bine with the Br. Thus a smaller fraction of the 18 min. activity becomes water-soluble. Primary recombination or deactivation might, of course, occur also. Substitution into carbon bisulfide occurs slightly less often than into carbon tetrachloride.

Alcohol or aniline acts to release the 18 min. bromine in inorganic form either by being attracted by Br atoms undergoing transition and reacting with them enough to prevent recombinations or substitutions or by reaction with the newly formed organic bromides while they are still activated.

This tentative picture is based on the following experimental findings. (1) A portion (roughly 25%) of the 18 min. activity ejected from organic compounds in the gas and in the liquid will interchange with Br_2 or react with reducing agents, but is not extracted by water. (2) Another portion is readily extracted by pure water. (3) The amount of 18 min. bromine which goes into or remains in organic form is reduced to a minimum by gaseous conditions or by adding alcohol or aniline to liquids. (4) Substitution into carbon bisulfide is observed and into carbon tetrachloride is confirmed. The substitution into carbon tetrachloride occurs either from bromine or alkyl bromides. (5) The products from the gas phase at 21 mm. pressure do not show preference for either negative or positive charged plates. (6) A small dependence of the amount of extraction from BrO_3^- on the presence of Br^- may indicate that an intermediate form is involved there.

BERKELEY, CALIFORNIA RECEIVED JULY 7, 1941

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Colorimetric Detection and Determination of Palladium with Compounds Containing the *p*-Nitrosophenylamino Group[1]

BY LYLE G. OVERHOLSER AND JOHN H. YOE

A study of the reaction of *p*-nitrosodiphenylamine (I) with palladous chloride and its application to the colorimetric detection and determination of palladium has been presented in a previous paper.[2] Further studies on a large number of aromatic amines revealed that compounds containing the *p*-nitrosophenylamino group, *p*-$NOC_6H_4N<$, namely, *p*-nitrosoaniline (II), *p*-nitrosodimethylaniline (III), and *p*-nitrosodiethylaniline (IV) form similar highly colored complexes with palladous salts. These complexes are all of the same general type as exemplified by palladous dichlorodiammine, $Pd(NH_3)_2Cl_2$. This compound has been reported to exhibit *cis-trans* isomerism; hence it is possible that those prepared in this Laboratory may exist in *cis–trans* isomeric forms, though no experimental evidence to substantiate this view is at hand.

Numerous amines give complexes with palladous chloride but generally the product obtained is yellow. Thus aniline[3] and *p*-nitroaniline[4] both give yellow complexes with palladous chloride. In contrast, the complex of (I) with palladous chloride is dark purplish-brown, that of (II) dark brown, and of (III) and (IV) bright red. Diethylaniline, dimethylaniline, *p*-aminophenol, *p*-chloroaniline, and *p*-phenylenediamine do not give highly colored complexes with palladous salts. All this evidence indicates that the nitroso group must be present in order to form highly colored complexes and that the *p*-$NOC_6H_4N<$ structure is responsible for the characteristic reaction with palladous salts.

The presence of the nitroso group also results in a more selective reaction for palladium. Thus, diphenylamine and its amino or hydroxy derivatives give highly colored reactions with numerous oxidizing agents, whereas the nitroso derivative reacts only with strong oxidizing agents. Similarly, *p*-aminodiethylaniline gives reactions with weaker oxidizing agents than does *p*-nitrosodiethylaniline

Ogburn[5] reported reactions of palladous chlo-

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[1] This investigation was supported partly by a grant-in-aid from the Carnegie Corporation of New York. It is the second of a projected series based upon studies of organic reagents in inorganic analysis. These studies are being conducted as a coöperative effort in which ten institutions are participating under the direction of John H. Yoe. Those coöperating with the University of Virginia are: Hampden-Sydney, Mary Baldwin, Randolph-Macon (Ashland), Virginia Military Institute, Virginia Polytechnic Institute, Washington and Lee, William and Mary, University of North Carolina, and Tulane University. Original manuscript received November 12, 1940.

[2] J. H. Yoe and L. G. Overholser, THIS JOURNAL, **61**, 2058 (1939).

[3] A. Gutbier and A. Krell, *Ber.*, **39**, 1292 (1906).

[4] A. Gutbier and C. Fellner, *Z. anorg. Chem.*, **95**, 129 (1921).

