5; barometer, 763 millimeters.

| | Calculated for $C_{14}H_{12}O_3N_2$ (per cent). | Found (per cent). |
|---|---|---|
| Nitrogen | 10.93 | 10.96 |

0.1974 gram dissolved in absolute alcohol required 7.70 cubic centimeters of N/10 sodium hydroxide for neutralization. Theory, 7.71 cubic centimeters.

The absorption spectrum of anilidophthalamic acid is plotted in fig. 6, and indicates by the band heading at $\frac{1}{\lambda}=3700$ that the structure is analogous to phthalhydroxamic acid and correctly represented by the above formula.

PHTHALYLPHENYLHYDRAZINE

If the alcohol solution of phthaloxime and phenylhydrazine be heated on the water bath for an hour, the reaction proceeds further with the splitting off of one molecule of water. A neutral yellow compound is formed identical with Hötte's phthalylphenylhydrazine. The same product results when anilidopthalamic acid is heated, the reaction going to completion rapidly at 100°. This compound crystallizes from alcohol in long yellow prisms, and melts at 182° uncorrected.

(1) 0.1854 gram gave 20.0 cubic centimeters nitrogen over water at 29°; barometer, 762.5 millimeters.

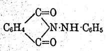
(2) 0.1740 gram gave 18.8 cubic centimeters nitrogen over water at 30°; barometer, 763.7 millimeters.

(3) 0.2230 gram gave 0.5761 gram $CO_2$ and 0.0821 gram $H_2O$.

[27] *Journ. f. prakt. Chem.* (1887), II, 35, 268.

| | Calculated for $C_{14}H_{10}O_2N_2$ (per cent). | Found (per cent). |
|---|---|---|
| Carbon | 70.58 | 70.44 |
| Hydrogen | 4.20 | 4.09 |
| Nitrogen | 11.76 | 11.82 |
| | | 11.77 |

The absorption spectrum of phthalylphenylhydrazine is also plotted in fig. 6. It shows a well-developed ultra-violet band heading at $\frac{1}{\lambda}=3600$ and a step-off extending from $\frac{1}{\lambda}=2400$ to 3060. The characteristics of this spectrum throw grave doubt upon the symmetrical structure,




given by Hötte. We have found his method of preparation analogous in every way to the formation of phthaloxime from phthalic anhydride and hydroxylamine. The replacement of the oxime group of phthaloxime by the phenylhydrazine residue corresponds to similar reactions studied by Just,[28] and undoubtedly results in a similar structure. Moreover, a careful study of the absorption spectrum in comparison with those of various phenylhydrazines and osazones described by Baly and Tuck [29] and by Baly, Tuck, and Marsden [30] leads us to believe that this compound may not be a hydrazone. We hope to continue this investigation, and in a later article to present conclusive evidence concerning the structure of this interesting compound and its derivatives.

[28] *Ber. d. deutschen chem. Ges.* (1886), **19**, 1205.
[29] *Journ. Chem. Soc. London* (1906), **89**, 982.
[30] *Ibid.* (1907), **91**, 1572.

119450——4

# ILLUSTRATIONS

PLATE I

Yellow phthaloxime. 1/1000 molar solution. Thickness of layer, 32 to 2 millimeters.

PLATE II

FIG. 1. Potassium salt of white phthaloxime in 90 per cent alcohol. 1/100 molar solution. Thickness of layer, 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 30, 50, 75, and 100 millimeters.
2. Silver salt of white phthaloxime in pyridine. 1/100 molar solution. Thickness of layer, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, and 22 millimeters.

TEXT FIGURES

FIG. 1. Full curve=white phthaloxime.
Dot curve=yellow phthaloxime.
Dash curve=benzoate of white phthaloxime.
2. Full curves=white phthaloxime with $\frac{1}{16}$, $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, and 1 equivalent of sodium ethoxide.
Dot curves=yellow phthaloxime with corresponding alkali.
3. Salts of white phthaloxime in 90 per cent alcohol.
Full curve=potassium salt.
Dash curve=sodium salt.
Dot curve=barium salt.
Dash and dot curve=ammonium salt.
4. Full curve=white phthaloxime in pyridine.
Dash curve=white phthaloxime in 50 per cent pyridine and 50 per cent water.
Dot curve=silver salt of white phthaloxime in pyridine.
5. Salts of white phthaloxime in pyridine containing 14 per cent water.
Full curve=silver salt.
Dash curve=potassium salt.
Dot curve=sodium salt.
Dash and dot curve= ammonium salt.
6. Full curve=phthalhydroxamic acid.
Dash curve=phthalylphenylhydrazine.
Dot curve=anilidophthalamic acid.