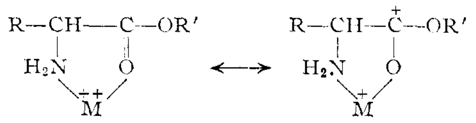
glycine ester results in an electron pull away from the carbon of the carbonyl group, thus facilitating attack by OH^-. The cupric complex of glycine ester is more stable than the nickel complex, resulting in a higher specific rate constant, as is seen in Table III. The values of log k_1 of the glycine ester complexes are about the same as those of the corresponding ammonia complexes, and for this reason we have not drawn the glycine ester complex as a chelate.

On the other hand, we have shown that the nickel complex of cysteine ester is probably a chelate, with the amino group and sulfhydryl ion as the predominant binding sites. On comparing the thermodynamic and kinetic data on the glycine and cysteine esters, it may seem strange at first that the specific rate constants for the alkaline hydrolysis of cysteine ester, in the presence of nickel ion, is not larger than 2.28 l.-mole^{-1} sec.$^{-1}$. If one remembers however that the net charges for the NiA_2 complexes are +2 and 0 for glycine ester and cysteine ester, respectively, then it is reasonable to assume that the net charge on the complex would facilitate the alkaline hydrolysis of glycine ester, but not cysteine ester.

The slower hydrolysis of cysteine ester, relative to glycine ester, both esters in the absence of divalent cation, is likewise explained. The negative charge of the cysteine ester anion inhibits the attack by OH^-, whereas no such inhibiting factor exists for the uncharged glycine ester. Calcium ion does not form complex with cysteine ester, and the data show that calcium does not catalyze the hydrolysis of the ester.

According to Kroll,[9] the actual intermediate complex required for the hydrolysis of amino acid esters is



He studied the cobalt induced hydrolysis of methyl esters of glycine and cysteine at pH 7.9 (Co^{++}, 0.016 M; ester concn., 0.016 M) and reported the following specific rate constants: $k_{\text{glycine ester}} = 0.0262$ sec.$^{-1}$ at 25°, $k_{\text{glycine ester}} = 0.0156$ sec.$^{-1}$ at 25.4°, $k_{\text{cysteine ester}} = 0.0121$ at 25°. The inhibition of ester hydrolysis for cysteine ester was attributed to the strong competition of sulfhydryl ion for the metal ion, so that the binding of the carbonyl oxygen to the metal ion is decreased. In these experiments Kroll used 0.14 M tris-(hydroxymethyl)-aminoethane as buffer (ester concn., 0.016 M) and did not take into account the interaction between the metal ion and the buffer constituent.

Benesch and Benesch[10] found that the reactivity of tris toward silver is of the same order as that of ammonia. We have found that the formation constants of copper(II) and nickel complexes with tris and with glycine esters are also of the same order of the values for the corresponding metal complexes of ammonia. In the light of these observations, Kroll's conclusion about the inhibition of cysteine ester hydrolysis is subject to reservations.

Acknowledgments.—The authors greatly appreciate support of the National Science Foundation and the American Philosophical Society which made this work possible.

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[9] H. Kroll, THIS JOURNAL, **74**, 2036 (1952).

[10] R. E. Benesch and R. Benesch, *ibid.*, **77**, 2749 (1955).

PITTSBURGH, PA.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, TEXAS SOUTHERN UNIVERSITY]

Interaction of Palladium(II) Nitrate and of Palladium(II) Sulfate Solutions with 1,2,3-Benzotriazole[1]

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RECEIVED JANUARY 16, 1956

A quantitative study of the reaction of palladium(II) sulfate and of palladium(II) nitrate solutions with 1,2,3-benzotriazole has been made. In these reactions, precipitation tests and elemental analyses showed that two palladium substitution compounds and two palladium substitution, coördination compounds were formed.

In a previous study, the preparation of two palladium coördination compounds that are formed in the interaction of palladium(II) chloride with 1,2,3-benzotriazole has been reported.[2] Palladium(II) chloride has been determined both gravimetrically and amperometrically using 1,2,3-benzotriazole as a precipitant.[3]

The purpose of the present study was to investigate the interaction of palladium(II) nitrate and of palladium(II) sulfate systems with 1,2,3-benzotriazole in an attempt to elucidate the chemistry of the reactions.

Experimental

Materials and Preparation of Solutions.—A dilute nitric acid solution of palladium(II) and a dilute sulfuric acid solution of palladium(II) were prepared from palladium metal powder, obtained from A. D. Mackay, Inc. These solutions were standardized using modifications of the Gilchrist–Wichers scheme.[4]

Standard 1,2,3-benzotriazole solution was prepared as described by Wilson and Wilson.[2] All other materials used were C.P. reagent grade chemicals.

Analytical Methods.—The determinations of carbon, hydrogen and nitrogen content in the compounds reported under "Procedure" were performed by Laboratory of Microchemistry, Tiedcke, N. J. Analyses of all other elements were carried out in our laboratory using conventional

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[1] This work was supported by a grant from the National Science Foundation.

[2] R. F. Wilson and L. E. Wilson, THIS JOURNAL, **77**, 6204 (1955).

[3] R. F. Wilson and L. E. Wilson, *Anal. Chem.*, **28**, 93 (1956).

[4] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 338–383.

methods. All precipitates were filtered using fine porosity, sintered-glass crucibles.

