

Summary

The suppressive effect of increasing resistance in the cell circuit on the maximum in the polarographic c. v. curve of mercurous ions, first discovered by Brdicka, has been confirmed. It has also been found that the maxima of oxygen, lead ions, nickel ions, and zinc ions, are all more or less suppressed by a large resistance in series

with the cell, and it is concluded that the effect is of general occurrence. An explanation of this effect has been given, based on the fact that the e. m. f. actually applied across the cell decreases during the life of each mercury drop when a large external resistance is in series with the cell.

BERKELEY, CALIFORNIA

RECEIVED MARCH 1, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Studies on Inner Complexes¹

BY HELMUT M. HAENDLER WITH GEORGE MCP. SMITH

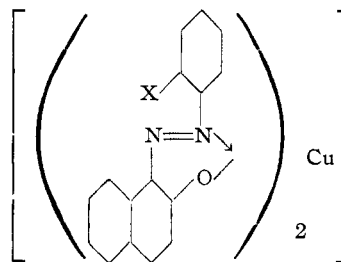
1. ortho-Hydroxy Azo Dye Inner Complexes

In a recent article² the formation and properties of various inner complexes of ortho-quinone monoximes were discussed. Because of the low solubility of these complexes, namely, of phenanthrenequinone monoxime and chrysenequinone monoxime, in the simpler organic solvents, it was decided to extend the study to include inner complexes of ortho-hydroxy azo dyes. Complexes of the latter type had been prepared and characterized by Drew and Landquist³ and were reported to be appreciably soluble in liquids such as xylene and nitrobenzene, a circumstance which gave greater promise of suitability for absorption spectra measurements.

The possible number of variable substituent groups in the azo dye is large, and the effects of position isomerism and changes in the substituents themselves can be followed. The dyes selected were derivatives of 2-naphthol, with a phenyl or substituted phenyl group joined to the naphthol through an azo linkage. The substituents chosen were the methyl, chloro, methoxy, and ethoxy groups, each located on the phenyl ring in its three possible isomeric positions.

The dyes give evidence of possible reaction with several different metal salts, notably those of copper, cobalt, and nickel. The complexes of copper being the most readily prepared, they alone were considered. These complexes, in which the chelating group has the classification C,C,N-

N,OH,⁴ have the structure shown, the system forming a stable six-membered ring.



In general, the characteristics of the copper complexes are identical. They are all some shade of brown when in a finely divided state and often exhibit a greenish or purplish cast when crystalline. They are soluble in many organic solvents although the solubility varies over a wider range than the other properties. The complexes with substituents in ortho position are the most soluble, dissolving to some extent in solvents like alcohol or acetone. They are usually so soluble in dioxane, benzene, xylene, etc., as to make crystallization extremely difficult. The para substituted complexes are the least soluble, the meta complexes lying in an intermediate position. All the complexes are soluble in both pyridine and nitrobenzene. Concentrated sulfuric acid decomposes them.

Experimental

ortho-Hydroxy Azo Dyes.—The dyes were prepared in the usual manner by coupling the proper diazotized amine with 2-naphthol in alkaline solution. All had been prepared previously, and references are given in Table I. The melting points of the dyes are also listed and were found to exceed, in general, the reported values, possibly because of the greater purity of the amines now available.

(1) This paper and that cited in reference 2 represent abstracts from a thesis presented by H. M. Haendler to the University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Haendler with Smith, *THIS JOURNAL*, **61**, 2624 (1939).

(3) Drew and Landquist, *J. Chem. Soc.*, 299 (1938).

(4) Haendler and Geyer, *THIS JOURNAL*, **60**, 2813 (1938).