[5] S. C. Ogburn, Jr., THIS JOURNAL, **48**, 2493 (1926).

ride with (II) and (III) but did not identify the products formed. We have made a further study of the reactions and also the reaction of (IV). The complexes have been identified and the reagents containing the *p*-$NOC_6H_4N<$ structure have been applied to the colorimetric detection and determination of palladium present as palladous chloride or palladous nitrate.

Methods and Materials

The experimental methods, both visual and spectrophotometric, were essentially the same as those previously given.[2] The materials included those previously described, as well as the following.

Palladous Nitrate.—Metallic palladium was dissolved in *aqua regia* and repeatedly evaporated with concentrated nitric acid until chloride-free. The final solution was made up to contain 1 mg. of palladium per ml. and was 1 *M* with respect to nitric acid.

***p*-Nitrosodimethylaniline.**—A solution of the reagent (Eastman No. 188) was prepared by dissolving 25 mg. of the solid in 50 ml. of 95% ethanol and diluting to 100 ml. with water. The solution was filtered whenever solid material remained undissolved.

***p*-Nitrosodiethylaniline.**—(Eastman No. 522.) The preparation was the same as for *p*-nitrosodimethylaniline.

***p*-Nitrosoaniline.**—This compound was prepared from *p*-nitrosophenol by the method of Fischer and Hepp.[6]

Sodium Acetate-Hydrochloric Acid Buffer.—A buffer having a *p*H of approximately 4.8 was prepared by adding 80 ml. of 1 *M* hydrochloric acid to 200 ml. of 1 *M* sodium acetate and diluting to 1 liter with water.

Sodium Acetate-Nitric Acid Buffers.—Chloride-free sodium acetate was prepared by recrystallizing a C. P. product three times from distilled water. A buffer having a *p*H of 1.2 was prepared by adding 320 ml. of 1 *M* nitric acid to 200 ml. of 1 *M* sodium acetate and diluting to 1 liter with chloride-free water. Dilution of 25 ml. of the buffer to 100 ml. with water gives a solution with a *p*H of 1.8. Another buffer with a *p*H of 4.7 was prepared as above, except that 80 ml. of 1 *M* nitric acid was used.

Reaction of Palladous Chloride with *p*-Nitrosoaniline, *p*-Nitrosodimethylaniline and *p*-Nitrosodiethylaniline

p-Nitrosoaniline, *p*-nitrosodimethylaniline and *p*-nitrosodiethylaniline react with palladous chloride to give complexes of the type $Pd[NOC_6H_4NH_2]_2Cl_2$. The complex formed with *p*-nitrosoaniline is a dark brown solid, while those formed with the dimethyl and diethyl reagents[7] are dark red. Although these complexes are of the same type as that of the diphenyl complex, they differ in solubility. The former are sparingly soluble in water, ethanol, and acetate buffers; the diphenyl complex, on the other hand, is insoluble in water and acetate buffers but is readily soluble in ethanol. All the complexes dissolve in strong acids or bases.

Preparation of Palladous Dichloro-bis-*p*-nitrosodimethylaniline, $Pd[NOC_6H_4N(CH_3)_2]_2Cl_2$.—Twenty milliliters of palladous chloride containing 20 mg. of palladium was diluted to approximately 500 ml. with water and to it was added 40 ml. of a filtered alcoholic solution, containing 100 mg. of *p*-nitrosodimethylaniline. The suspension was allowed to stand several hours before being filtered through a sintered glass crucible. The solid was washed with three 5-ml. portions of water and dried at 110° for three hours. *Anal.* Calcd. for $C_{16}H_{20}N_4O_2PdCl_2$: C, 40.20; H, 4.22; Pd, 22.32; Cl, 14.84. Found: C, 40.08; H, 4.36; Pd, 22.22; Cl, 14.74.

Preparation of Palladous Dichloro-bis-*p*-nitrosodiethylaniline, $Pd[NOC_6H_4N(C_2H_5)_2]_2Cl_2$.—The procedure was the same as for the dimethyl complex except that *p*-nitrosodiethylaniline was used. *Anal.* Calcd. for $C_{20}H_{28}N_4O_2PdCl_2$: C, 44.98; H, 5.31; Pd, 19.98; Cl, 13.28. Found: C, 45.28; H, 5.23; Pd, 19.93; Cl, 13.17.

