that the cyclohexane molecule is to some extent distorted on adsorption so that each CH_2 group has surface contact.

Summary

Isotherms are given for benzene and cyclohexane on Graphon at temperatures of 5.5 and 28.6°. The area covered per molecule is found to be *ca.* 38 Å.^{2} for cyclohexane and 41 Å.^{2} for benzene. Both indicate that the molecules lie flat on the surface. The isotherms and isosteric heats of adsorption computed from them show that in the first layer cyclohexane is more strongly held than benzene. In the multilayer region benzene is the more strongly adsorbed.

Areas per molecule are given for a variety of adsorbates, as obtained from isotherms on Graphon and carbon blacks. These are compared with areas computed from models.

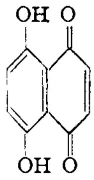
CLAREMONT, CALIFORNIA RECEIVED APRIL 12, 1950

[CONTRIBUTION FROM THE DEPARTMENTS OF RADIATION BIOLOGY AND BIOCHEMISTRY, UNIVERSITY OF ROCHESTER SCHOOL OF MEDICINE AND DENTISTRY]

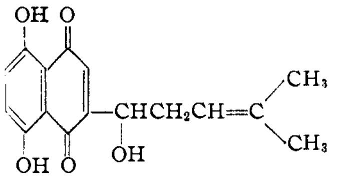
Beryllium Complexes with Naphthazarin and Alkannin[1]

BY A. L. UNDERWOOD, T. Y. TORIBARA AND W. F. NEUMAN

Previous papers[2,3] have described the use of naphthazarin (I) and alkannin (II) as reagents for the spectrophotometric determination of microgram quantities of beryllium. It was of interest, therefore, to know the nature of the materials formed by the interaction of beryllium with these dyes.



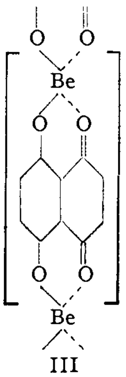
I



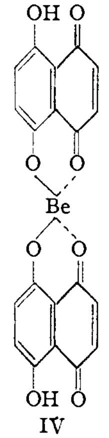
II

In certain instances, true compounds of the chelate type are formed from metal ions and so-called "lake-forming" dyes, but in others, the reaction appears to be non-stoichiometric with adsorption phenomena playing a predominant role.[4] Dubsky, *et al.*,[5] studied the products formed when beryllium solutions were mixed with naphthazarin or alkannin solutions in the presence of ethylenediamine; they concluded that ethplenediamine reacted with naphthazarin or alkannin to form ketimine compounds which then yielded chelate complexes with beryllium, but the data adduced to support this idea seem inconclusive. Thus, it appeared that the products formed from beryllium and alkannin or naphthazarin under the conditions of the analytical method[2] could not be characterized without further investigation.

It was found that beryllium reacts with naphthazarin or alkannin to form two definite complexes depending upon the ratio of the reactants in solution. The following structures (III) in which the ratio is one beryllium atom to one dye molecule and (IV) in which one beryllium atom reacts with two dye molecules are assigned using naphthazarin (I) as the dye.



III



IV

The portion of structure III in the brackets is taken as the unit which probably forms a polymer. Certain chemical evidence favors this interpretation as well as the fact that the structure proposed is based on beryllium's maximum coördination number of 4.

The evidence for the structures of these complexes was obtained from spectral studies, use of the method of continuous variations[6,7,8] and *p*H titrations.

Experimental

Apparatus.—All spectrophotometric data were obtained with a Beckman model DU quartz spectrophotometer, using matched Corex curvettes. *p*H titration curves were obtained with a Beckman model H 2 glass electrode *p*H meter.

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[1] This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, N. Y. Presented before the Division of Physical and Inorganic Chemistry, Detroit, Michigan, April, 1950.

[2] Underwood and Neuman, *Anal. Chem.*, **21**, 1345 (1949).

[3] Toribara and Underwood, *ibid.*, **21**, 1352 (1949).

[4] For example, see Liebhafsky and Winslow, THIS JOURNAL, **69**, 1130 (1947); Porter and Weiser, *J. Phys. Chem.*, **31**, 1383, 1704 (1927).

[5] Dubsky, Langer and Wagner, *Mikrochemie*, **22**, 108 (1937).

[6] Job, *Ann. Chim.*, [10] **9**, 113 (1928).

