

morning. The residue was dissolved in water (30 ml.) and filtered. Sodium iodide (0.5 g.) in water (3 ml.) was added to the filtrate and the precipitate was allowed to stand overnight, filtered, washed with sodium iodide solution, a little ice water and then ether, and air dried (yield 0.67 g.); $[\alpha]_{3461} - 5900^\circ$. Further fractions, 0.19 g., $[\alpha]_{3461} - 6500^\circ$; 0.06 g., $[\alpha]_{3461} - 4500^\circ$, were obtained by evaporating the filtrate stepwise. Total yield was 0.92 g. (98.5%), average $[\alpha]_{3461} - 5920^\circ$.

The product of the above preparation (0.89 g.) was transposed to the chloride and treated with sodium *d*-antimonytartrate (0.36 g.). The diastereoisomer which resulted (0.78 g.) had $[\alpha]_{3461} - 5400^\circ$. It was recrystallized from hot water twice giving a final product with $[\alpha]_{3461} - 6700^\circ$. This diastereoisomer gave an iodide on decomposition which had $[\alpha]_{3461} - 7500^\circ$. The filtrate from the resolution yielded an iodide which had zero rotation. The original complex formed was therefore a mixture containing 88% *L*-[Co-*d*-EPE]I and 12% *D*-[Co-*d*-EPE]I.

***D*-1,4-Methyl-1,8-bis-(salicylideneamino)-3,6-dithiaoctanecobalt(III) Iodide 1-Hydrate.**—The diastereoisomer *D*-[Co-*l*-EPE]-*l*-SbOtart·4H₂O (1.8 g.) was converted to the iodide and fractionally crystallized. The best fraction had $[\alpha]_{3461} + 7500^\circ$. *Anal.* Calcd. for [CoC₂₁H₂₄N₂S₂O₂]I·H₂O: C, 41.7; H, 4.3; N, 4.6. Found: C, 41.7; H, 4.4; N, 4.5.

Preparation and Resolution of 1,4-Methyl-1,8-bis-(salicylideneamino)-3,6-dithiaoctanecobalt(III) Iodide.—The preparation was identical with that described above save that 1,4-methyl-1,8-diamino-3,6-dithiaoctane was used. The yield was 0.86 g. (95%) having an average rotation $[\alpha]_{3461} + 5170^\circ$.

This product was resolved using sodium *l*-antimonytartrate. The diastereoisomer was collected immediately on forming. The filtrate was treated with excess sodium iodide (0.6 g.) and the precipitated iodide collected quickly and washed with a little water and then ether (yield 0.02 g.). It had $[\alpha]_{3461} - 2500^\circ$, while the diastereoisomer had $[\alpha]_{3461} + 5000^\circ$ which improved to +6500° on recrystallization.

These results indicate that the original compound formed was a mixture of *D*-[Co-*l*-EPE]I (84%) and *L*-[Co-*l*-EPE]I (16%).

The rotatory dispersion curves for the isomers *L*-[Co-*d*-EPE]I and *D*-[Co-*l*-EPE]I were prepared for 0.01% solutions in a 1-dm. tube using a Shimadzu manual spectrophotometer with a photoelectric polarimeter attachment. They are shown in Fig. 2 together with the curve for *D*-[Co-EEE]I.

Acknowledgment.—The authors are indebted to the Microanalytical Service of the Department of Medical Chemistry for the microanalyses recorded.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH 13, PENNSYLVANIA]

Copper Complexes of *o*-Hydroxy Schiff Bases and the Hydrolysis of the Schiff Bases¹

BY KUMAR K. CHATTERJEE, NOEL FARRIER, AND BODIE E. DOUGLAS

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Copper complexes (2:1) of *N*-salicylideneaniline (III), *N*-salicylidene-*p*-anisidine (IV), *N*-(2-hydroxy-3-methoxybenzylidene)-*p*-anisidine (V), and *N*-(2-hydroxy-3-methoxybenzylidene)-aniline (VI) have been prepared in water-ethanol solution. Similar methods did not yield the chelates of the Schiff bases derived from *o*-aminophenol (*N*-benzylidene-*o*-hydroxyaniline (I) and *N*-(4-methoxybenzylidene)-*o*-hydroxyaniline (II)) because of hydrolytic cleavage of the Schiff bases. The Cu chelate (2:1) of II was prepared in absolute ethanol. The hydrolytic cleavage of the Schiff bases was followed spectrophotometrically. All of the Schiff bases were found to hydrolyze in a matter of minutes in 50% v./v. water-dioxane and almost instantaneously in acidified water-dioxane. The spectra of the conjugate acids of the Schiff bases could be obtained in absolute ethanol in which gaseous HCl is dissolved. In this medium the decomposition was slow enough for the spectra to be recorded in most cases.