TABLE I
 o-HYDROXY AZO DYE INNER COMPLEXES

Name of dye	M. p., °C.	Formula	Solvent for inorg. comp. ^a	Solvent for recryst. of complex	Yield, %	Copper anal., %
						Calcd. Found
1-Phenylazo-2-naphthol ⁵	131.5-132.5	[Cu(P) ₂] ^{3,14}	EtOH-H ₂ O	Nitrobenzene	85
1-(o-Tolylazo)-2-naphthol ⁶	130.5-131.5	[Cu(o-Me-P) ₂]	EtOH-H ₂ O	Xylene	85	10.8 10.8
1-(m-Tolylazo)-2-naphthol ⁷	139-140	[Cu(m-Me-P) ₂] ³	EtOH-H ₂ O	Xylene	80
1-(p-Tolylazo)-2-naphthol ⁸	135.5-137	[Cu(p-Me-P) ₂]	EtOH-H ₂ O	Nitrobenz.-xylene	90	10.8 11.1
1-(o-Chlorophenylazo)-2-naphthol ⁸	165-166	[Cu(o-Cl-P) ₂]	Me ₂ CO-H ₂ O	Dioxane	50	10.1 9.8
1-(m-Chlorophenylazo)-2-naphthol ⁸	158-159	[Cu(m-Cl-P) ₂]	Me ₂ CO-H ₂ O	b	35	10.1 10.3
1-(p-Chlorophenylazo)-2-naphthol ⁹	160.5-161.5	[Cu(p-Cl-P) ₂]	EtOH-H ₂ O	Nitrobenz. ^c	70	10.1 10.0
1-(o-Anisylazo)-2-naphthol ¹⁰	179.5-180.5	[Cu(o-MeO-P) ₂]	EtOH-H ₂ O ^d	i-Amyl alc.	70	10.3 10.3
1-(m-Anisylazo)-2-naphthol ¹¹	143.5-144.5	[Cu(m-MeO-P) ₂]	EtOH-H ₂ O	Toluene ^c	85	10.3 10.1
1-(p-Anisylazo)-2-naphthol ¹²	138-139	[Cu(p-MeO-P) ₂]	EtOH-H ₂ O	Xylene	60	10.3 10.3
1-(o-Phenetylazo)-2-naphthol ¹⁰	141	[Cu(o-EtO-P) ₂]	EtOH-H ₂ O ^d	None	80	9.8 9.8
1-(m-Phenetylazo)-2-naphthol ¹³	101-102	[Cu(m-EtO-P) ₂]	EtOH-H ₂ O	Xylene ^c	90	9.8 10.0
1-(p-Phenetylazo)-2-naphthol ¹⁰	134-135	[Cu(p-EtO-P) ₂]	EtOH-H ₂ O	Nitrobenz., then tol.	60	9.8 9.9

^a All in ratio of 1:1 by volume. ^b Purified by extraction with nitrobenzene and precipitation of the complex from extract with ethyl ether. ^c Precipitated with petroleum ether. ^d Ammonium hydroxide added.

Inner Complexes of the Azo Dyes.—The complexes, two of which had been noted previously, were prepared by the addition, in twofold excess, of cupric acetate, dissolved in dilute alcohol or acetone, to a nearly saturated solution of the azo dye in the corresponding organic solvent. As a more definite example, the preparation of 1-(o-tolylazo)-2-naphtholato-copper (II) is given. To a solution of 2.0 g. of cupric acetate in 30 ml. of water there was added 30 ml. of 95% ethyl alcohol. This solution, after filtration, was run dropwise into a hot, nearly saturated solution of 2.6 g. of 1-(o-tolylazo)-2-naphthol (0.01 mole) in ethyl alcohol. After twenty-four hours, the crystals were filtered off, washed with alcohol, dried, and recrystallized from a suitable solvent, in this case, xylene.

In two instances it was found advisable to add several ml. of 6 N ammonium hydroxide to the mixed solutions to hasten the formation and coagulation of the precipitate. Because of the very finely divided state of the freshly precipitated complex, centrifugation was resorted to in several cases. The solvent for recrystallization depends on the complex, and this and other data, including analytical results, are presented in Table I.

2. Inner Complex Absorption Spectra

The visible absorption spectra of ten of the oxime complexes included in the earlier paper,² of the ortho-hydroxy azo dye complexes listed in Table I, and of the parent organic compounds were measured from a more or less qualitative standpoint to determine what predominant variations, if any, might occur. Original tests on the oxime complexes reported indicated too low a solubility for suitable absorption work, but it has

since been found that satisfactory solutions of these oxime complexes could be prepared with pyridine, with the exception of the too insoluble lead complexes.

There is extremely close similarity between the spectra of closely related complexes and rather than attempt to show curves for all forty spectra the positions of the maxima and the magnitudes of the molecular extinction coefficients are given in Table II.

As would be expected from the observed colors of the oxime complexes the variations in spectra are greater than with the copper azo complexes reported here. The formation of the metal complexes of the oximes is accompanied by an increase in intensity and a variable widening of the absorption band. It was found that the introduction of the extra ring system in chrysenequinone monoxime as contrasted to phenanthrenequinone monoxime occasioned a slight broadening of the absorption band and an increase in intensity, and this relationship between these two ring systems is maintained throughout the spectra of the complexes.