[7] Job, *ibid.*, [11] **6**, 97 (1936).

[8] Vosburgh and Cooper, THIS JOURNAL, **63**, 437 (1941).

Reagents.—The preparation of pure naphthazarin and alkannin has been described.[8] For the spectrophotometric studies reported below, a solution of naphthazarin in redistilled 1,4-dioxane, 4.61×10^{-4} *M*, was employed. The beryllium stock solution prepared by dissolving the metal (spectroscopically better than 99.9% pure) in hydrochloric acid, the buffer consisting of a 0.5 *M* boric acid solution in 10% mannitol adjusted to *p*H 5.0 with sodium hydroxide, and the gum arabic solution employed to stabilize the beryllium–dye color lakes, were the same as described previously.[2] The acid beryllium stock solution was diluted to give a 4.61×10^{-4} *M* solution for the spectrophotometric studies; such diluted solutions were prepared fresh daily to prevent concentration changes due to adsorption of beryllium on the walls of the glass container. For the *p*H titrations, where extraneous hydrochloric acid was undesirable, solutions approximately 0.1 *N* in beryllium were prepared from beryllium sulfate recrystallized from water. Because of the uncertain degree of hydration of the crystals, the solutions were analyzed gravimetrically for beryllium. Solutions 0.100 *N* in alkannin and naphthazarin in redistilled 1,4-dioxane were used in these titrations. Carbonate-free sodium hydroxide solutions, standardized against potassium acid phthalate, were employed.

Absorption Spectra Studies of Beryllium–Naphthazarin Complexes.—The curves shown in Fig. 1 indicate the changes in the naphthazarin spectrum when beryllium is added in various molar ratios, the same quantity of dye being present in each case. The solutions are buffered at a *p*H of 6.7, the original buffer of *p*H 5.0 changing to this value when diluted.[9] When beryllium and dye are present in equimolar quantities, an absorption peak appears at about 540 mμ, together with a slight hump in the neighborhood of 600 mμ. When the molar ratio of dye to beryllium is 2:1, the peak at 540 mμ recedes, but the hump near 600 mμ becomes more pronounced. These observations may be tentatively interpreted as indicating the existence of two complexes: the first with a combining ratio of 1:1 showing an absorption maximum at 540 mμ, and a second with a combining ratio of 2 dye:1 beryllium exhibiting a peak near 600 mμ. Further, the relative stabilities are apparently such that some 2:1 complex exists even when the mixing ratio is 1:1. Where there is a threefold molar excess of dye, it appears that only a mixture of 2:1 complex and free dye exists, as shown by the fact that the 3:1 curve passes through the intersection of the curves for 2:1 complex and free dye.

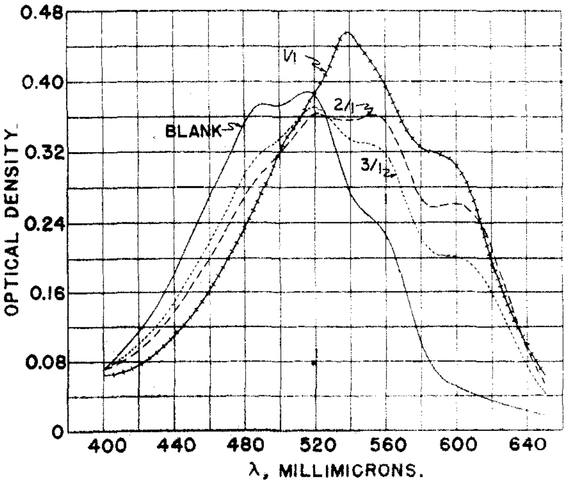

Fig. 1.—Variation of Dye/Be Ratio > 1, using constant amount of dye.

It can be seen from Fig. 2 that when beryllium is increased beyond the 1:1 ratio, the peak at 540 mμ persists even out to tenfold excesses, and no new peaks appear. Further, the hump at 600 mμ disappears while the height of the 540 mμ peak increases. This suggests that there are no complexes containing more beryllium than the 1:1 complex but that excess beryllium serves to force all the dye into the 1:1 form.