Preparation of Palladous Dichloro-bis-*p*-nitrosoaniline, $Pd[NOC_6H_4NH_2]_2Cl_2$.—The procedure was the same as for the dimethyl complex except that *p*-nitrosoaniline was used. *Anal.* Calcd. for $C_{12}H_{12}N_4O_2PdCl_2$: C, 34.15; H, 2.85; Pd, 25.30; Cl, 16.81. Found: C, 34.60; H, 3.32; Pd, 25.20; Cl, 16.77.

Relative Absorption Curves for Dimethyl and Diethyl Reagents and for their Palladous Chloride and Nitrate Complexes.—Data for all the absorption curves were obtained with a photoelectric spectrophotometer constructed by Barton and Yoe.[8]

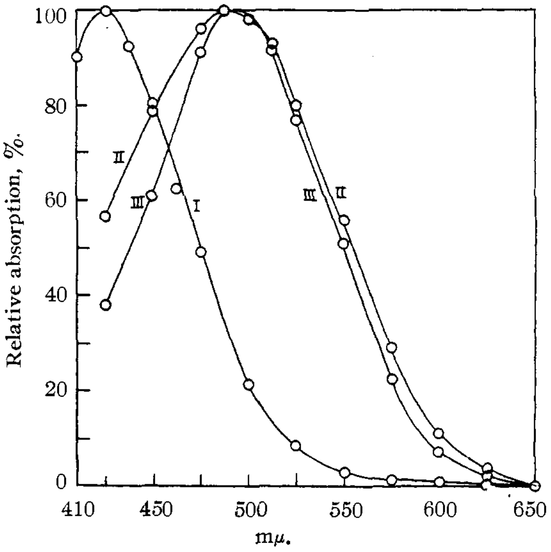

Fig. 1.—Relative absorption of *p*-nitrosodiphenylamine and its complexes: I, reagent; II, $Pd[C_6H_5NHC_6H_4NO]_2(NO_3)_2$(?); III, $Pd[C_6H_5NHC_6H_4NO]_2Cl_2$.

In Fig. 1 the absorption curves for the diphenyl reagent and its complexes are given for comparison with those of the dimethyl and diethyl reagents. Curve I was obtained for the following solution: 25 ml. of the sodium acetate-hydrochloric acid buffer (*p*H 1.4) plus 2 ml. of the diphenyl reagent, diluted to 100 ml. with water. The palladous

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[6] O. Fischer and E. Hepp, *Ber.*, **20**, 2471 (1887).

[7] For the sake of brevity, *p*-nitosodiethylaniline will be referred to as diethyl reagent and its complex with palladous chloride as the diethyl complex, and similarly for the use of dimethyl and diphenyl compounds.

[8] C. J. Barton and J. H. Yoe, *Ind. Eng. Chem., Anal. Ed.*, **12**, 166 (1940).

chloride complex of Curve III was obtained for a solution prepared as for Curve I except for the presence of 80 γ of palladium as the chloride. The palladous nitrate complex of Curve II is comparable to that of Curve III except that palladium was added as the nitrate and 25 ml. of a sodium acetate–nitric acid buffer (pH 1.2) was used in place of the hydrochloric acid buffer.

The absorption curves for the dimethyl reagent and its complexes are given in Fig. 2. The reagent Curve I is for the following solution: 25 ml. of sodium acetate–hydrochloric acid buffer (pH 4.8) plus 1 ml. of the dimethyl reagent and diluted to 100 ml. with water. The palladous chloride complex Curve III is for a solution prepared as I except for the addition of 80 γ of palladium as the chloride. Curve II is the corresponding curve for palladous nitrate, using a sodium acetate–nitric acid buffer (pH 4.7) in place of the hydrochloric acid buffer.