During the course of the investigation of the spectra of some Schiff bases and their metal complexes, several new copper complexes were isolated. The Schiff bases derived from *o*-aminophenol did not give the corresponding copper chelates by the usual preparative methods because of hydrolysis of the ligand in the presence of water. An investigation of the changes in the spectra of the Schiff bases in water-dioxane and in acid solution as a function of time was carried out in order to determine the importance of hydrolysis in the present work and in other studies in the literature.

Lane and Kandathil² reported a series of *o*-hydroxy Schiff bases of three types: Type A, derived from *o*-aminophenol and benzaldehyde or *p*-substituted benzaldehydes; type B, derived from salicylaldehyde and aniline or *p*-substituted anilines; and type C, derived from 2-hydroxy-3-methoxybenzaldehyde and aniline or *p*-substituted anilines. The acid dissociation constants of these compounds and the formation constants of some of their metal chelates were determined by potentiometric titrations. No hydrolysis of the Schiff bases was noted, even though Charles and Freiser³ reported that they were unable to carry out potentiometric titrations of Schiff bases of *o*-aminophenol (type A) because of hydrolysis of the ligand. Eichhorn and Bailar⁴ observed that hydrolysis of the ligand prevented the preparation of metal complexes of the Schiff bases obtained from 2-thiophenylaldehyde and *o*-aminophenol. Eichhorn and Marchand⁵ found that Schiff bases of

this type were made more susceptible to hydrolytic cleavage by coordination to copper(II) (and presumably by protonation).

Experimental

The following Schiff bases were prepared by condensing the appropriate aldehyde and amine²: *N*-benzylidene-*o*-hydroxyaniline (I), *N*-(4-methoxybenzylidene)-*o*-hydroxyaniline (II), *N*-salicylideneaniline (III), *N*-salicylidene-*p*-anisidine (IV), *N*-(2-hydroxy-3-methoxybenzylidene)-*p*-anisidine (V), and *N*-(2-hydroxy-3-methoxybenzylidene)-aniline (VI). The melting points agreed closely with those reported and elemental analyses were available for all of the Schiff bases and for the copper chelates of all except I. Commercial *o*-aminophenol used in these preparations and for the spectra was recrystallized several times from 50% water-ethanol in an atmosphere of nitrogen.

Dioxane was purified⁶ within a couple of weeks of the time used.

The spectra were recorded on a Cary Model 14 recording spectrophotometer. The pH titrations were carried out as described in the reference cited by Lane.⁷

Preparation of Copper Chelates.—The copper chelates of III, IV, V, and VI were prepared by the following general method.

An aqueous ethanolic solution of copper acetate was mixed with a warm ethanolic solution of the Schiff base in a molar ratio of 2:1 (ligand-metal), followed by addition of a 5% solution of sodium acetate in water with constant and rapid stirring. The precipitated copper compounds were allowed to settle for about 1 hr., filtered with suction, redissolved in the minimum quantity of warm ethanol, and recrystallized by the addition of water to the ethanolic solution. The products were filtered and washed several times with 50% ethanol and finally dried *in vacuo* at room temperature for several days.

(1) This work was supported by the Atomic Energy Commission, Contract AT(30-1)2274.

(2) T. J. Lane and A. J. Kandathil, *J. Am. Chem. Soc.*, **83**, 3782 (1961).

(3) R. G. Charles and H. Freiser, *ibid.*, **74**, 1385 (1952).

(4) G. L. Eichhorn and J. C. Bailar, Jr., *ibid.*, **75**, 2905 (1953).

(5) G. L. Eichhorn and N. D. Marchand, *ibid.*, **78**, 2688 (1956).

(6) A. Weissberger and E. S. Proskauer, "Organic Solvents," Oxford University Press, London, 1935, p. 140.

