remained. On cooling the hot filtered solution, a white crystalline product was obtained which contained 26.9% of palladium. The value calculated for $BzH_2[Pd(CN)_4]$ is 26.8%. Since the residue might be a decomposition product of the salt, an aqueous solution of the recrystallized product, $BzH_2[Pd(CN)_4]$ was heated. Hydrogen cyanide was evolved and an insoluble product was obtained. Its palladium content was 30.8% corresponding to the value 31.2% calculated for dicyanobenzidinepalladium, $[BzPd(CN)_2]$.

β-Naphthoquinoliniumtetracyanopalladate(II) $Nq_2H_2[Pd(CN)_4]$.—The white crystalline precipitate obtained by mixing a hydrochloric acid solution of the base with tetracyanopalladic(II) acid was filtered, washed with water, alcohol and ether and dried at 50°. It contained 19.0% of palladium, 63.1% of carbon and 3.8% of hydrogen. The corresponding values calculated for $Nq_2H_2Pd(CN)_4$ are 18.7, 63.1 and 3.5%. The salt lost hydrocyanic acid on standing forming nearly pure dicyanodinaphthoquinoline palladium which contained 21.4% of palladium. The calculated value is 20.6%.

Oxiniumtetracyanopalladate(II) $Ox_2H_2[Pd(CN)_4]$.—This yellow crystalline product, obtained by the general method, was not decomposed by hot water. It contained 21.0% of palladium. The value calculated for $Ox_2H_2[Pd(CN)_4]$ is 21.3%. The solid salt had a strong yellow fluorescence in ultraviolet light.

Nitroniumtetracyanopalladate(II) $NtH_2[Pd(CN)_4]$.—This white crystalline product which is not decomposed by hot water, was obtained by the general method. The amount of palladium in the compound was 20.8%. The value calculated for $NtH_2[Pd(CN)_4]$ is 20.3%.

Acknowledgment.—One of us, G.B.H., wishes to express his appreciation to the Ministery of Agriculture of Brazil for permission to work in the laboratories of the Departmento da Producão Mineral and to the University of Minnesota for the sabbatical leave.

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[CONTRIBUTION FROM THE LAB. PROD. MINERAL, MINISTERIO DA AGRICULTURA, RIO DE JANEIRO]

Coördination of Organic Bases with Palladium(II) Cyanide

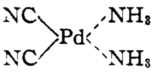
BY F. FEIGL AND G. B. HEISIG[1]

Palladium(II) cyanide coördinates ammonia and many organic nitrogen bases such as pyridine, ethylenediammine, quinoline, α,α'-dipyridyl, o-phenanthroline, benzidine, oxine, diphenylamine, "tetrabase" forming crystalline compounds which are homologs of the diammine, β-naphthoquinone forming a homolog of the monoamine. The reaction is one between a Lewis acid and base, respectively. Many amines including alkaloids in neutral or acid solutions coördinate with palladium(II) cyanide forming adsorption complexes (lakes). In the case of acid-base indicators the colors of the lakes are essentially the same as those of the acid solutions of the indicators. An explanation is proposed which is based on resonance and the Lewis theory of acids and bases. The colored oxidation products of uncolored amines form lakes with palladium(II) cyanide. These lakes are obtained by adding palladium(II) cyanide to the slightly colored, acidified hydrogen peroxide solutions of the amines. Two explanations for the formation of these lakes are offered. Examples of the analytical use of the lakes of acid-base indicators with palladium(II) cyanide are described.

Many analytical textbooks state that palladium(II) cyanide dissolves in ammonia, but the product formed is not mentioned. A search of the literature showed that in 1841 Fehling[2] isolated a white crystalline product whose empirical formula is $Pd(CN)_2 \cdot 2NH_3$. This compound is somewhat soluble in hot water and ammonia. From the standpoint of coördination chemistry and modern concepts of chemical bonds[3] palladium(II) should have a coördination number of 4. Therefore, the product may be an electrolyte—formula I—or a non-electrolyte—formula II

