[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY, TULANE UNIVERSITY]

The Factors Affecting the Directive Influence of the Nitro Group in the Nitro Complexes of Palladium(II)[1]

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Although the existence of the *cis* series of palladous ammines has been questioned,[4] Grunberg and Shulman[5] were able to prepare the *cis*-dichlorodiammine palladium(II) complex with physical and chemical properties different from its *trans* isomer.

The compound *cis*-dinitrodiammine palladium(II) was prepared by Mann[6] and was found to differ from the *trans* compound isolated by Lang[7] in all its properties. An X-ray investigation showed the *cis* complex to have 8 molecules per unit cell as compared to one for the corresponding *trans* compound. Such a large number of molecules per unit cell is usually found for the unsymmetrical *cis* compounds.[8,9,10]

The dimer $Pd(NH_3)_4Pd(NO_2)_4$ was found to have an X-ray powder photograph distinctly different from either the *cis* or *trans* monomeric complexes.[6]

The *cis*-dinitrodiammine palladium(II) isomer is unusual in that its preparation[6] seemingly constitutes a complete reversal of Tschernaiev's rule of *trans* elimination.[11] Since the nitro group has one of the strongest *trans* influences,[12,13] the addition of nitrite ions to a solution of $Pd(NH_3)_4^{+2}$ ions should result in the formation of the *trans*-$Pd(NH_3)_2(NO_2)_2$ rather than its *cis* isomer.[6] Similarly allowing ammonia to react with $Pd(NO_2)_4^{-2}$ ions *cis*-$Pd(NO_2)_2(NH_3)_2$ should be formed rather than its *trans* isomer obtained by Mann.[6]

Since an attempt to duplicate Mann's work revealed that the *trans*-dinitrodiammine palladium(II) isomer was formed after the successive removal of two or three crops of the *cis*-dinitrodiammine compound, a detailed study of the conditions affecting the reaction was undertaken.

Experimental

(1) **Special Reagents.**—The C.P. palladous chloride used was obtained from Eimer and Amend, New York, N. Y. All other chemicals and reagents used were of standard C.P. quality.

(2) **Tests Used to Differentiate between the *cis* and *trans* Isomers.**—The tests used to distinguish between the *cis*- and *trans*-dinitrodiammine complexes were essentially the same as those employed by Mann.[6] The *cis*-dinitrodiammine palladium(II) isomer in aqueous solution forms an almost colorless solution upon the addition of potassium iodide. The aqueous solution of the *trans* isomer forms a red colored solution within an hour upon the addition of the iodide. The melting point of the *cis* compound is 233–234° with no evolution of a gas, whereas the *trans* isomer melts at 230–231° with evolution of a gas.

The ignition test also constitutes a rapid and essentially accurate means of differentiation. Ignition of the *trans* compound in a crucible results in an exothermic decomposition, heat and light are often given off, and a gray porous residue is left. The *cis* isomer decomposes quietly leaving a black or gray compact residue. All three of these tests were used in assigning the *cis* or *trans* configuration to each crop of crystals. Grunberg's oxalate test[14] is not applicable to the nitro palladium complexes as interconversion takes place forming the mono-oxalato complex in either case. Several attempts were made to prepare the bi-oxalato complex from the *trans* isomer and oxalic acid, but all attempts were unsuccessful. The thiourea test[15] was also found to be unreliable. The order of addition, the *p*H or the presence of a large excess of thiourea produced similar results with both isomers. All attempts to obtain a constant palladium analysis from the amorphous brown precipitate failed.

(3) **Preparations. A.** ***trans*-Dichlorodiammine Palladium(II).**—The *trans*-dichlorodiammine palladium(II) complex was prepared by treating an aqueous solution of the tetrammine with a slight excess of dilute hydrochloric acid in the manner described by Drew and co-workers.[4]

Anal. Calcd. for $Pd(NH_3)_2Cl_2$: Pd, 50.40; Cl, 33.5. Found: Pd, 50.17; Cl, 33.0.

B. ***trans*-Dinitrodiammine Palladium(II).** (a) **Lang's Method.**[7]—The *trans*-dinitrodiammine complex was prepared by the action of silver nitrite upon the *trans*-dichlorodiammine complex. The product upon recrystallization from hot water was found to melt at 231–232° with evolution of a gas.