(7) H. Freiser, R. G. Charles, and W. D. Johnston, *J. Am. Chem. Soc.*, **74**, 1383 (1952).

This method was found unsuitable for the preparation of copper complexes of Schiff bases derived from *o*-aminophenol (I and II). The products obtained in this way gave evidence of extensive hydrolysis of the Schiff bases. The copper chelate of II was obtained by mixing a saturated solution of copper acetate (hydrated) in absolute ethanol with a slightly warm solution of the Schiff base in absolute ethanol. The copper compound crystallized from the solution on cooling. It was washed with cold absolute ethanol and dried *in vacuo* for several days. Attempts to prepare the copper complex of I by this method were unsuccessful.

The copper(II) complex of *o*-aminophenol was prepared in the same manner as the complexes of III, IV, V, and VI. The precipitated complex was digested on a steam bath for about 1 hr., cooled, filtered, washed several times with water followed by cold ethanol, and dried *in vacuo* for several days.

The copper content of the complexes was determined by iodometric titrations after decomposition of the complexes by boiling with a mixture of nitric and perchloric acids. Analyses for C, H, and N were performed by Alfred Bernhardt of the Max-Planck Institute.

Results and Discussion

Copper Chelates.—The copper(II) chelates of types B and C prepared were those of III, reddish brown, 13.97% Cu found (calcd. 13.94); IV, olive-brown, 12.19% Cu (calcd. 12.33); V, purple, 11.06% Cu (calcd. 11.04); and VI, dark brown, 12.11% Cu (calcd. 12.33). All complexes were quite insoluble in water, but fairly soluble in chloroform, and sparingly soluble in ethanol and dioxane.

The products obtained from the attempts to prepare copper complexes of I and II in the presence of water contained a much higher percentage of Cu than should be present for a 2:1 complex of the Schiff bases. The Cu content of the complex obtained from I was 20.65% (13.93% calcd.). The copper content of the complex obtained from II was 16.55% (12.32% calcd.). Both complexes are greenish brown and rather similar in appearance to the *o*-aminophenol complex. A separate liquid layer formed, and the odor of benzaldehyde was very obvious after the copper acetate solution was mixed with the solution of I. The Cu analyses indicated that the solid compounds obtained were not pure samples of the 2:1 *o*-aminophenol complex (22.7% Cu calcd.). Another sample of the Cu compound obtained from I and hydrated copper acetate in absolute ethanol gave an elemental analysis of 48.94 C, 4.72 H, 8.97 N, and 17.6% Cu. The calculated percentages for a 2:1 chelate of I are 68.5 C, 4.4 H, and 6.15% N. The calculated percentages for a 2:1 chelate of *o*-aminophenol are 51.4 C, 4.28 H, and 10.0% N. A sample of the *o*-aminophenol chelate gave the following analysis; 47.59 C, 4.71 H, and 10.08% N. The C/N ratio based on the analysis of the compound obtained from I is 5.45. The calculated value for *o*-aminophenol is 5.14 and that for I is 11.1. The product obtained is apparently a slightly impure chelate of *o*-aminophenol and could not contain the Schiff base in either a 1:1 or 2:1 ratio because of the low C/N ratio found. A 1:1 complex would also be expected to be more soluble in water than the product obtained. The copper(II) product obtained from I in aqueous ethanol did not show the characteristic C=N infrared absorption band at about 1615 cm^{-1} as shown by the chelates of the other Schiff bases.

The copper complex of II obtained in the absence of water was almost black, although, when the crystals were crushed, the powder was brown. The analysis gave 12.24 Cu (calcd. 12.31), 65.57 C (calcd. 65.3), 4.75 H (calcd. 4.65), and 5.47% N (calcd. 5.44). After the crystals were isolated they could be kept in contact with water for an extended period of time without change, presumably because of the great insolubility of the compound. It was not evident that any of the complex dissolved. The great insolubility of the 2:1

complex of the Schiff base is believed to be responsible for the failure to obtain purer complexes of *o*-aminophenol in the attempts to prepare the complexes of the Schiff bases in the presence of water. A pure sample of the 2:1 chelate of I was not obtained.