$[Pd(NH_3)_4][Pd(CN)_4]$

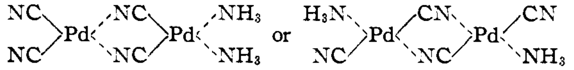
I



II

We prepared the diammine by warming a suspension of palladium(II) cyanide in an excess of ammonia. The palladium(II) cyanide first dissolves and then a white crystalline product which contains 55.3% of palladium, 12.3% of carbon and 3.1% hydrogen, precipitates. The calculated values for $[Pd(NH_3)_2(CN)_2]$ are 55.3, 12.4 and 3.1%, respectively. Since palladium(II) sulfide is not precipitated from the hot aqueous solution by ammonium sulfide, tetrammine palladium(II) ions are not present. The absence of cyanide ions in the aqueous solution was shown by the non-precipitation of silver cyanide on the addition of silver nitrate. These facts eliminate formula I; therefore, formula II is the correct one.

The diammine reacts with 0.1 *N* acetic acid forming a white crystalline product which contained 60.5% of palladium. This value corresponds to 60.7% of palladium calculated for the monammine. The product is not palladium(II) cyanide, for it does not form palladium sulfide when moistened with ammonium sulfide. Since palladium has a coördination number of four and not three as given by the formula $PdNH_3(CN)_2$, it is probable that the formula should be twice the simple one. In this case the compound can be thought of as an addition compound of palladium(II) cyanide and its diammine. The empirical formula is $Pd(CN)_2 \cdot [Pd(NH_3)_2(CN)_2]$ and the coördination formulas are



Homologs of the monammines have analogous formulas.

We also found that an addition reaction took place between a suspension palladium(II) cyanide and amines dissolved in water or organic solvents. The products were crystalline organic homologs of dicyanodiamminepalladium(II) or microscopically amorphous adsorption complexes although in a few cases both types of products formed simultaneously. The lakes, adsorption complexes, formed by the action of palladium(II) cyanide

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[1] On sabbatical leave from the University of Minnesota, Minneapolis, Minn.

[2] R. Fehling, *Ann.*, **39**, 119 (1841).

[3] L. Pauling, "The Nature of the Chemical Bond," Ithaca, N. Y., 1940, p. 99.

with dyes were amorphous. The term adsorption[4] complex is used to describe the amorphous products formed by the coördination of a nitrogen with a palladium ion on the surface of palladium cyanide. A second palladium ion is coördinated with the first to bring the number of groups coördinated to four.

Homologs of Dicyanodiammine- and Monamminepalladium(II).—By heating a suspension of palladium(II) cyanide with the appropriate compound under the conditions specified, the following homologs of dicyanodiamminopalladium(II) were obtained.

Dicyanodipyridinepalladium(II) Cyanide.—An exothermal reaction took place almost immediately on adding the cyanide to pyridine. On the addition of an excess of alcohol and ether a white crystalline precipitate formed. The product contained 33.9% of palladium, 45.0% of carbon and 3.26% of hydrogen. The corresponding values for the bipyridine derivative, $PdPy_2(CN)_2$, are 33.7, 45.5 and 3.2% respectively. The analogous compound to the monoammine, $PdNH_3(CN)_2$, which was obtained by treating the diammine $[Pd(NH_3)_2(CN)_2]$ with dilute acetic acid, could not be obtained pure. An impure product containing 42.8% of palladium was obtained by heating the pure dipyridyl compound for an hour at 105° or by allowing the reaction product to crystallize from pyridine.

Dicyanodiquinolinepalladium $(Pdqn_2(CN)_2]$.—A suspension of palladium(II) cyanide in an excess of quinoline was heated. After cooling, a large volume of alcohol and ether was added to bring about the formation of a fine crystalline precipitate which contained 25.8% palladium. The value calculated from the formula $[Pdqn_2(CN)_2]$ is 25.6%.

Dicyanodioxinepalladium $[Pdox_2(CN)_2]$ **and the Adsorption Complex of Palladium(II) Cyanide and Oxine.**—A suspension of palladium(II) cyanide was heated in a saturated aqueous solution of 8-hydroxyquinoline (oxine). The oxine was replenished as the color of the solution diminished. The solid was washed by decantation with hot alcohol. From the hot wash alcohol light orange crystals of dicyanodioxinepalladium separated, which contained 23.5% of palladium. The calculated value for $[Pdox_2(CN)_2]$ is 23.8%. The residue was a microscopically amorphous, yellow adsorption complex of oxine and palladium(II) cyanide which contained 55.8% of palladium.