Anal. Calcd. for $Pd(NH_3)_2(NO_2)_2$: Pd, 45.83; N, 24.07. Found: Pd, 45.75; N, 23.70.

(b) **Formic Acid Method.**—Five grams of palladous chloride was dissolved in 150 ml. of a mixture of equal amounts of concentrated ammonia and water and the solution evaporated upon the steam-bath until only a faint odor of ammonia was noticeable. The solution was filtered and the volume adjusted to approximately 70 ml. Fourteen grams of sodium nitrite dissolved in 20 ml. of water was added and the solution cooled below 10° in an ice-bath. Four ml. of 90% formic acid solution was then added with stirring. The resulting precipitate was filtered off, washed with 100 ml. of water, alcohol and finally ether. The product, a fine yellow powder, was dried at 100–110° for one hour. The melting point was found to be 227–228° with evolution of a gas; yield approximately 55%.

Anal. Calcd. for $Pd(NH_3)_2(NO_2)_2$: Pd, 45.83; N, 24.07. Found: Pd, 45.57; N, 24.55.

C. ***cis*-Dinitrodiammine Palladium(II).**—The *cis*-dinitrodiammine palladium(II) isomer was prepared by treating an ammoniacal solution of the *trans*-dichlorodiammine compound with a concentrated solution of sodium nitrite in the manner described by Mann.[6] The product was found to melt at 234–235° with no evolution of a gas.

D. **Potassium Nitropalladite.**—Potassium nitropalladite was prepared according to the general instructions given by Gibbs.[16] Five grams (0.028 mole) of palladous chloride

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[2] Abstracted in part from the Ph.D. dissertation of N. L. Cull, June, 1950.

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[6] F. G. Mann, D. Crowfoot, D. Gattiker and W. Wooster, *J. Chem. Soc.*, 1642 (1935).

[7] J. Lang, *J. prakt. Chem.*, **83**, 415 (1861).

[8] E. G. Cox, H. Saenger and W. Wardlaw, *J. Chem. Soc.*, 182 (1934).

[9] E. G. Cox and G. H. Preston, *ibid.*, 1089 (1933).

[10] E. G. Cox, F. W. Pinkard, W. Wardlaw and K. C. Webster, *ibid.*, 459 (1935).

[11] E. Tschernaiev, *Ann. inst. platine* (*U. R. S. S.*), **4**, 261 (1926).

[12] A. Grunberg, *Bull. acad. sci.* (*U. R. S. S.*) *Classe sci. chem.*, 350 (1943).

[13] M. M. Yakshin, *Compt. rend. acad. sci.* (*U. R. S. S.*), **32**, 555 (1941).

[14] A. A. Grunberg, *Helv. Chim. Acta*, **14**, 455 (1931).

[15] J. Kurnakov, *J. prakt. Chem.*, **50**, 483 (1894).

[16] W. Gibbs, *Am. J. Sci.*, **34**, 341 (1862).

was allowed to react with 10.2 g. (0.12 mole) of potassium nitrite dissolved in 250 ml. of water and the solution brought to a boil. The solution was evaporated on the steam-bath to a volume of approximately 50 ml. and then filtered and the filter paper washed with 10 ml. of water. The combined washing and filtrate were then poured slowly with stirring into 300 ml. of 95% ethyl alcohol. A lemon-yellow precipitate settled out immediately. After standing for an hour, it was filtered, washed with alcohol and finally with ether. The product, a light yellow, non-hygroscopic powder was dried for one hour at 100–110°; yield approximately 90% of the monohydrate.

Anal. Calcd. for $K_2Pd(NO_2)_4 \cdot H_2O$: Pd, 27.60. Found: Pd, 27.30.

(4) **Reaction Mechanism Studies.**—A study of the reactions between dichlorodiammine palladium(II), ammonia and sodium nitrite in aqueous solution was undertaken using a Beckman *p*H meter, model G, equipped with a high alkalinity lithium glass electrode. The meter was standardized daily during runs against standard buffer solution *p*H 10 purchased from the National Technical Laboratories, South Pasadena, California. The procedure employed consisted of measuring the initial *p*H of the solution and the *p*H as each crop of crystals were removed. The crystals formed slowly from the mother liquor as it stood in a desiccator over concentrated sulfuric acid (see Prepn. C). The decrease in *p*H with time was due primarily to the absorption of ammonia from the reaction mixture by the sulfuric acid. It was noted that, on measurement of the *p*H after the sodium nitrite had been added to the ammoniacal solution of the dichlorodiammine palladium complex, an initial increase in *p*H occurred. After passing through a maximum the *p*H then gradually decreased with time. The mother liquor after removal of the crystals was again placed in a vacuum desiccator over concentrated sulfuric acid. The crystals were weighed and placed in labeled weighing bottles.