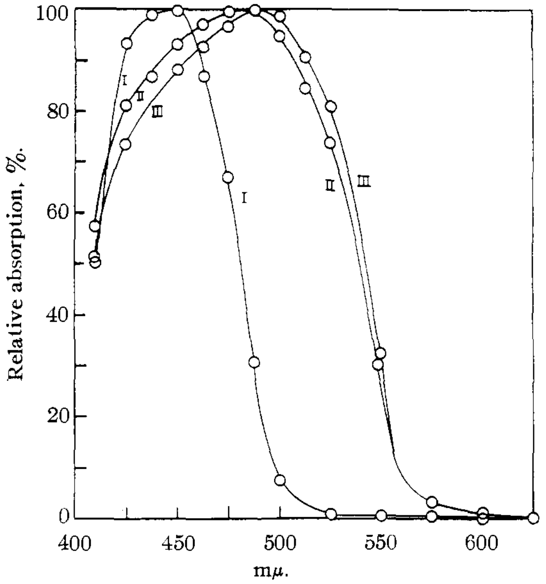

Fig. 2.—Relative absorption of p-nitrosodimethylaniline and its complexes: I, reagent; II, $\mathrm{Pd[NOC_6H_4N(CH_3)_2]_2(NO_3)_2}$(?); III, $\mathrm{Pd[NOC_6H_4N(CH_3)_2]_2Cl_2}$.

The corresponding curves for p-nitrosodiethylaniline given in Fig. 3 are for solutions similar to those in Fig. 2 except for the different reagent employed.

A comparison of the curves in Figs. 2 and 3 shows the similarity of the dimethyl and diethyl reagents; the diphenyl reagent of Fig. 1 gives a different type of curve. It is important to observe that the absorption of the dimethyl and diethyl reagents can be eliminated without appreciably decreasing the sensitivity of the method. Thus, at 525 mμ, the absorption due to the reagent is about 1 per cent. compared to about 80% for the palladous chloride complex, a much more favorable ratio than is obtainable for the diphenyl reagent.

Colorimetric Determination of Palladium with p-Nitrosodimethylaniline.—The colorimetric method previously given,[2] employing p-nitro sodiphenylamine, is satisfactory, provided certain precautions are observed. From a study of the reactions of the dimethyl and diethyl reagents, it was evident, however, that these reagents possess certain advantages over the diphenyl reagent. Accordingly, a thorough study was made of these reactions and a critical comparison with the diphenyl reagent will be given in this paper. Because the dimethyl and diethyl reagents are very similar in their behavior, only the results obtained for the dimethyl reagent will be presented, although the diethyl reagent may be used with equal satisfaction.

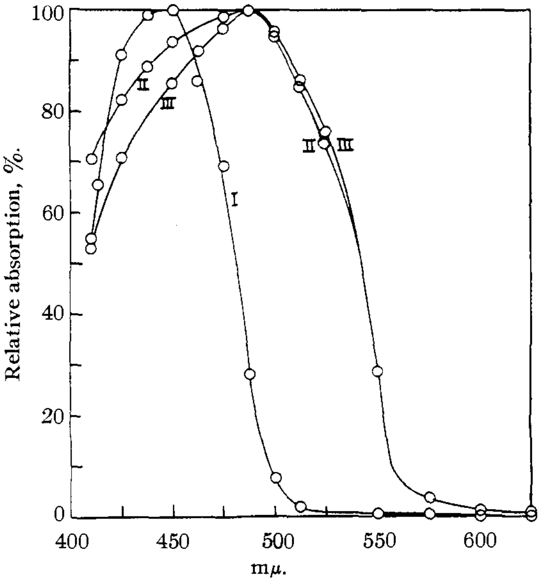

Fig. 3.—Relative absorption of p-nitrosodiethylaniline and its complexes: I, reagent; II, $\mathrm{Pd[NOC_6H_4N(C_2H_5)_2]_2(NO_3)_2}$(?); III, $\mathrm{Pd[NOC_6H_4N(C_2H_5)_2]_2Cl_2}$.

The general procedure is similar to that used with the diphenyl reagent and is as follows: transfer 25 ml. of the sodium acetate–hydrochloric acid buffer (pH 4.8) to a 100-ml. volumetric flask, add the palladous chloride solution, 1 ml. of the dimethyl reagent, dilute with water to the mark and thoroughly mix. Comparison of the colors may be made five minutes after the addition of the reagent, using 50-ml. Nessler tubes (220 mm.) or 100-ml. tubes (160 mm.) in a roulette comparator[9] equipped with Corning Filter No. 512. The increments of palladium employed in the standards are the same as those used with the diphenyl reagent.