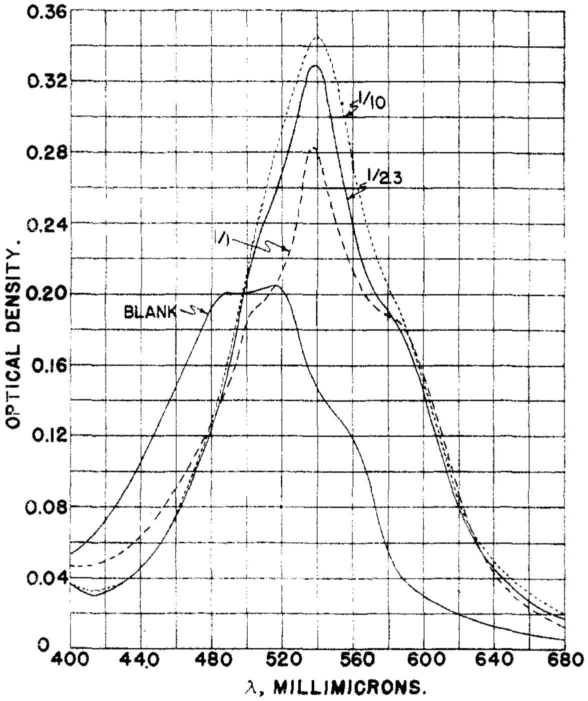

Fig. 2.—Variation of Dye/Be ratio <1, using constant amount of dye.

Thus, the absorption spectra suggest the existence of two and only two complexes. It is convenient to denote their empirical formulas by DyeBe and $\text{DyeBe}_{1/2}$ because the same quantity of dye was used for all the curves in the series. The direct absorbance readings are proportional to the molar absorptivity values, and the heights of the curves may be used in comparing ϵ values.

Method of Continuous Variations.—Confirmation of the previous conclusions was obtained by the method of continuous variations. This method was first described by Job,[6] who later pointed out[7] that it was not generally applicable when two or more complexes were formed. Vos-

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[9] It should be noted that since a mixture of dioxane and water is under consideration, the question of *p*H may become somewhat complicated. Directly measured, uncorrected *p*H values are recorded here.

burgh and Cooper,[8] however, extended the theory and showed that the method could be used in certain favorable cases, even where more than one complex existed. In this work the theoretical equations for two complexes as developed by Vosburgh and Cooper were used, but a different approach was employed in the selection of the wave lengths.

The quantity x ml. of a beryllium solution of molarity M was added to $(10 - x)$ ml. of a dye solution, also of molarity M, and the total volume was adjusted to V ml. with water. The terms C_1, C_2, C_3, C_4 are, respectively, the concentration of beryllium, dye, complex DyeBe and $\text{DyeBe}_{1/2}$ in the final solution with ϵ_1, ϵ_2, ϵ_3 and ϵ_4 the corresponding molar absorptivities. A is the absorbance, $\log_{10}I_0/I$. Y is the difference between the observed absorbance and that which would have been obtained from the quantity of dye added if no reaction with beryllium had occurred. Since cells of 1-cm. path length were used and the beryllium solution is colorless, the equation is obtained

$$Y = A - \epsilon_2(10 - x)M/V \qquad (1)$$

which simplifies after appropriate substitutions to

$$Y = (\epsilon_3 - \epsilon_2)C_3 + (\epsilon_4 - \epsilon_2)C_4 \qquad (2)$$

Equation (2) if differentiated is essentially the same as equation (13) of Vosburgh and Cooper.[8]

If it is assumed that both complexes are quite stable, it may be shown that the maximum concentration of either complex is at that value of x when the two components are present in the theoretical combining ratio for that complex. Thus a plot of Y *vs.* x should show a maximum or minimum at the theoretical composition of either complex depending upon the wave length selected. Vosburgh and Cooper[8] eliminated one of the terms of equation (2) by selecting a wave length where two of the colored components had the same molar absorptivities. This procedure was not very satisfactory in this study as shown by the curve at 520 mμ in Fig. 3. A minimum is observed at the theoretical ratio for $\text{DyeBe}_{1/2}$, but it is not well-defined.