Hydrolysis of The Schiff Bases.—Lane and Kandathil assumed that no hydrolysis of the Schiff bases occurred because equilibrium was attained rapidly during the titrations. We repeated the pH titrations of compounds I, II, and *o*-aminophenol in 50% v./v. water-dioxane. The three titration curves could be superimposed on one another. The titration curves for the three ligands carried out in the presence of copper(II) perchlorate were also the same within experimental error. Presumably the pH values do not drift during the titrations because hydrolysis of these Schiff bases is essentially complete before the titrations are begun. On addition of the Schiff base to the perchloric acid solution before beginning the titration, there is a yellow color produced which fades within a few seconds. This is believed to be the protonated Schiff base which decomposes rapidly.

The acid dissociation constants reported² for four compounds of type A were all very close together, perhaps within experimental error ($\text{p}K_{\text{NH}} = 4.27-4.31$ and $\text{p}K_{\text{OH}} = 11.65-11.79$). The values for $\text{p}K_{\text{OH}}$ are very close to that reported for *o*-aminophenol⁷ (11.57), but the values for $\text{p}K_{\text{NH}}$ are significantly higher than that for *o*-aminophenol (3.75). Our value for $\text{p}K_{\text{NH}}$ for all three compounds (including *o*-aminophenol) is 4.17, in reasonable agreement with the values of Lane. Thus we check the values of $\text{p}K_{\text{NH}}$ and $\text{p}K_{\text{OH}}$ reported by Lane and Kandathil for compounds of type A, but as values for *o*-aminophenol, not the Schiff bases.

In order to verify the hydrolysis of the Schiff bases of *o*-aminophenol and to examine the possibility of the hydrolysis of compounds of types B and C, spectral studies were carried out. The spectrum of I in dioxane shows two broad absorption maxima at about 270 and 350 $\text{m}\mu$ (Fig. 1). A spectrum of I in 50% v./v. water-dioxane completed 4 min. and 10 sec. after mixing showed a decrease in these two maxima and the appearance of a maximum at about 245 $\text{m}\mu$. As time passed, the maximum at 270 $\text{m}\mu$ continued to decrease and shifted to 285 $\text{m}\mu$. Benzaldehyde has an absorption band at 285 $\text{m}\mu$ and *o*-aminophenol has one at 287. The intense absorption band at 350 $\text{m}\mu$ essentially disappeared in water-dioxane or in aqueous acid solution. The absorption band at 245 $\text{m}\mu$ which increased with time in water-dioxane can be attributed to the bands of benzaldehyde (250 $\text{m}\mu$) and *o*-aminophenol (233 $\text{m}\mu$). In aqueous acid solution the spectrum did not change with time, although a faint yellow color, which faded rapidly, developed on adding the Schiff base to acid solution before dilution. The 285 $\text{m}\mu$ band observed in water-dioxane is decreased in intensity and broadened to the shorter wave-length side in acid solution. The corresponding band of *o*-aminophenol decreases in intensity in acid solution and shifts to shorter wave length. The 245 $\text{m}\mu$ band of the final solution in water-dioxane is also decreased in intensity in acid solution as expected, since the 233 $\text{m}\mu$ band of *o*-aminophenol is also shifted to shorter wave length in acid solution and would contribute less to absorption in this region. The hydrolytic cleavage of the Schiff base occurs slowly in water-dioxane, but it is essentially complete on mixing in acid solution.

Similar changes are observed in the spectrum of II in water-dioxane (Fig. 2). The intense absorption band of the final solution can be attributed to the 280 $\text{m}\mu$ band of 4-methoxybenzaldehyde and the 278 $\text{m}\mu$ band of *o*-aminophenol. The changes in the curve in acid