Dicyano-α,α′-dipyridylpalladium $[Pd(\alpha,\alpha'\text{-dip})(CN)_2]$.—A suspension of palladium(II) cyanide in alcohol containing an excess of α,α′-dipyridyl was heated two days on a water-bath. Analysis of the residue showed that it was impure $Pd\text{-}\alpha,\alpha'\text{-dip}(CN)_2$; the palladium content was 36.8%, while that calculated for the compound is 33.9%. The residue was again suspended in an alcoholic solution of the base and heated. After several days, an analysis showed that the insoluble material was the pure diammine. It contained 34.1% of palladium.

Dicyanoethylenediaminepalladium $[Pden(CN)_2]$.—On the addition of an excess of ethylenediamine to palladium(II) cyanide, a clear solution was obtained as the result of a strong exothermal reaction. A large volume of water was added and then a slight excess of hydrochloric acid. A light colored crystalline precipitate formed which was washed with water, alcohol, ether and dried for a half-hour at 110°. The product contained 53.0% of palladium, while that calculated for $Pden(CN)_2$ is 48.8%. When a more concentrated solution of palladium cyanide in ethylenediamine was allowed to stand, long needle crystals formed which contained 48.4% of palladium. The per cent. of carbon and hydrogen was 22.6 and 4.3%, respectively. The calculated values are 22.0 and 3.7%.

Dicyano-*o*-phenanthrolinepalladium $[Pd\text{-}o\text{-phen}(CN)_2]$.—A suspension of palladium(II) cyanide in a nearly saturated aqueous solution of *o*-phenanthroline was heated below the boiling point for approximately a day. Alcohol was then added, the hot solution filtered and the precipitate washed with hot alcohol and finally with ether. A white crystalline precipitate was obtained which contained 31.1% of palladium. The value calculated for $[Pd\text{-}o\text{-phen}(CN)_2]$ is 31.6%.

Dicyanodi-β-naphthoquinolinepalladium $[Pd\beta Nq(CN)_2]_2$.—Alcohol was added to the cooled melt of β-naphthoquinoline (m.p. 93.5°) and the residue was washed with alcohol and dried. A white crystalline product, a homolog of dicyanomonamminepalladium(II), which contained 31.0% of palladium was obtained. The calculated value for $PdNq(CN)_2$ is 31.5%.

The homologs of the diammine can also be prepared by heating the dihydrogen salts of tetracyanopalladium(II) acid.[5]

β-Palladium(II) Cyanide Lakes.—Palladium(II) cyanide forms lakes with many classes of dyes. If the dye is an acid–base indicator, the color of the lake is essentially the same as the color of the indicator in an acid solution as can be seen from Table I.

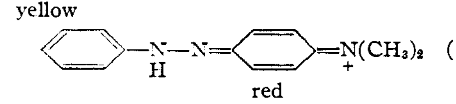
The lake of Rhodamine B has the color of the indicator in a neutral solution since it is not a strong enough Lewis acid to change the resonating system.

The lakes are formed not only from neutral aqueous or alcoholic solutions of the indicator, but also from acidified solutions as is shown in column 7 of Table I. The percentage of palladium in the lakes is considerably less than the percentage of palladium in the cyanide (67.2%) and indicates that an appreciable amount of indicator is present in the adsorption complex.

The adsorption complexes of the bases β-naphthoquinoline, diphenylamine, benzidine and tetramethyldiaminodiphenylmethane (tetrabase) were prepared by heating a suspension of palladium(II) cyanide in an alcoholic solution of the respective bases. The amount of palladium in the adsorption compounds was 56.9, 62.3, 59.3 and 59.5%, respectively. The adsorption complexes of the last three bases were also obtained by heating a suspension of palladium(II) cyanide in aqueous hydrochloric acid solutions of the bases of diphenylamine and benzidine. The amount of palladium in these products was 62.2 and 54.4%, respectively. The adsorption complexes of diphenylamine, benzidine and the tetrabase are not white but colored. The reason for obtaining colored adsorption complexes from these colorless bases will be discussed.