When both complexes are stable, at the value of x where one complex is a maximum, there should be very little of the other complex present. In equation (2) one of the terms becomes negligible in the region of the maximum of the other term. Further, the absorption in the region of the maximum is due principally to one complex, while in the intermediate values of x, both complexes contribute. To obtain a maximum at the theoretical composition for either of the complexes, certain relationships must be fulfilled. The maximum for the DyeBe complex should occur when x is 5 ml. while the maximum for the $\text{DyeBe}_{1/2}$ complex should occur when x is 3.3 ml. As both formulas are based on a unit quantity of dye, the ratio of the maximum quantities of each complex will be 6.7 moles of $\text{DyeBe}_{1/2}$ to 5 moles of DyeBe, or $C_{4\max.}/C_{3\max.}$ is 1.33. To get a maximum in Y corresponding to the theoretical ratio for $\text{DyeBe}_{1/2}$, a wave length must be selected such that $(\epsilon_3 - \epsilon_2) < 1.33\ (\epsilon_4 - \epsilon_2)$, and to get a maximum at the ratio for DyeBe, $(\epsilon_3 - \epsilon_2) > 1.33\ (\epsilon_4 - \epsilon_2)$.

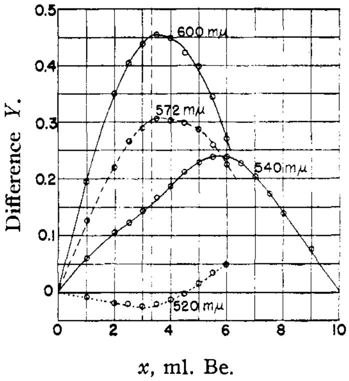

Fig. 3.—Plot of Y *vs.* x in the application of the method of continuous variations for the system naphthazarin-beryllium.

The Y value selected here was defined as the difference between the observed absorbance and that calculated for no interaction with the beryllium. The latter term is simply the absorbance of the total amount of dye used. For each sample containing beryllium, another with the same amount of dye and no beryllium was prepared. The spectrophotometer was set to zero against the free dye sample corresponding to each beryllium sample. Thus the value of Y was obtained directly from the spectrophotometer reading, and the compositions of both complexes were determined using the Y function at different wave lengths.

In Fig. 1 the heights of the curves were employed in comparing ϵ values to pick the wave lengths used in applying the method of continuous variations as shown plotted in Fig. 3. At 572 mμ the ratio $(\epsilon_3 - \epsilon_2)/(\epsilon_4 - \epsilon_2) = 1.28$ and $(\epsilon_4 - \epsilon_2)$ is large enough to give a good maximum at the theoretical ratio for the $\text{DyeBe}_{1/2}$. At 600 mμ the ratio $(\epsilon_3 - \epsilon_2)/(\epsilon_4 - \epsilon_2) = 1.21$ and $(\epsilon_4 - \epsilon_2)_{600} = 1.38\ (\epsilon_4 - \epsilon_2)_{572}$, both factors being favorable to give a sharper peak for the $\text{DyeBe}_{1/2}$ at 600 mμ than at 572 mμ. At 540 mμ the ratio $(\epsilon_3 - \epsilon_2)/(\epsilon_4 - \epsilon_2) = 2.18$, and a maximum would be expected at the ratio for the DyeBe. The maximum obtained is actually displaced somewhat toward the right. However, the absorption spectra indicate no complexes containing more beryllium than the 1:1 complex, and the best explanation for the displacement of the maximum is that the 1:1 complex is sufficiently unstable that the excess of beryllium is required to force all the dye into this form. The linearity of the curve except in the region of the maximum for values of x from 0 to 3.3 and from 5 to 10 indicates that no complexes with more than 2:1 or less than 1:1 dye to beryllium exist. The fact that curves are as obtained rather than straight lines indicates that both complexes are somewhat unstable, and an excess of either component is necessary to complex all of the other.

Effect of *p*H.—The colors of the free dye and of solutions containing beryllium were found to change with *p*H.[2,3] With the free dye the change in color may be ascribed to changes in the structure caused by ionization, as each dye molecule has two ionizable hydrogens. Figure 4 shows the shift in the spectra of naphthazarin caused by changing the *p*H. In the structure postulated for the 1:1 complex (III), both hydrogens have been displaced, and no further changes would be expected by changing the *p*H once the complex has been formed. Figure 5 shows that changing the *p*H has very little effect on the spectra of solutions in which beryllium was present in excess.