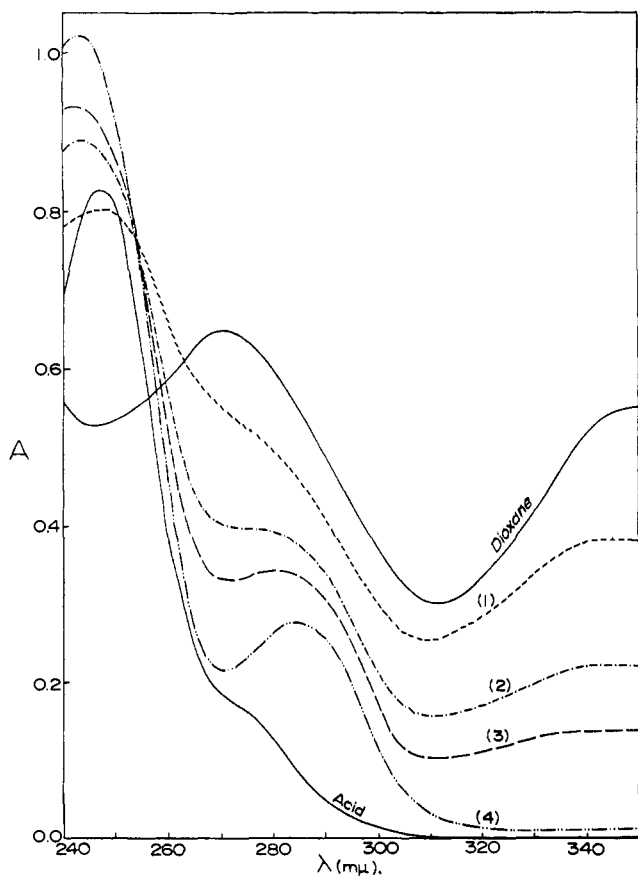


Fig. 1.—Optical absorption curves for $4.48 \times 10^{-5} M$ N-benzylidene-*o*-hydroxyaniline (I) in pure dioxane, 50% v./v. dioxane-0.005 *M* HClO₄ (aqueous), (1-4) 50% v./v. water-dioxane, times of completion of curves after mixing: (1) 4 min. 10 sec.; (2) 8 min. 45 sec.; (3) 12 min. 50 sec.; and (4) 37 min. 15 sec.

solution are those to be expected from the changes in the spectrum of *o*-aminophenol in acid solution. The changes in the spectra of VI (Fig. 3) and III (Fig. 4) can also be explained from knowledge of the spectra of the hydrolysis products. Similar changes in water-dioxane and in acidified water-dioxane solutions of IV and V can be accounted for in the same way.

A sample of V, kindly supplied by Father Lane, was found to be identical with our sample by mixture melting point determination and by the spectra in ethanol and in dioxane. Both samples were found to behave as described in water-dioxane. In 50% water-ethanol similar changes with time in the spectra of both samples were observed. A sample of N-(4-methylbenzylidene)-*o*-hydroxyaniline, also provided by Father Lane, was found to give spectral changes with time in water-dioxane and water-ethanol which were comparable with those of I and II.

The absorption curves of the Schiff bases studied are similar in dioxane and in absolute ethanol. The positions of the maxima are essentially the same, but the relative peak heights vary somewhat. However, the curves are altered significantly in absolute ethanol containing HCl (added as gaseous HCl). The resulting curves of the protonated Schiff bases are not at all the same as those in acidic solutions of water-dioxane. These curves change with time, but slowly enough to permit the spectra to be recorded. Figure 5 shows the absorption curve of V in dioxane, ethanol, acidified ethanol, and acidified water-dioxane. The addition of HCl to the Schiff base in ethanol causes the absorption

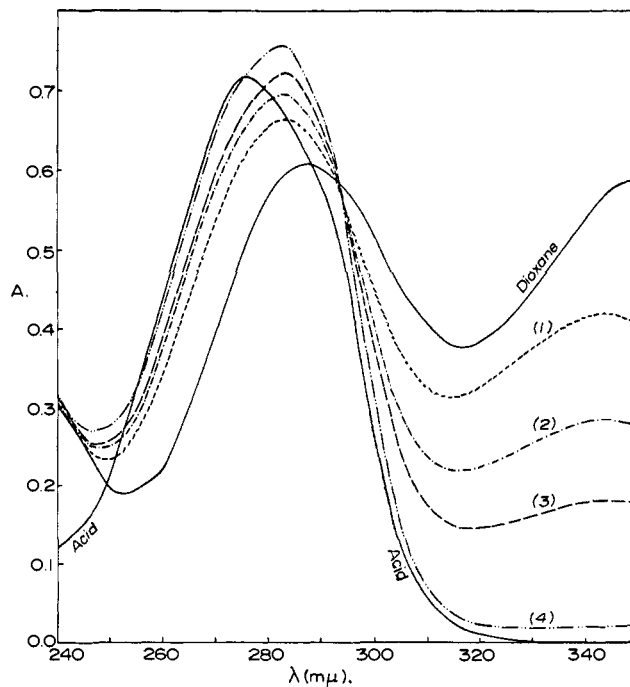


Fig. 2.—Optical absorption curves for $4.48 \times 10^{-5} M$ N-(4-methoxybenzylidene)-*o*-hydroxyaniline (II) in pure dioxane, 50% v./v. dioxane-0.005 *M* HClO₄ (aqueous), (1-4) 50% v./v. water-dioxane, times of completion of curves after mixing: (1) 4 min. 10 sec.; (2) 8 min. 45 sec.; (3) 13 min. 40 sec.; and (4) 40 min.