That it is the amine and not its hydrochloride which is adsorbed was shown by the constancy of the chloride content of a known volume of hydrochloric acid in which palladium(II) cyanide was suspended before and after the formation of a lake of malachite green.

We believe that the analogous behavior of solid palladium(II) cyanide and hydrogen ion in causing the same change in the color of indicators is of interest from a theoretical standpoint. The reaction between palladium(II) cyanide and an amine is the reaction of a Lewis acid and base, respectively. A question arises as to the role of palladium(II) cyanide in the process which leads to the color change. The color change of an aminoazo-indicator by hydrogen ion was formerly explained by the simple formation of a quinoid ring[6] and more recently by the behavior of an indicator dye as a resonating system.[7] In the case of methyl yellow (dimethylaminoazobenzene) the change to a quinoid structure by H^+ was represented by equation I.



(I)

Acid–base indicators are usually colored due to the electronic oscillations in conjugated systems. The change in color of methyl yellow, for example, from yellow to red on the addition of an acid is brought about by the stabilization

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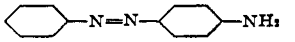
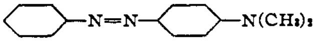
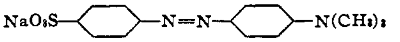
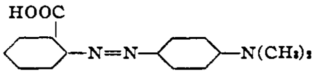
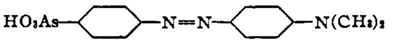
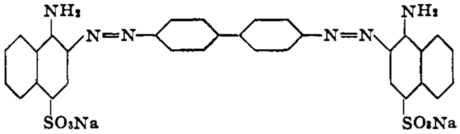
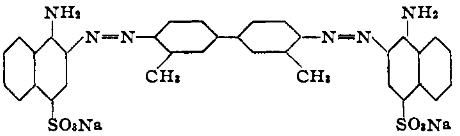
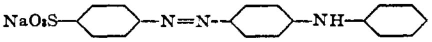
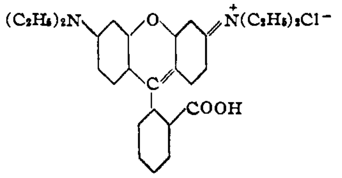
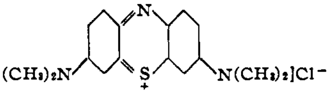
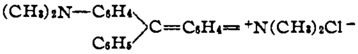
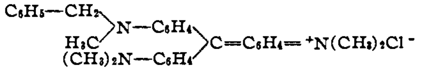
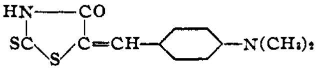
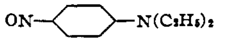
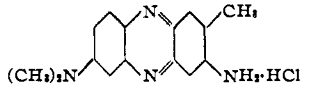
[4] F. Feigl and H. W. Zocher propose the term adsorption compound for these and similar products in a forthcoming paper; see also F. Feigl, *Anal. Chem.*, **21**, 1310 (1949); F. Feigl, "Specific Selective Sensitive Reactions," Academic Press, New York, N. Y., 1949, pp. 547–567.

[5] F. Feigl and G. B. Heisig, This Journal, **73**, 5360 (1951).

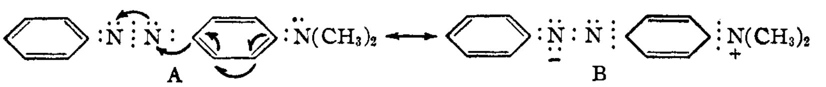
[6] Kolthoff and Rosenblum, "Acid Base Indicators," New York, N. Y., 1938, p. 228.

[7] W. F. Luder and S. Zuffanti, "Electronic Theory of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 97. See also G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," New York, N. Y., 1941, p. 180; G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 308ff (1939). We are indebted to Dr. M. Calvin of the University of California for suggestions to consider the color change as a resonance phenomenon.