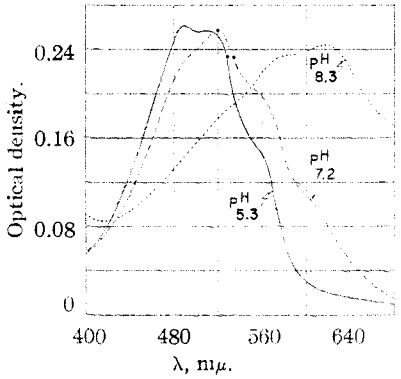

Fig. 4.—Spectra of naphthazarin at different *p*H's.

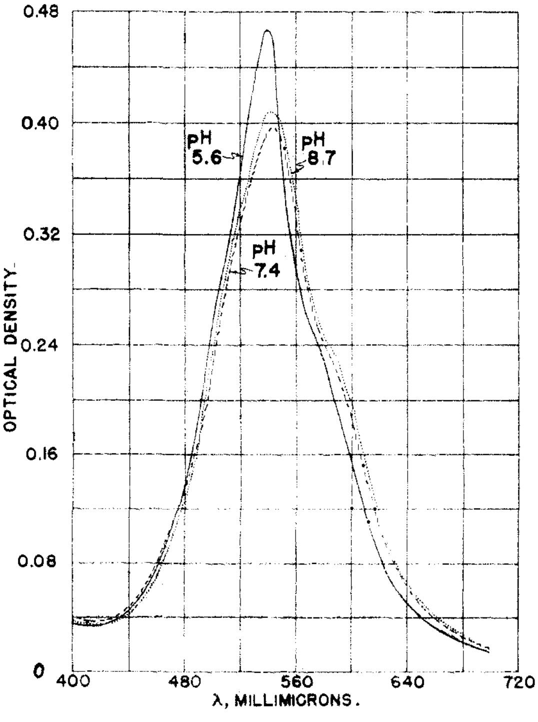

Fig. 5.—Spectra of Be–naphthazarin complex at different *p*H's.

In the analytical procedure[1] (an excess of dye is used forming the 2:1 dye to beryllium complex) it was shown that when a beryllium solution was read against a free dye solution of the same *p*H, the net reading remained essentially constant in the *p*H range 5.5 to 8. This indicates that the spectra of the 2:1 complexes not only shift with *p*H, but also that they shift similarly to those of the spectra of the free dye. The structure for the 2:1 complex (IV) shows ionizable hydrogens remaining, and Fig. 6 shows the effect of changing *p*H on the spectra of the complex.

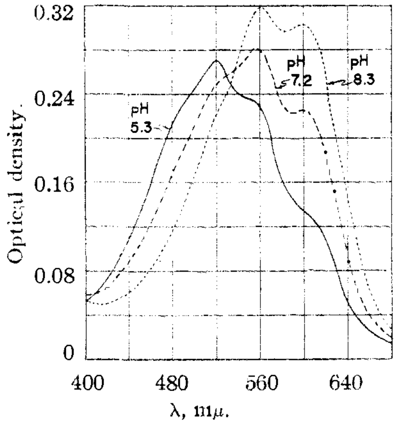

Fig. 6.—Spectra of Be(naphthazarin)$_2$ complex at different *p*H's.

A very useful method serving to confirm the postulations from the spectral data was the use of *p*H titration curves. A beryllium sulfate solution and a naphthazarin solution were titrated separately with sodium hydroxide. The beryllium and the naphthazarin were then mixed[10] in proportions to form the 1:1 and the 2:1 dye to beryllium complexes and each solution was titrated with sodium hydroxide. Figure 7 shows the curves of equimolar quantities of beryllium and naphthazarin titrated singly and when mixed. The fourth curve is calculated on the basis of no interaction. The buffering in the lower *p*H region of the

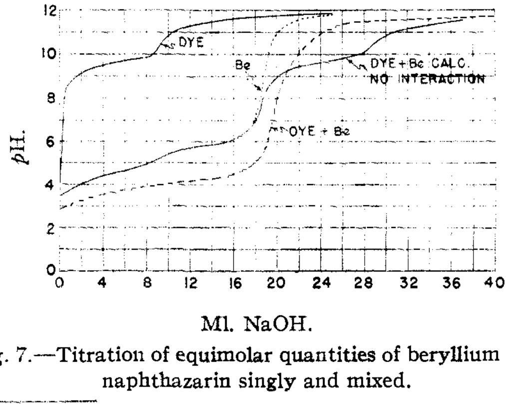

Fig. 7.—Titration of equimolar quantities of beryllium and naphthazarin singly and mixed.