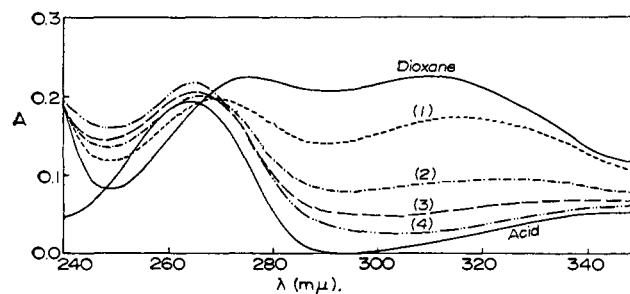


Fig. 3.—Optical absorption curves for $2.24 \times 10^{-5} M$ N-(2-hydroxy-3-methoxybenzylidene)-aniline (VI) in pure dioxane, 50% v./v. dioxane-0.005 *M* HClO₄ (aqueous), (1-4) 50% v./v. water-dioxane, times of completion of curves after mixing: (1) 4 min. 10 sec.; (2) 8 min. 50 sec.; (3) 13 min. 50 sec.; and (4) 30 min. 50 sec.

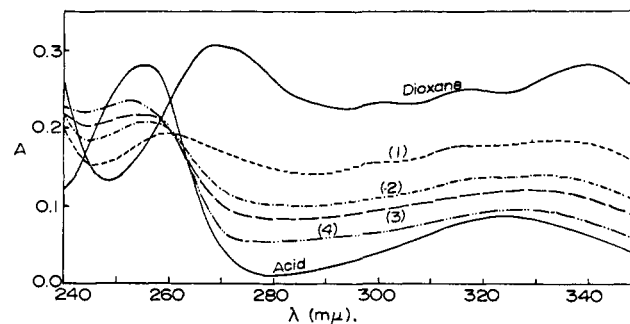


Fig. 4.—Optical absorption curves for $2.24 \times 10^{-5} M$ N-salicylideneaniline (III) in pure dioxane, 50% v./v. dioxane-0.005 *M* HClO₄ (aqueous), (1-4) 50% v./v. water-dioxane, times of completion of curves after mixing: (1) 5 min. 5 sec.; (2) 11 min. 30 sec.; (3) 15 min. 55 sec.; and (4) 25 min. 35 sec.

bands to diminish in intensity and shift to longer wave length, but in acidified water-dioxane the spectrum is essentially that of the substituted aldehyde.

Since the solutions used for the spectrophotometric studies were necessarily much more dilute than those used for potentiometric titrations, it was necessary to consider the concentration effect. Solutions which were 0.02 *M* in Schiff bases I and III were prepared in 50% v./v. water-dioxane and solutions which were 0.04 *M* in I and III were prepared in 50% v./v. 0.005 *M* HClO₄-dioxane. At time intervals aliquots of these solutions were removed and diluted with dioxane to give 10⁻⁵ *M* solutions. The spectra of these solutions revealed that hydrolysis proceeded in the more concentrated water-dioxane solutions so that it was nearly complete within about 1 hr. Hydrolysis in the more concentrated acid-dioxane solutions was complete within the few seconds required for mixing. The hydrolysis was quenched by dilution with a large volume of dioxane.