Procedure.—Three samples, each containing 0.143 mmole of palladium, of the stock palladium(II) sulfate solution were treated with sodium acetate to neutralize excess sulfuric acid. These solutions were heated to about 60°, and a 2.5% solution of 1,2,3-benzotriazole (dissolved in 50% acetic acid) was added until the mole ratio of reagent to palladium was about 5 to 1. The precipitates which were formed were digested for 10 minutes, and then they were filtered. These precipitates were washed several times with dilute acetic acid (1:100), and finally several times with warm distilled water. After drying the precipitates at 130° for 1 hour to constant weight, the following weights of the three precipitates were obtained: 56.1, 56.0, 56.0 mg. *Anal.* Calcd. for the gray colored precipitate: Pd, 27.2; C, 36.8; H, 2.32; N, 21.4; SO_4, 12.3. Found: Pd, 27.2; C, 36.5; H, 2.34, N, 21.6; SO_4, 12.3. Formula of the compound appears to be $[Pd(C_6H_4NN_2)(C_6H_4NHN_2)]_2(SO_4)$.

Three aliquots of the standard palladium(II) sulfate solution were treated with sodium acetate and 0.200 mmole of a 0.100 molar standard 1,2,3-benzotriazole solution, in amounts such that the molar concentration of palladium remained in slight excess. After standing at room temperature for 12 hours, the precipitates were filtered, washed, dried and weighed in the usual manner. The following weights were obtained from the three beige colored precipitates: 54.6, 54.5, 54.6 mg. *Anal.* Calcd. for the precipitates: Pd, 39.1; C, 26.4; H, 1.48; N, 15.4; SO_4, 17.6. Found: Pd, 39.1; C, 26.5; H, 1.69; N, 15.4; SO_4, 17.6. Formula of compound corresponds to $[Pd(C_6H_4NN_2)]_2(SO_4)$.

Samples of the standard palladium(II) nitrate solution, each containing 0.114 mmole of palladium were treated with 10 ml. of acetate buffer (2 *M* in acetic acid and in sodium acetate) and were heated to about 60°. The palladium was precipitated using an excess of 2.5% benzotriazole solution; the precipitates after being digested for 10 minutes were filtered, washed, dried and weighed in the usual way. The yellow precipitates gave the following weights: 46.2, 46.3, 46.3 mg. *Anal.* Calcd. for the precipitate: Pd, 26.3; C, 35.5; H, 2.24; N, 24.2. Found: Pd, 26.3, C, 35.7; H, 2.38; N, 24.0. The data correspond to the formula $Pd(C_6H_4NN_2)(C_6H_4NHN_2)(NO_3)$.

Aliquots of the standard palladium(II) nitrate solution were treated with 10 ml. of acetate buffer and 0.200 mmole of 1,2,3-benzotriazole solution, in amounts such that palladium remained in excess. These precipitates after standing at room temperature for 12 hours were filtered, washed, dried and weighed as usual. The weights of the yellow-colored precipitates were: 57.3, 57.3, 57.4 mg. *Anal.* Calcd. Pd, 37.2; C, 25.1; H, 1.41; N, 19.5. Found: Pd, 37.2; C, 25.3; H, 1.56; N, 19.4. The data indicate that the formula is $Pd(C_6H_4NN_2)(NO_3)$.

Discussion

Elemental analyses and weight relations obtained in this study indicated that two palladium substitution type compounds and two substitution, coördination type compounds were produced. On the basis of the elemental analyses; the observed formulas are $[Pd(C_6H_4NN_2)(C_6H_4NHN_2)]_2(SO_4)$, $[Pd(C_6H_4NN_2)]_2(SO_4)$, $Pd(C_6H_4NN_2)(C_6H_4NHN_2)(NO_3)$ and $Pd(C_6H_4NN_2)(NO_3)$, and their formula weights are 783.93, 545.69, 405.94 and 286.82, respectively. The experimental results indicate that the interaction of 1,2,3-benzotriazole with excess palladium ions involves the removal of an acidic hydrogen and the reaction is probably

$$Pd^{++} + C_6H_4NHN_2 \longrightarrow [Pd(C_6H_4NN_2)]^+ + H^+ \quad (1)$$

However, when excess 1,2,3-benzotriazole is present the course of the reaction probably includes the addition of another reagent molecule by coördination

$$[Pd(C_6H_4NN_2)]^+ + C_6H_4NHN_2 \longrightarrow [Pd(C_6H_4NN_2)(C_6H_4NHN_2)]^+ \quad (2)$$

Hence, in excess palladium, nitrate and sulfate ions give the following reactions

$$[Pd(C_6H_4NN_2)]^+ + NO_3^- \longrightarrow Pd(C_6H_4NN_2)(NO_3)\downarrow \quad (3)$$

$$2[Pd(C_6H_4NN_2)]^+ + SO_4^= \longrightarrow [Pd(C_6H_4NN_2)]_2(SO_4)\downarrow \quad (4)$$

In excess 1,2,3-benzotriazole, the reactions appear to follow the path

$$[Pd(C_6H_4NN_2)(C_6H_4NHN_2)]^+ + NO_3^- \longrightarrow Pd(C_6H_4NN_2)(C_6H_4NHN_2)(NO_3)\downarrow \quad (5)$$

$$2[Pd(C_6H_4NN_2)(C_6H_4NHN_2)]^+ + SO_4^= \longrightarrow [Pd(C_6H_4NN_2)(C_6H_4NHN_2)]_2(SO_4)\downarrow \quad (6)$$

The four compounds produced in the above reactions are soluble in solutions which contain an excess of cyanide or thiocyanate ions, but the precipitates are insoluble in most organic solvents and in most inorganic acids. The dried precipitates are stable up to at least 300°. As yet, it has not been possible to carry out X-ray examination of these compounds; the investigation of the structure of these interesting compounds will be pursued further.

Houston 4, Texas