Effect of Salts.—The dimethyl complex is slightly less sensitive to the presence of salts than is the diphenyl. Thus, 0.01 M sodium chloride is without effect and 0.03 M causes no deter-

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(9) Yoe and Crumpler, *Ind. Eng. Chem., Anal. Ed.*, **7**, 78 (1935).

minable error using the diphenyl reagent; the corresponding limits for the dimethyl reagent are 0.03 and 0.05 *M*, respectively. The effect is similar in both cases, *i. e.*, a decrease in the color intensity is produced.

Effect of Hydrogen-ion Concentration.—The yellow color of the dimethyl reagent increases in intensity through the *p*H range 0.9–5.2, showing the most rapid change from *p*H 0.9 to 3.0. Above *p*H 3.0 the intensity increases slowly, the difference between *p*H 4.4 and 5.2 being detected only with difficulty. The intensity of the color of the dimethyl complex increases most rapidly from *p*H 2.0 to 3.9. From *p*H 4.4 to 5.2 there is no detectable change. Using the diphenyl reagent, 0.5 ml. of 1 *M* hydrochloric acid is without effect and 0.75 ml. causes no serious interference; the corresponding limits using the dimethyl reagent are 0.75 and 1.0 ml., respectively. The diphenyl complex has a maximum color intensity at a *p*H of 3.0, but it cannot be used at this *p*H because of the formation of turbid solutions. In contrast, the dimethyl complex has a maximum color intensity at approximately *p*H 4.8 and also yields clear solutions, making the reagent applicable at the *p*H of maximum sensitivity. Under conditions of maximum sensitivity, however, the diphenyl reagent is more sensitive than the dimethyl.

Formation and Stability of Color.—The most serious objection to the diphenyl reagent is its slow reaction rate and the instability of suspensions of the colored complex. On the other hand, the dimethyl complex, which is sparingly soluble in the buffer used, probably yields true solutions and thus the disadvantages inherent to a colloidal state may be avoided. About thirty minutes is required for maximum color development when the diphenyl reagent is employed and the color is not stable for more than one or two hours. The dimethyl reagent, on the other hand, requires not more than five minutes for maximum color development and the color is stable for three or four hours. Solutions of the diphenyl complex give a precipitate on standing a day; those of the dimethyl complex remain clear for weeks. The effect of temperature on the dimethyl complex is less marked than for the diphenyl. With the former a temperature difference of 20° causes no error, provided the solutions stand about ten minutes before color comparison. On heating solutions of the dimethyl complex to 90–100° no appreciable fading occurs; under such treatment, the diphenyl complex is precipitated.

As in the case of the diphenyl reagent, the order of addition of reagent and of palladium has no effect. Palladous chloride should not be allowed to remain in the acetate buffer (*p*H 4.8) longer than ten minutes before adding the reagent, in order to avoid a decrease in the color intensity due probably to adsorption on the glassware.

Interference of Certain Ions.—The ions that interfere with the dimethyl reagent are the same as those which interfere with the diphenyl reagent. With the exception of cupric and ferric ions, the dimethyl reagent compares favorably with the diphenyl. The limiting concentrations of certain interfering ions for the two reagents are given in Table I. The data were obtained with the roulette comparator.[9]

TABLE I

Ion	Dimethyl, p. p. m.	Diphenyl, p. p. m.
Cu^{++}	3	50
Fe^{+++}	2	30
Co^{++}	10	10
Ni^{++}	15	20
$AuCl_4^-$	0.5	1
$RhCl_5^=$	1	1
$IrCl_6^=$	1	1
$PtCl_6^=$	20	20

Sensitivity and Accuracy.—The sensitivity is the same as for the diphenyl reagent, *i. e.*, 1 : 200,000,000 using either the roulette comparator or 50-ml. Nessler tubes (220 mm.). The accuracy as determined in the roulette comparator using Corning Filter No. 512 is: 0.5–12, 0.25; 13–25, 0.5; 26–35, 1; 35–45, 2 γ. The method is most suitable for solutions containing less than 25 γ of palladium.