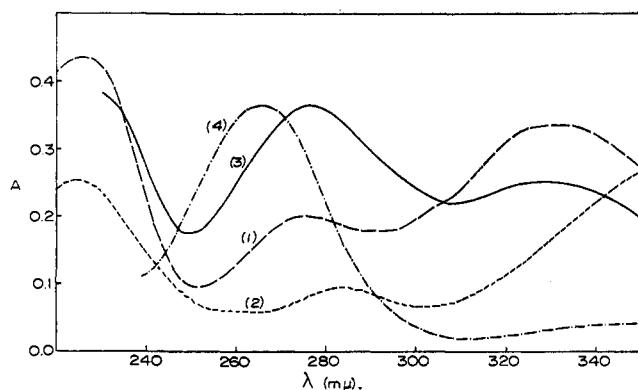


Fig. 5.—Absorption spectra of N-(2-hydroxy-3-methoxybenzylidene)-*p*-anisidine (V): (1) 2×10^{-5} *M* Schiff base in absolute ethanol and (2) in a 0.02 *M* solution of HCl (dissolved in gaseous HCl) in absolute ethanol; (3) 2.14×10^{-5} *M* Schiff base in dioxane and (4) in 50% v./v. dioxane-0.005 *M* HClO₄ (aqueous).

Although no attempt was made to follow the kinetics of the hydrolytic cleavage of the Schiff bases, the times recorded for the spectral changes permit crude comparisons. The hydrolysis of I or II was almost complete within 5 min. in the water-dioxane solutions of the same concentrations as used for the spectral studies of the other compounds (ca. 2×10^{-5} *M*). The curves shown (Fig. 1 and 2) are for solutions 2–2.5 times as

concentrated as the others in order to be able to follow the hydrolysis. The approximate half-lives for the other compounds were: III, 6 min.; IV, 10 min.; V, 9 min.; and VI, 9 min. The unsubstituted *o*-hydroxy Schiff bases hydrolyze more rapidly than those with methoxy substituents. The faster hydrolysis of the Schiff bases of *o*-aminophenol as compared to those of types B and C was apparent from the difficulty in preparing the copper chelates of type A Schiff bases.

The spectrophotometric studies followed the hydrolysis of the Schiff bases in the presence of water and acid. It is worth considering the effect of the metal ions also. Eichhorn and Marchand⁵ reported that coordination with a metal ion stabilized the Schiff bases of salicylaldehyde types B and C toward hydrolytic cleavage, while those Schiff bases which do not involve the C=N linkage as part of the chelate ring are made more susceptible to hydrolytic cleavage by coordination. In the copper(II) complexes of Schiff bases derived from *o*-aminophenol, the C=N bond is not a part of the chelate ring. The acquisition of a formal positive charge on the nitrogen as a result of coordination or protonation probably makes the C of the C=N bond more susceptible to attack by water to bring about the hydrolytic cleavage of the C=N bond. The copper complex of *o*-aminophenol should be considerably more stable than that of the corresponding Schiff bases because of the greater basicity of the NH₂ group compared to the C=N group. The complexes of the Schiff bases of types B and C give a stable chelate ring only as long as the C=N bond remains unbroken. These complexes of the Schiff bases should be more stable than those of either the aldehyde or amine alone.

Although all of the Schiff bases studied cleave very rapidly in the presence of both water and acid, cleavage causes difficulty in the preparation of the copper chelates in the presence of water only for the Schiff bases of type A. Since the Schiff bases can be prepared in or recrystallized from aqueous ethanol, equilibrium must be established between the Schiff base and the aldehyde and amine. In the presence of excess amine or in the basic solution produced from partial hydrolysis in concentrated solutions, the Schiff base is fairly stable. In dilute solutions the hydrolysis is nearly complete. During potentiometric titrations the initial acidic solution should cause almost complete cleavage of the Schiff bases, but some reformation might occur as the solutions become more basic during the titrations. The interpretation of the results of such titrations would be difficult because of the complex equilibria involved.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

The Electronic Structures of Octahedral Metal Complexes. I. Metal Hexacarbonyls and Hexacyanides

By HARRY B. GRAY AND N. A. BEACH

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The bonding in metal hexacarbonyls and hexacyanides is described in terms of molecular orbitals. Vapor phase electronic spectra for the metal hexacarbonyls are reported in the range 3500–1700 Å. A molecular orbital energy level scheme is presented which is able to account for the observed d-d and charge-transfer absorption bands in the d⁶ metal complexes. The charge-transfer transitions all are assigned as metal (d) to ligand (π^*).

Introduction

Transition metal carbonyls and cyanides are among the simplest complexes in which both metal-to-ligand

and ligand-to-metal types of π -bonding are of importance. Thus a knowledge of the electronic energy levels for typical metal carbonyls and cyanides is very desirable.