TABLE I

Dyestuff					Lake	
			Color of Soln.		Color from (% Pd)	
Name	Class	Structure	Neutral	Acid	Neutral soln.	Acid soln.
Aminoazobenzene	Amino azo		y	r	r	r
Methyl yellow	Amino azo		y	r	r (59.6%)	r (54.1%)
Methyl orange	Amino azo		y	r	r (61.2%)	r (60.8%)
Methyl red	Amino azo		r	r	v	v
p-Dimethylaminoazophenylarsenic acid	Amino azo		y	p	v	v
Congo red	Amino azo		r	b	v	dye ppt.
Benzopurpine	Amino azo		r	db	rb	..
Tropaolin OO	Amino azo		r	p	br	v
Rhodamine B	Xanthone		mag	or	p (52.7%)	v
Methylene blue	Thiazine		b	b	b (47.9%)	b
Malachite green	Triphenylmethane		b	ol	bg	g
Gentian violet	Triphenylmethane		v	g	b	g
p-Dimethylaminobenzalrhodamine	Rhodamine condensation product		y	r	r	r
p-Nitrosodiethylaniline	Nitrosoamine		y	y	or	or
Neutral red	Phenazine		r	r	r	r

of resonance structure (B) by coördination of a hydrogen ion on the negative nitrogen



The small arrows connecting the symbols in (A) show electron pair shifts which result in the formation of a quinoid ring and leave the nitrogen of the dimethylamino and the azo groups with a formal positive and negative charge, respectively. When a hydrogen ion coördinates with electrons on the negative nitrogen, an ion is formed whose positive charge is localized on the nitrogen of the dimethylamino group. The coördination of a palladium ion on the surface of the acid palladium cyanide with the electrons on the negative nitrogen, stabilizes the dicovalent nitrogen and the color changes due to the difference in the electronic oscillating system.

The following equations show the similarity in the formation of the red coördination products of methyl yellow with a hydrogen ion or palladium cyanide.

The same general assumptions which explain the behavior of methyl yellow are valid for the other aminoazo-indicators, and when modified, also for non-azo indicators.[8]

Many organic bases are oxidation-reduction indicators, *i.e.*, within a certain *p*H range, and in the presence of oxidizing agents having a suitable oxidation potential, they are oxidized, and the oxidized form has a different color from that of the reduced form.[9] The color change is associated

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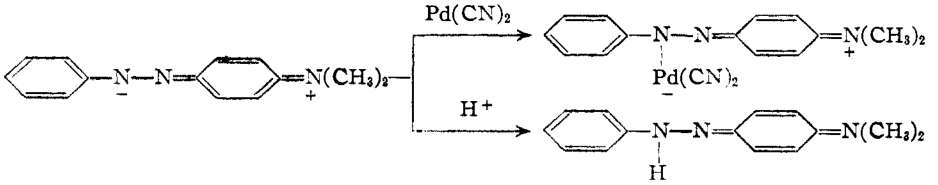
[8] The change of color of acid-base indicators coördinated on the surface of palladium(II) cyanide is analogous to the color change without the addition of an acid of acid-base indicators at the interface of water-benzene, etc., emulsions observed by Deutsch, *Ber.*, **60**, 1036 (1927); *Z. physik. Chem.*, **136**, 353 (1928). Perhaps explanations analogous to those given for the change in color on the surface of palladium(II) cyanide will hold for those observed by Deutsch.

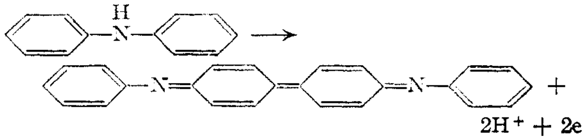
[9] The terms oxidized and reduced forms of an oxidation-reduction indicator are used in this part in the conventional sense. This usage is hardly correct. The terms oxidized and reduced forms, correctly used, imply isomerism, whereas actually the oxidized form is a new compound produced by the oxidation of the reduced form. The oxidation may or may not be followed by side reactions, rearrangements, etc.



with a change in the structure, whereby usually a non-quinoid aromatic amine is oxidized to the quinoid form. The general reaction may be represented by the equation

$$\text{amine} + \text{oxidizing agent} + \text{Pd(CN)}_2 \rightleftharpoons \text{lake oxidized amine} + \text{reduction products of the oxidizing agent}$$