The solutions of the copper, nickel, and cobalt complexes appear to be those of the inner complex itself, but the similarity of the cadmium, manganese, and uranyl complex spectra indicates that these form addition compounds with the pyridine, as was previously reported for the cadmium complex.²

The azo dyes referred to in this paper are all some shade of red in the solid state, and the spectra of the dyes in nitrobenzene solution show no characteristic mutations. The maxima occur at approximately the same wave length and vary but slightly in intensity. There is no definite

- (5) Liebermann, *Ber.*, **16**, 2860 (1883).
- (6) Zincke and Rathgen, *ibid.*, **19**, 2490 (1886).
- (7) Haager and Dohr, *Monatsh.*, **27**, 273 (1906).
- (8) Niementowski, *Chem. Zentr.*, **73**, II, 938 (1902).
- (9) Orton and Everatt, *J. Chem. Soc.*, 1020 (1908). First prepared with amyl nitrite but use of sodium nitrite is simpler.
- (10) Charrier and Ferreri, *Gazz. chim. ital.*, **41**, II, 717 (1911).
- (11) Reverdin and DeLuc, *Ber.*, **47**, 1540 (1914).
- (12) Hantzsch, *Ann.*, **325**, 249 (1902).
- (13) Reverdin and Lokietek, *Bull. soc. chim.*, **4**, 17, 409 (1915).
- (14) Elkins and Hunter, *J. Chem. Soc.*, 1598 (1935).

TABLE II
 ABSORPTION SPECTRA DATA

	Max. m μ	ϵ
Phenanthrenequinone monoxime	410	800
Chrysenequinone monoxime	415	1300
Phenanthrenequinonemonoximato-		
Cadmium	390	4150
	620	150
Copper (II)	470	5650
Cobalt (II)	510	5200
Manganese (II)	445	4300
	800	300
Nickel (II)	450	5000
Uranyl	410	4350
Diethanolato(-)-uranyl	410	5800
Chrysenequinonemonoximato-		
Copper (II)	475	5900
Manganese (II)	475	6550
	835	2000
Nickel (II)	475	5550
Uranyl	410	6500
Diethanolato(-)-uranyl	400	7300
-2-Naphthol		
1-Phenylazo	505	1600
1-(<i>o</i> -Tolylazo)	505	2000
1-(<i>m</i> -Tolylazo)	505	2000
1-(<i>p</i> -Tolylazo)	500	1400
1-(<i>o</i> -Chlorophenylazo)	500	2200
1-(<i>m</i> -Chlorophenylazo)	500	2150
1-(<i>p</i> -Chlorophenylazo)	505	2350
1-(<i>o</i> -Anisylazo)	530	1750
1-(<i>m</i> -Anisylazo)	500	2000
1-(<i>p</i> -Anisylazo)	510	2250
1-(<i>o</i> -Phenetylazo)	530	2150
1-(<i>m</i> -Phenetylazo)	500	2400
1-(<i>p</i> -Phenetylazo)	515	2300
-2-Naphtholato-copper (II)		
1-Phenylazo	495	10500
1-(<i>o</i> -Tolylazo)	495	3650
1-(<i>m</i> -Tolylazo)	500	5450
1-(<i>p</i> -Tolylazo)	505	10250
1-(<i>o</i> -Chlorophenylazo)	505	4400
1-(<i>m</i> -Chlorophenylazo)	470	7500
1-(<i>p</i> -Chlorophenylazo)	510	9350
1-(<i>o</i> -Anisylazo)	530	4650
1-(<i>m</i> -Anisylazo)	505	6700
1-(<i>p</i> -Anisylazo)	500	9150
1-(<i>o</i> -Phenetylazo)	530	4750
1-(<i>m</i> -Phenetylazo)	505	6850
1-(<i>p</i> -Phenetylazo)	510	8650

variation although several minor changes have been noticed. A slight shift of absorption to the red can be seen in the dyes having substituent methoxy and ethoxy groups, particularly in ortho and para substituted compounds.

Solutions of azo dye inner complexes in nitrobenzene also show but little variation in spectra. The effect of the formation of the complex by completion of the chelate ring is to widen the

absorption band considerably, shifting the maximum slightly to the red, and increasing the intensity of absorption. The relationship between the spectra of the azo dyes and the corresponding complexes remains about the same in all cases. On the basis of one mole of dye the spectra of the methyl and chloro complexes with this group in ortho position approach the spectra of the dyes themselves although the difference between the other complexes and the corresponding dyes remains considerable. It seems possible, therefore, that the structure in these two may be different.

Any apparent variation due to substituent groups is less than with the azo dyes alone; changes due to position, however, are more marked. The magnitude of the extinction coefficient increases conspicuously from ortho substituted, through meta, to para substituted complexes, a relation similar in form to that observed with solubilities.

It is apparent that because of the complexity of the molecule any structural interpretation of the spectra secured is impossible. The exact nature of both the oximes and the azo dyes is still indefinite. Naturally, before any statements more conclusive than those presented can be made, considerable work must be undertaken. It is proposed to extend the study of relative effects through consideration of series of simpler compounds.

It seems extremely probable that the increase in intensity noted with the complexes is less dependent upon the nature of the substituent groups in the dyes than upon the formation of the chelate linkage.

Experimental

The compounds tested were prepared as described above, with the following exceptions and additions.

Phenanthrenequinone Monoxime.—The oxime, prepared as described,² was purified by crystallization from ethyl alcohol; m. p. 161–162°.