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(10) When the dye and beryllium solutions were mixed, part of the dye came out of solution. As the *p*H was raised, the complex formed also came out of solution. Despite the heterogeneity of the system the reaction proceeded stoichiometrically as shown.

mixture curve can be ascribed only to hydrogen ions released through the interaction of beryllium and the dye. A computation shows that two equivalents of hydrogen ion are released for every beryllium ion (or dye molecule) in accord with the proposed structure (III). The curve for the mixture crosses the "no interaction" curve and the *p*H rises rapidly after the two equivalents of hydrogen have been neutralized.

Figure 8 shows the curves obtained in a similar manner when 2 moles of dye are present for every mole of beryllium. Computation again shows that two equivalents of hydrogen are released for every beryllium ion. In this case, however, continued addition of alkali gives a curve which closely follows the "no interaction" curve. This shows that the residual hydrogens on the 2:1 dye to beryllium complex behave similarly to the hydrogens on the free dye. Another possible interpretation of this curve is that the two hydrogens released may be caused by the formation of the 1:1 complex followed by titration of the excess dye. However, the spectral studies indicate that the latter is not true. As the spectra of the 1:1 complex does not change with *p*H, the net reading between a beryllium solution containing excess dye and a free dye solution would not remain constant in the *p*H range 5.5 to 8 as has been shown.[2] The structure for the 2:1 complex (IV) is consistent with both the titration and spectral data.

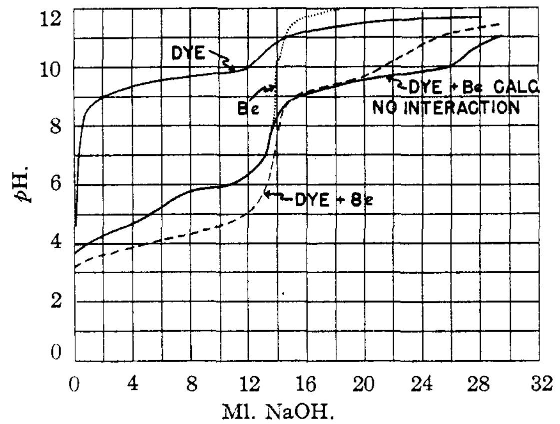

Fig. 8.—Titrations of solutions containing 2 moles of naphthazarin per mole of beryllium.

These titration curves were repeated using alkannin in place of naphthazarin, with essentially identical results as shown in Figs. 9 and 10. Although the beryllium:alkanin system has not been investigated by the method of continuous variations, apparently it is similar to that of the beryllium:naphthazarin system.

Preparation of Pure Beryllium-Naphthazarin Complexes.—Preliminary attempts to prepare a pure complex led to anomalous results; after it was found that two complexes could be formed, it was possible to isolate materials containing approximately the appropriate amounts of beryllium for both complexes by mixing the reactants in the same ratios as the combining ratios.

The quantity of 2.1080 g. of naphthazarin was dissolved in 200 ml. of 1,4-dioxane, and 25 ml. of a beryllium solution, containing 50 mg. of beryllium, was added. This represents a twofold molar excess of dye. Sodium hydroxide solution was added until the red color of the dye gave way to the purple color characteristic of the complex. The clear solution was diluted with water to give 350 ml., and heated to 50–60°, when a fine precipitate appeared. This was collected by centrifugation, washed 3 times with water, dried, washed 3 times with benzene, and finally dried in a vacuum desiccator. The beryllium content was determined by ignition to beryllium oxide.

Anal. Calcd. for $C_{20}H_{10}O_8Be$: Be, 2.33. Found: Be, 2.27.

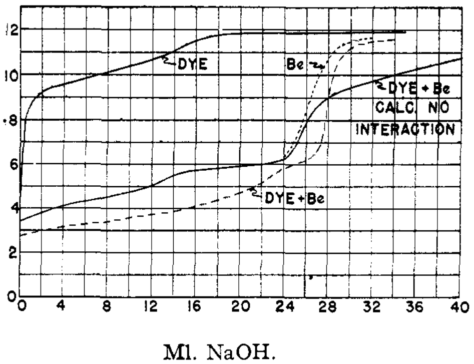

Fig. 9.—Titration of equimolar quantities of alkannin and beryllium singly and mixed.