For diphenylamine the structure change to a quinoid form is given by the equation[10]



In this equation the formation of a colorless intermediate product is not included, since it is not involved in our explanation. We have studied the behavior of diphenylamine, diphenylbenzidine and diphenyldiamine-*p*-sulfonic acid, and found that a slightly acid solution containing hydrogen peroxide remains colorless or slightly colored until palladium(II) cyanide is added. Immediately, a lake forms which has the color of the oxidized form of the oxidation–reduction indicator. Even in the absence of hydrogen peroxide, the palladium(II) cyanide is slightly colored. We have prepared the colored palladium(II) cyanide lakes of the oxidized form of diphenylamine and found that the amount of palladium is 59.3%, which corresponds to the amount of palladium found in the lakes of acid–base indicators as can be seen from columns 6 and 7 of Table I.

There are two explanations for the formation of the lake of the oxidized form of diphenylamine, etc., from a solution which contains an oxidizing agent whose oxidation potential is not sufficient to cause the formation of enough of the oxidized form to change appreciably the color of the solution. The first involves the displacement of the equilibrium between the reduced and oxidized forms of the oxidation–reduction indicator by the coördination of the oxidized form to form a lake (adsorption complex) with palladium(II) cyanide. A second possibility is that the reduced form of the indicator is adsorbed on the surface of the palladium(II) cyanide and then it is more reactive than in the solution. This behavior is analogous to the increase in the oxidation potential of an oxidizing agent with an increase in the concentration of the hydrogen ions. To check the second assumption we prepared the adsorption complexes of diphenylamine and palladium(II) cyanide and found that the slightly colored adsorption complex is changed to the dark blue lake of the oxidized form of the indicator by the addition of acidified hydrogen peroxide. The same color change in the color of the solution of diphenylamine was brought about by the addition of concentrated hydrochloric acid instead of palladium(II) cyanide. It is possible that the processes assumed in both explanations occur simultaneously.

The colored oxidation products formed when palladium(II) cyanide is added to an acidified solution of hydrogen peroxide which contained one of the following colorless organic amines: aniline, ethylaniline, diethylaniline, phenylenediamine, benzidine,[11] diaminobenzidine,[12] 2,7-diaminodiphenylene oxide, tetramethyldiaminodiphenylmethane (tetrabase), dianisidine or oxine[13] form adsorption complexes (lakes) with the palladium(II) cyanide. We have prepared the lakes of palladium(II) cyanide with benzidine and tetramethyldiaminodiphenylmethane (tetrabase) by treating palladium(II) cyanide with acid solutions of the bases containing hydrogen peroxide and found that the amount of palladium is about 55% which is essentially the same as that in the adsorption complexes discussed previously. Unlike other colorless amines, benzidine and tetrabase do not form colorless adsorption complexes with palladium(II) cyanide. The color of the products showed that they contained some of the oxidized form of the base. It seems that the adsorbed uncolored base is unstable and is oxidized by the oxygen in the air. This is in agreement with the assumption that the reactivity of the adsorbed base is greater than that in the dissolved state. In agreement with this assumption is the fact that the colors of the tinted adsorption complexes of benzidine and tetrabase with palladium(II) cyanide are deepened on the addition of hydrogen peroxide. The adsorption complex of palladium(II) cyanide with benzidine is changed to the deep colored lake of the oxidized form of the base by treatment with an acidified solution of hydrogen peroxide. The tetrabase in the palladium(II) cyanide adsorption complex is activated to such an extent that it is readily oxidized by the oxygen of the air.

Analytical Aspects of the Lakes of Palladium(II) Cyanide.—As previously noted, the formation of lakes of palladium(II) cyanide with dyes occurs practically immediately and can be used in analytical chemistry. For example, small amounts of palladium(II) cyanide can be spotted on filter paper or on a spot plate with a drop of a solution of a dye. Since the lakes are intensely colored, very small amounts of palladium(II) cyanide can be detected. In fact, the lake formed from such a small amount of palladium(II) cyanide that it cannot be detected by the eye, can readily be seen. For this purpose the best acid-base indicator is an alcoholic solution of methyl yellow which forms a brilliant red lake. To detect a small quantity of palladium(II) cyanide, the material to be tested must not be acid. Moreover, a distinction between palladium(II) cyanide and silver cyanide or copper(I) cyanide can be made very rapidly by adding methyl yellow.[14]