Phenanthrenequinonemonoximato - cobalt(II).—This complex, first reported by Ciusa,¹⁵ was prepared by addition, in two-fold excess, of a solution of cobalt acetate in 50% ethyl alcohol to a hot, nearly saturated alcohol solution of the oxime. The complex was purified by precipitation from nitrobenzene solution with ethyl ether.

Phenanthrenequinonemonoximato - nickel(II).—This complex, also reported by Ciusa, was prepared as was the cobalt complex, using nickel acetate.

Absorption Spectra.—The spectra were determined by measurement of percentage transmission, at definite wave lengths, of the solutions compared to the pure solvent as a

(15) Ciusa, *Gazz. chim. ital.*, **66**, 591 (1934).

standard. The new Coleman Regional Spectrophotometer was used. The accuracy of the instrument compares very favorably with that of other apparatus, usually visual in operation, used for the same purpose. The compounds were weighed directly into volumetric flasks, made up to volume, and an aliquot taken if necessary. The concentrations used were in the neighborhood of 0.001 *M*. The extinction coefficients were calculated from Beer's law.

Summary

1. Several new copper inner complexes of closely related ortho-hydroxy azo dyes of 2-naphthol have been prepared.

2. The complexes have been isolated in the crystalline state and are all sufficiently soluble in organic solvents to permit absorption spectra measurements.

3. The absorption spectra of phenanthrenequinone monoxime, chrysenequinone monoxime, and ten of their metal inner complexes were measured in pyridine solution and the observed variations discussed.

4. The absorption spectra of thirteen ortho-hydroxy azo dyes and the thirteen corresponding copper inner complexes were measured in nitrobenzene and the observed variations discussed.

5. The color of the inner complexes in both cases is apparently influenced less by the character of the substituent group in the organic portion than by the formation of the chelate bond.

SEATTLE, WASHINGTON

RECEIVED MARCH 15, 1940

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

α - and β -N-Dialkylamino- α,β -unsaturated Ketones

BY NORMAN H. CROMWELL

Although β -N-dialkylamino- α,β -unsaturated ketones have been prepared by André,¹ by adding secondary amines to phenylacetylacetylenes, it seems desirable to use cheaper, more readily obtainable starting materials.

The condensation of benzoylacetone with ammonia and primary amines has been shown by Beyer² to give 1-phenyl-3-aminobutene-2-one-1 and 1-phenyl-3-N-alkylaminobutene-2-one-1, respectively, or their tautomeric imines. Also Combes³ has shown that acetylacetone could be condensed with diethylamine to give 2-N-diethylamino-pentene-2-one-4.

The investigation of Ruhemann and Watson⁴ has led these workers to the conclusion that dibromobenzalacetophenone reacted with ammonia and amines to give β -amino- α,β -unsaturated ketones. The more recent work of Dufraisse, *et al.*,⁵ has shown conclusively that the main product from this type of reaction is not the β - but the α -amino- α,β -unsaturated ketone. Dufraisse was interested in this reaction, mainly, as a means of preparing 1,2-diketones.

The research described in the present paper is

(1) André, *Compt. rend.*, **152**, 525 (1911); *Ann. chim.*, [8] **29**, 575 (1913).

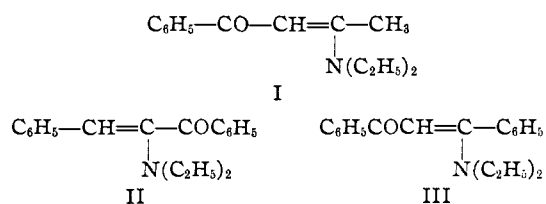
(2) Beyer, *Ber.*, **20**, 2180 (1887); *ibid.*, **24**, 1669 (1891).

(3) Combes and Combes, *Bull. soc. chim.*, [3] **7**, 778 (1892).

(4) Ruhemann and Watson, *J. Chem. Soc.*, **85**, 1181 (1904).

(5) Dufraisse and Moureu, *Bull. soc. chim.*, [4] **41**, 861 (1927).

an extension of these methods to the preparation of the following unsaturated amino ketones



The unsaturated amino-ketone II was prepared from the corresponding dibromide, while I and III were prepared by the condensation of diethylamine with the corresponding 1,3-diketones. The yield of compound III was too low to make this method of preparative value, and is reported here merely for reasons of comparison with the readily obtainable compound I. Both of these condensations had to be carried out in sealed tubes above 100°.

The structure of II was elucidated by its hydrolysis to the corresponding 1,2-diketone, which was identified through a suitable derivative. The structure of I was apparent by analogy with the investigations of Beyer,² while III had been prepared from benzoyl-phenylacetylene, previously, by André.¹

The study of these two reactions and their products is being extended.