Spectrophotometric Study of the Dimethyl Complex.—The greater stability of the colored solution of the dimethyl complex, as well as the elimination of the absorption by the reagent using a wave band of 525 mμ, makes the dimethyl reagent more suitable for spectrophotometric studies than the diphenyl. Even the small absorption by the dimethyl reagent can be completely eliminated either by using the reagent solution as the standard, or by applying a correction factor. At low palladium concentrations, use of the reagent solution as the standard is satisfactory. Solutions containing 10 to 20 γ of palladium were prepared as for the visual studies. Measurements of the absorption of these solutions showed the dimethyl complex to be stable for at least four hours. After one day the absorption decreased by approximately 5% and after five days by about 10%.

A test of the conformity of solutions of the dimethyl complex to the Lambert–Beer law is given in Fig. 4. The values were obtained for solutions prepared according to the recommended procedure using a wave band of 525 mμ and corrected for absorption by the reagent. The straight line conformity is within the limits of experimental error up to a concentration of 1:5,000,000 (20 γ in 100 ml.). Above this concentration, a deviation occurs and this becomes greater with increasing concentration. The optimum range for the visual method corresponds to the concentrations at which the Lambert–Beer law is applicable.

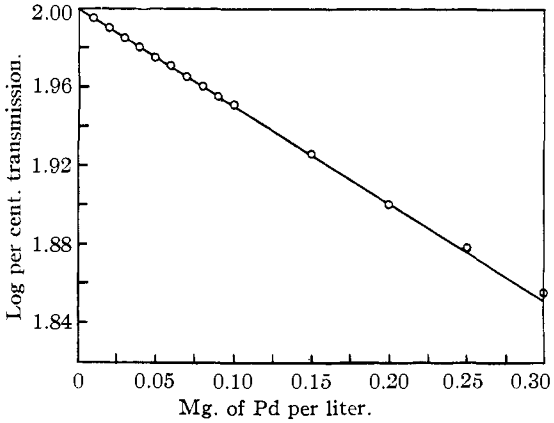

Fig. 4.—Conformity of palladous dichloro-bis-*p*-nitrosodimethylaniline to the Lambert–Beer law.

Reactions with Palladous Nitrate.—All the reagents react with palladous nitrate to give colored complexes similar to those obtained with palladous chloride. The diphenyl complex is insoluble and can be isolated readily. The others are soluble and can be obtained only in an impure state by a partial evaporation of the solutions.

Colorimetric Determination of Palladium as the Nitrate.—The procedures for the determination of palladium as the chloride are not applicable if silver is present. The presence of silver chloride causes turbidity and if the silver is removed by precipitation as the chloride, part of the palladium is lost. By using *p*-nitrosodiphenylamine for the determination of palladium as the nitrate, however, the method may be applied directly to solutions containing silver. The character of the reaction is similar to that with palladous chloride and hence will not be given in detail.

Recommended Procedure.—Pipet 25 ml. of a sodium acetate–nitric acid buffer (*p*H 1.2) into a 100-ml. volumetric flask, add the palladous nitrate, 2 ml. of the diphenyl reagent, dilute to the mark with water, and mix thoroughly. Let stand for twenty to thirty minutes before making the color comparison.

All reagents must be chloride-free to avoid turbidity, if silver is present, and even in the absence of silver this precaution is necessary since small amounts of chloride cause a marked decrease in color intensity.

The sensitivity is the same as for the determination of palladous chloride. The rate of color development for the nitrate is about equal to that of the chloride, but the stability is slightly greater. The temperature effect is comparable in the two methods. The reaction is affected by changes in concentration of salts or hydrogen-ion; 0.5 ml. of 1 *M* nitric acid and 5 millimoles of salts (exclusive of buffer) being the maximum allowable.

With the exception of silver, the interference of metallic ions (interference of platinum group metals was not determined) is comparable to that in the determination of palladium as the chloride. When palladium is determined as the nitrate, the silver concentration should not exceed 20 mg. (200 p. p. m.); larger amounts cause a slight decrease in the intensity of the color. In some cases this interference may be eliminated by the addition of approximately the same amount of silver to the standards as is present in the unknown. At a concentration of 500 p. p. m. of silver, the intensity is reduced about 10%, thus making it possible to determine 0.01% of palladium in 50 mg. of silver with an error of 10%.

p-Nitrosodimethylaniline and *p*-nitrosodiethylaniline may also be used for the determination of palladous nitrate in a method comparable to that employed for the determination of palladous chloride by these reagents. A sodium acetate–nitric acid buffer (*p*H 4.7) and palladous nitrate standards are used. No special advantage over the diphenyl reagent is obtainable, the reaction being slow and only slightly more stable. The temperature effect is less than for the diphenyl reagent but the interference of cupric and ferric ions is disadvantageous. The effect of the silver ion is comparable to that obtained when the diphenyl reagent is used.