The formation of the red lake of palladium(II) cyanide with methyl yellow can be used to detect such a small quantity of the indicator that the solution is not colored noticeably. This can be done by adding a small amount of palladium(II) cyanide to the solution, which in this case can also be acid, and shaking with ether the suspension of the lake formed. The lake collects at the ether and water interface. A very small amount of the lake is easily seen. The palladium(II) cyanide in this case acts as a collector or trace-catcher. Thus dyes which form lakes with palladium(II) cyanide may be differentiated from those which do not.

We were able to show quickly that the tetrachloropalladate(II) ion reacts with silver cyanide to form palladium(II) cyanide, according to the equation

$$2\text{AgCN} + \text{PdCl}_4^{=} \rightleftharpoons \text{Pd(CN)}_2 + 2\text{AgCl} + 2\text{Cl}^-$$

by dissolving silver cyanide in ammonia, impregnating filter paper with the solution, drying, spotting with a solution of tetrachloropalladate(II) ions, and warming. Immediately on applying a drop of methyl yellow, a red lake formed which proved the presence of palladium(II) cyanide. This can be made the basis for a new spot test for palladium.

Congo red and benzopurpurine 4B are not readily differentiated by ordinary analytical procedures, because they differ only by two methyl groups, but can be differentiated by the difference in the color of their palladium(II) cyanide

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[10] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Rev. Ed., The Macmillan Co., New York, N. Y., 1946.

[11] This compound was recently used as an analytical reagent by Halste, *Anal. Chim. Acta*, **2**, 402 (1948), who kindly furnished us a sample.

[12] This compound was recently used by N. M. Cullinane and S. J. Chard, *Analyst*, **73**, 95 (1948), who kindly furnished us with a sample.

[13] Elgriwe, *Z. anal. Chem.*, **118**, 98 (1939), observed that magnesium hydroxide in an ammoniacal solution of *p*-aminophenol becomes blue when the mixture is shaken. The color is probably due to the oxidation of the amine to colored products which are not obtained in the absence of $Mg(OH)_2$. This is analogous to the behavior of oxidation–reduction indicators and oxidizable amines with palladium(II) cyanide. An explanation analogous to that proposed for palladium(II) cyanide will probably explain the observations of Elgriwe.

[14] These results are not wholly in agreement with those reported by C. Walling, THIS JOURNAL, **72**, 1166 (1950). However, the conditions are not the same. The differences are being further investigated by one of us.

lakes. The lakes formed by adding a drop of a solution containing at least 0.2 mg./ml. of the respective dyes to a little solid palladium(II) cyanide on a piece of filter paper are dark blue and red-pink, respectively. Hence it is easy to differentiate between drops of solutions which contain at least approximately 0.2 mg. of dye per milliliter.

Palladium(II) cyanide also forms adsorption complexes with many alkaloids. Dilute hydrochloric acid solutions of caffeine, theobromine, quinine, ephedrine and berberine were prepared which gave a turbidity on the addition of phosphomolybdic acid. About 5 ml. of these solutions was shaken with palladium(II) cyanide and filtered. On the addition of phosphomolybdic acid, the solution remained clear, showing that the alkaloids were completely adsorbed by the palladium(II) cyanide. Some of the caffeine adsorption complex with palladium(II) cyanide was prepared by heating a suspension of the cyanide in an aqueous solution of caffeine. After drying the residue at 110° the palladium content was found to be 52.5%. Thus in spite of its large molecular volume, caffeine forms the same type of adsorption complex as do the amines which have a smaller molecular volume. It is thus possible to concentrate alkaloids by forming adsorption complexes with palladium(II) cyanide and decomposing the complex in a suitable manner.