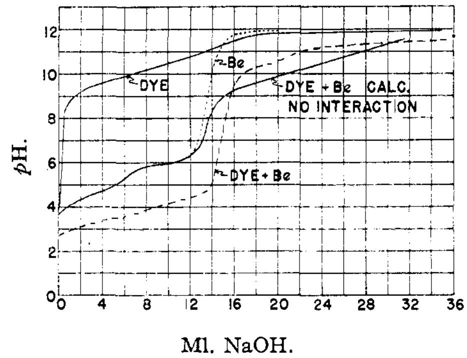

Fig. 10.—Titration of solutions containing 2 moles of alkannin per mole of beryllium.

This procedure was repeated, mixing equimolar quantities of beryllium and naphthazarin.

Anal. Calcd. for $C_{10}H_4O_4Be$: Be, 4.57. Found: Be, 4.16.

The deviation of the analytical value from the calculated one in the latter case may be explained on the basis that the 1:1 complex is contaminated with a small amount of the 2:1 complex. Further purification of the complexes was not possible; both materials were extremely insoluble in all the common solvents, and neither compound would sublime.

The titration data have shown that both hydrogens on naphthazarin come off during the formation of the 1:1 complex with beryllium. The structure postulated (III) is based on beryllium's maximum coördination number of four which is exhibited in other compounds[11,12] involving analogous functional groups. Since both sets of functional groups on the naphthazarin molecule are involved in the 1:1 complex with beryllium, a polymeric structure seems the most probable. The insolubility of the complex in all the common solvents and its inability to sublime are properties consistent with this view.

Summary

1. Absorption spectra studies indicate that beryllium and naphthazarin react in solution to form two complexes, represented empirically by DyeBe and DyeBe$_{1/2}$, the predominance of one or the other depending on the ratio of the reactants.

2. The method of continuous variations has been critically employed to confirm the existence of the two complexes.

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(11) Morgan and Moss, *J. Chem. Soc.*, **105**, 189 (1914).

(12) Mills and Gotts, *ibid.*, 3121 (1926).

3. Further studies of absorption spectra together with pH titration curves have made possible the postulation of structures for the two complexes. Titration curves indicate that the compound alkannin, which has not been studied spectrophotometrically, forms complexes analogous to those of naphthazarin.

4. Materials have been isolated, the compositions of which approximate those expected for the postulated structures.

ROCHESTER, NEW YORK RECEIVED JUNE 14, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Cuprous Oxide as a Catalyst. I. Preparation and Promotion by Metallic Oxides[1]

BY F. E. BROWN, RALPH E. MENZEL, MEREDITH M. STEWART AND PHILIP A. LEFRANCOIS

Few references to any catalytic action of cuprous oxide are found in the literature prior to 1937, and none of these references describe the treatment necessary to produce and retain the power to catalyze hydrogenations at moderate temperatures, 120 to 200°. Adkins and his collaborators[2,3] have described catalysts containing copper oxide and some of the other oxides which promote or stabilize or unite with copper oxide but these catalysts become inactive when the copper is reduced to the monovalent state.[4,5]

In 1937 Menzel[6] announced the discovery of the catalytic effect of cuprous oxide. Stewart[7] and Lefrancois[8] confirmed Menzel's discovery and extended the investigation of promoters.

General Procedure

The hydrogenation of furfural to form furfuryl alcohol was the reaction chosen for testing the catalysts. All experiments were conducted, batchwise, in one of the two electrically heated rocker type bombs described below. One, made in our shop, was copper lined and had a capacity of 3.85 l. In the experiments reported in this paper this bomb was charged with 3.00 moles of furfural. Calibration showed that when one mole of hydrogen reacted the pressure of the hydrogen decreased about 100 p. s. i., if the pressure was calculated to what it would be at 0°. The second was a commercial, unlined, chromium-nickel steel hydrogenation bomb. Its measured capacity was 0.495 l. It was charged with 0.50 mole of furfural and when one mole of hydrogen reacted the pressure decreased about 680 p. s. i. if pressures are reduced to 0°. These bombs will be called the "3.85-l. bomb" and "0.495-l. bomb," respectively.

Preparation of Catalysts.—Four catalysts well known for their use in hydrogenations in the moderate temperature range were prepared for comparison with cuprous oxide catalysts.