TABLE I

STUDY OF $Pd(NH_3)_2(NO_2)_2$ FORMATION FROM $Pd(NH_3)_2Cl_2$

Soln. no.	Total % *cis*	Total % *trans*	Total % yield	Time at reacn., hr.	*p*H at transition	Remarks
1-A	52.3	27.2	79.5	48	9.33	Mann's cond.[a]
2-A	40.9	31.9	72.8	104	9.52	Mann's cond.[a]
3-A	52.5	23.0	75.5	114	9.70	Mann's cond.[a]
1-B	52.5	23.0	75.5	114	9.70	Mann's cond. (8:1)[a]
2-B	50.0	20.6	70.6	114	9.65	NO_2^-:Pd(II) (6:1)
3-B	36.4	13.7	50.1	96	9.48	NO_2^-:Pd(II) (4:1)
4-B	50.3	6.9	57.2	115	9.42	NO_2^-:Pd(II) (2:1)
5-B	40.9	27.6	68.5	96	9.80	NO_2^-:Pd(II)(10:1)
6-B	43.4	27.3	70.7	96	9.87	NO_2^-:Pd(II)(12:1)
1-C	45.5	20.6	66.1	96	9.94	NH_3:Pd(II)(3.2:1)
2-C	59.2	20.6	79.8	96	9.98	NH_3:Pd(II)(6.4:1)
3-C	52.5	23.0	75.5	114	9.70	Mann's cond. (8:1)[a]
4-C	43.2	23.0	66.2	96	9.96	NH_3:Pd(10.2:1)
1-D	52.5	23.0	75.5	114	9.70	Mann's cond. 0.38 *M*[a]
2-D	4.6	50.2	54.8	129	9.94	Pd(II) .24 *M*
3-D	-0-	73.2	73.2	156	...	Pd(II) .16 *M*
4-D	-0-	75.4	75.4	228	...	Pd(II) .12 *M*
1-E	-0-	77.6	77.6	42	...	Temp. 35–40°
2-E	-0-	61.7	61.7	42	...	Temp. 35–40°
3-E	59.1	38.8	97.9	256	10.99	Temp. 10–13°
4-E	68.2	27.5	95.7	192	10.89	Temp. 10–13°
1-F	45.7	34.2	79.9	84	7.75	Substn. of NH_4NO_2 for $NaNO_2$
2-F	43.4	45.5	88.9	84	7.79	
1-G	-0-	82.0	82.0	178	...	Substn. *cis* and *trans* $Pd(NH_3)_2(NO_2)_2$ 25° as starting material
2-G	-0-	77.4	77.4	178	...	
3-G	-0-	63.8	63.8	68	...	
4-G	-0-	77.4	77.4	68	...	
5-G	-0-	59.4	59.4	160	...	Temp. 10°
6-G	-0-	69.0	69.0	160	...	Temp. 10°
1-H	61.5	9.0	70.5	239	9.88	Addn. of Cl^-, Temp. 10°.
2-H	52.4	9.0	61.4	239	9.77	
1-J	45.6	32.0	77.6	96	9.95	*cis*-$Pd(NH_3)_2Cl_2$ starting material
2-J	40.9	29.7	70.6	96	10.01	*trans*-$Pd(NH_3)_2Cl_2$ starting material

[a] 0.38 mole of $PdCl_2$ was dissolved in 3 moles of concd. NH_3. The mixture was heated and filtered. Three moles of NO_2^- ions was added and the mixture was allowed to crystallize in a desiccator over concd. H_2SO_4.

Several tests including the reaction with potassium iodide, the melting point and an ignition test were made to determine whether the product was *cis* or *trans*. A compilation of all the results obtained is given in Table I.

(A) **Mann's Conditions.**—Three individual runs were made under the conditions employed by Mann in the preparation of the *cis*-dinitrodiammine complex (see Prep. C). Results for solutions 1-A, 2-A and 3-A are given in Table I.