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In Situ X-Ray Diffraction Studies of Heterogeneous Reactions[1]

BY M. A. MOSESMAN

An apparatus embodying a metallic microreactor of approximately 0.002-ml. capacity, fabricated from high purity, machinable beryllium rod, has been developed and utilized for the investigation of the changes that occur in solid materials through chemical interaction with gaseous reactants in a flow system as revealed by *in situ* X-ray powder diffraction patterns. The construction of the apparatus is such as to permit operations at pressures and temperatures as high as 11 atmospheres and 650°, respectively, and flow rates as low as 1.0 ml./hr. The X-ray diffraction data obtained in the application of this apparatus to the determination of the stable oxidation states of iron in an ammonia synthesis catalyst and of molybdenum in bulk and alumina-supported molybdenum trioxide in reducing and oxidizing atmospheres identify Fe_3O_4, FeO and Fe in the former instance and MoO_3 and MoO_2 in the latter instances during the course of the reactions observed under the imposed operating conditions.

Introduction

The reliability and accuracy, as well as the limitations, of the X-ray powder diffraction technique for the examination and identification of solids and solid mixtures are well established,[2] but the application of this method in a conventional manner to the investigation of the changes that occur in solid materials participating in heterogeneous chemical reactions is generally time-consuming and laborious. Moreover, X-ray diffraction data obtained on samples necessarily removed from a reaction zone under reaction conditions frequently may be ambiguous unless adequate precautions are taken to insure that the atmospheres to which the sample is subjected subsequent to its removal are nonreactive. As a consequence, it is extremely desirable to have available for optimum results a means of obtaining *in situ* diffraction patterns under reaction conditions. A number of recent investigators[3–7] have developed X-ray cameras for obtaining diffraction data at elevated temperatures, under controlled atmospheres in some instances, or elevated pressures, but, in general, these apparatus are not readily adaptable to the study of solids in heterogeneous, dynamic reaction systems. The first report of an apparatus especially designed for obtaining X-ray diffraction patterns of powders in contact with a flowing gas under varying conditions of pressure and temperature was disclosed by Long.[8] The present research reports some further applications of this apparatus in the investigation of gas–solid reactions between ammonia synthesis catalyst, bulk molybdenum trioxide, and alumina-supported molybdenum trioxide and reducing or oxidizing atmospheres. In view of the generally limited dissemination of the foregoing reference, a brief description of the apparatus as currently constituted is also included.

Experimental

Apparatus.—The essential feature of the apparatus is the metallic microreactor of approximately 0.002-ml. capacity fabricated from high purity, machinable beryllium rod;[9] the selection of beryllium for construction of the microreactor was dictated by the need for a material possessing a low X-ray absorption coefficient[10] and a simple X-ray diffraction pattern and capable of withstanding operations at elevated pressures and temperatures. The design of the beryllium microreactor assembly is shown in Fig. 1. The microreactor A is mounted in a hollow steel housing B threaded internally at each end and provided with entrance and exit openings for the respective collimated and diffracted X-ray beams. Steel unions C exerting compressive force against specially made copper ferrules D on each end of the microreactor maintain the latter gas-tight and rigid within the housing. These unions also provide the means of attaching charge and exit gas lines. The microreactor-housing-union assembly is surrounded by a well-insulated resistance heater E wound upon a Pyrex tube containing openings that coincide with those of the housing. Appropriately sized openings are also provided through the insulating material for

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[1] Presented at the 119th Meeting of the American Chemical Society at Cleveland, Ohio, April, 1951.

[2] See, for example, W. T. Sproull, "X-Rays in Practice," McGraw-Hill Book Company, Inc., New York, N. Y., 1946.

[3] M. J. Buerger, N. W. Buerger and F. G. Chesley, *Am. Mineral.*, **28**, 285 (1943).

[4] J. J. Lander, *Rev. Sci. Instruments*, **20**, 82 (1949).

[5] J. W. Edwards, R. Speiser and H. L. Johnston, *ibid.*, **20**, 343 (1949).

[6] A. N. Lawson and N. A. Riley, *ibid.*, **20**, 763 (1949).

[7] P. Gordon, *J. Applied Phys.*, **20**, 908 (1949).

[8] R. W. Long, U. S. Patent 2,483,500.

[9] Obtained from Brush Beryllium Company, 3714 Chester Avenue, Cleveland, Ohio.

[10] H. Brackney and Z. J. Atlee, *Rev. Sci. Instruments*, **14**, 59 (1943).