(1) **Cu-Ba-Cr Oxide.**[9]—A precipitate is formed by adding a solution of ammonium carbonate to a solution containing copper nitrate, barium nitrate and chromium(III) nitrate. The precipitate is decomposed by heating to 230°. This catalyst is designated by "Cu-Ba-Cr-O-(C.F.A.) 230°."

(2) **Cu-Ba-Cr Oxide.**[10]—The Cu-Ba-Cr-O (C.F.A.) 230° catalyst is modified by suspension in a 10% solution of acetic acid, washing and drying at 110-120°. This catalyst is designated by "Cu-Ba-Cr-O (C.F.A.) washed."

(3) **The Cu-Ba-Cr-O** (C.F.A.) catalyst is decomposed at 160° instead of 230°. Its designation is "Cu-Ba-Cr-O (C.F.A.) 160°."

(4) **Cu-Cr Oxide.**[11]—Treatment of a solution containing copper sulfate and sodium dichromate with ammonium hydroxide produces a precipitate of $CuOHNH_4CrO_4$, which is decomposed at 200-400°. This catalyst is designated by "Cu-Cr-O (C.E.)."

The catalysts containing cuprous oxide were prepared in nearly all cases by grinding together, at room temperature, oxides of individual metals prepared separately. These oxides were prepared from chemicals of reagent grade or C. P. quality. The several ingredients were put into solution and the solutions were mixed slowly with constant stirring in the order indicated in the following directions, or treated as indicated.

(5) **Coprecipitated** Cu_2O **and** $Ca(OH)_3$.—One hundred fifty ml. of a 40% solution of sodium hydroxide is added to 43.8 g. of calcium nitrate, 100 g. of cupric nitrate trihydrate, and 100 g. of dextrose in 400 ml. of water. The mixture is heated to 85° for 30 min., filtered in a Büchner funnel, and washed until the wash water is clear. The precipitate is dried for 12 hr. in a vacuum desiccator, powdered and stored in a stoppered bottle.

(6) **Cu-Cr Oxide.**—A concentrated aqueous solution of CrO_3 is added to powdered $CuCO_3 \cdot Cu(OH)_2$ until effervescence ceases. To this solution, concentrated ammonium hydroxide is added until precipitation is complete. The precipitate is collected in a Büchner funnel, dried in air, pulverized, dried in a vacuum desiccator, heated to 160° and stored in a stoppered bottle.

(7) Cu_2O.—Two hundred fifty ml. of a 40% solution of sodium hydroxide is added to 1250 ml. of an aqueous solution of 250 g. of cupric nitrate trihydrate and 250 g. of dextrose. The mixture is digested for 30 min. at 85°, filtered in a Büchner funnel, and washed until the wash water is clear. The precipitate is dried *in vacuo* over anhydrone for 24-48 hr., powdered, dried for another 24 hr., and stored on a petri dish in a desiccator charged with phosphorus pentoxide. An analysis of the dark red product found 3.76% H_2O, 2.12% Cu and 94.12% Cu_2O.

(8) CaO.—Immediately before an experiment, a weighed sample of calcium hydroxide is ignited at 900-1000° until loss of weight indicates its conversion to calcium oxide (about 3 hr.), and cooled in a desiccator over phosphorus pentoxide.

(9) Cr_2O_3.—Three hundred ml. of concentrated ammonium hydroxide is added to 1 l. of an aqueous solution containing 250 g. of $Cr(NO_3)_3 \cdot 7.5H_2O$. The precipitate is collected in a Büchner funnel, dried 12 hr. at 110°, pul-

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[1] Abstracted in part from theses presented by Ralph E. Menzel, Meredith M. Stewart and Philip A. Lefrancois to the Graduate Faculty of Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931).

[3] Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

[4] Homer Adkins, "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," University of Wisconsin Press, Madison, Wis., 1937, p. 13.

[5] Adkins and Shriner, Catalytic Hydrogenation and Hydrogenolysis, Chap. 9 in "Organic Chemistry," Second Edition, Vol. I, Henry Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 788-789.

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[7] Stewart, *ibid.*, **16**, 134 (1941). U. S. Patent 2,400,959 (1946).

[8] Lefrancois, *Iowa State Coll. J. Sci.*, **19**, 41 (1944).

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[10] Connor, Folkers and Adkins, *ibid.*, **54**, 1144 (1932).

[11] Calingaert and Edgar, *Ind. Eng. Chem.*, **26**, 878 (1934).