Detection of Palladium.—All four of the reagents may be used for the detection of palladous chloride or nitrate, although *p*-nitrosoaniline is less sensitive than the others. The sensitivities determined on the spot-plate under different conditions are recorded in Table II. The tests were made by adding a drop of the reagent solution to 0.05 ml. of the palladous salt of the designated concentration. Results obtained for the diethyl reagent are similar to those for the dimethyl. The sensitivities for palladous nitrate are approximately the same as for the chloride.

TABLE II

Medium	Dimethyl	Diphenyl
Water	1:8,000,000	1:10,000,000
Buffer (*p*H 4.7)	1:8,000,000	1: 8,000,000
Buffer (*p*H 1.4)	1:5,000,000	1: 5,000,000

Summary

The reactions of *p*-nitrosodiphenylamine, *p*-nitrosoaniline, *p*-nitrosodimethylaniline and *p*-nitrosodiethylaniline, compounds containing the *p*-nitrosophenylamino group, *p*-$NOC_6H_4N<$, with palladous chloride and palladous nitrate, are described. The highly colored complexes are useful for the detection or colorimetric determination of small amounts of palladium. In the case of the chloride, the complexes have been isolated and found to have the general composition, Pd-$[NOC_6H_4N<]_2Cl_2$.

p-Nitrosodimethylaniline and *p*-nitrosodiethylaniline possess the following advantages over *p*-nitrosodiphenylamine as colorimetric reagents for palladous chloride: (1) faster reaction rate, (2) greater stability, (3) smaller temperature effect, (4) more suitable for spectrophotometric studies.

Relative absorption curves are given for solutions of the reagents and for those of their complexes.

Solutions of the *p*-nitrosodimethylaniline–palladous chloride complex were found to follow the Lambert–Beer law for concentrations of palladium up to 1 : 5,000,000.

A procedure is presented for the colorimetric determination of palladium in the presence of silver.

UNIVERSITY, VIRGINIA RECEIVED JULY 19, 1941

NOTES

t-Butyllithium

BY PAUL D. BARTLETT, C. GARDNER SWAIN AND ROBERT B. WOODWARD

In a number of cases organolithium compounds are found to be much less subject to hindrance in reactions involving addition to the carbonyl group than are the corresponding Grignard reagents.[1,2] The inaccessibility and theoretical interest of tri-*t*-butylcarbinol prompted us to investigate *t*-butyllithium, which had not been reported at the time of this work, and to compare it with *t*-butylmagnesium chloride in its reaction with hexamethylacetone.[3] We find that, like the Grignard reagent, *t*-butyllithium produces with hexamethylacetone only reduction and no addition.

Unsuccessful attempts were made to prepare *t*-butyllithium by the reaction of small pieces of lithium or of lithium globules (made by shaking molten lithium under mineral oil at 250° and cooling) with *t*-butyl chloride in ether or benzene or with *t*-butylmagnesium chloride. Metathesis between phenyllithium and *t*-butylmagnesium chloride was also tried unsuccessfully. However, a vigorous reaction between *t*-butyl chloride and lithium globules could be induced in dry ether under nitrogen by the addition of a little magnesium metal ($^1/_{35}$ of the weight of the lithium) and priming with a little *t*-butylmagnesium chloride. This suggests that a free-radical intermediate in the formation of the Grignard reagent may react with the lithium. A trace of magnesium would suffice for such a process, since it would be constantly regenerated from its chloride by lithium. There was no evidence of appreciable formation of lithium nitride. In a series of runs, the coarser the lithium used the more gas was given off in the formation of the *t*-butyllithium. This gas was

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[1] Wittig, *Ber.*, **68**, 924 (1935).

[2] Ziegler, *Angew. Chem.*, **49**, 455 (1936).

[3] Conant and Blatt, THIS JOURNAL, **51**, 1227 (1929). References to *t*-butyllithium have since appeared in papers by Gilman and coworkers, *ibid.*, **62**, 2813, 3206 (1940).