(B) **Effect of Variations in Nitrite Ion Concentration.**—The mole ratio of sodium nitrite to palladium was varied from a 2:1 ratio, *i.e.*, the theoretical amount necessary for complete reaction, up to a 12:1 ratio, which is higher than that used by Mann (8:1). Results for solutions 1-B through 6-B inclusive are shown in Table I.

(C) **Effect of Variations in Ammonia Concentration.**—Four runs, the results of which are given in Table I (Solutions 1-C, 2-C, 3-C and 4-C), were made in which the concentration was varied from a slight excess over theoretical, up to a slight excess over the amount employed by Mann.

(D) **Effect of Dilution.**—The molarity of the solutions used with respect to palladium was varied from 0.38 *M* (Mann's conditions) to 0.12 *M*. Table I shows the results obtained for solutions 1-D through 4-D inclusive.

(E) **Effect of Temperature Variation.**—The temperature studies at 40° were made by placing a desiccator in an oven regulated by a thermal regulator to ±2°. The solutions of dichlorodiammine palladium(II), ammonia and sodium nitrite were heated in a water-bath to 40° prior to mixing. No significant rise in temperature was noted on mixing. Measurements were made as rapidly as possible and the mother liquor replaced in the desiccator after each measurement. The low temperature studies were made in a similar manner by placing the desiccator in a refrigerator at 10–12°. Upon removal of the solutions for measurement, an ice-bath was used to keep the solutions at a low temperature. The temperature measurements at high and low temperatures are only qualitative studies. The results for solutions 1-E, 2-E, 3-E and 4-E are given in Table I.

(F) **Effect of Substitution of Ammonium Nitrite for Sodium Nitrite.**—A fresh ammonium nitrite solution, approximately 18%, specific gravity 1.18, obtained from J. T. Baker Chemical Co., Phillipsburg, New Jersey was used in this study. Two runs were made using an 8:1 molar ratio of ammonium nitrite to palladium; the results are shown in Table I, solutions 1-F and 2-F.

(G) **Effect of Substitution of** *cis*- **or** *trans*-$Pd(NH_3)_2(NO_2)_2$ **for** $Pd(NH_3)_2Cl_2$ **as a Starting Material.**—Studies, using the dinitrodiammine complex as the starting material instead of the dichlorodiammine compound (solutions 1-G and 2-G), were made with the *trans*-dinitrodiammine complex as prepared by the formic acid method. Solutions 3-G and 4-G utilized the *cis* and *trans* nitro complexes, respectively, as obtained from Mann's conditions. Solutions 5-G and 6-G were run at low temperatures using the method described in Section E. Results are shown in Table I.

(H) **Effect of Using** $Pd(NH_3)_2(NO_2)_2$ **as a Starting Material and Adding Two Equivalents of Sodium Chloride.**—One and eight-tenths grams of $Pd(NH_3)_2(NO_2)_2$ was dissolved in 10 ml. of water and five ml. of concentrated ammonia. This solution was added to a solution of 3.9 g. of sodium nitrite and 1.1 g. of sodium chloride in 15 ml. of water after both solutions had been cooled to 10° in an ice-bath. The resulting mixture was placed in a desiccator over concentrated sulfuric acid and maintained at a temperature of 7–10° in a refrigerator. Fractions were removed, the *p*H measured and the precipitates tested to determine whether they were *cis* or *trans*. It was found that under these conditions a large yield (over 50%) of the *cis* isomer was obtained.

Discussion

(1) **Reactions between** $Pd(NH_3)_2Cl_2$**, Ammonia and Sodium Nitrite.**—A mechanism is postulated, involving the formation of the $[Pd(NH_3)(NO_2)_2Cl]^-$ ion, which not only explains all of the observed phenomena, but also is in complete accord with Tschernaiev's rule of *trans* elimination.

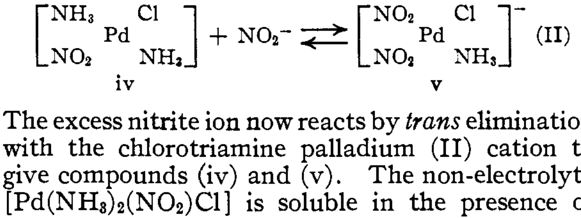
The first of the solution equilibria to be considered is the reaction of the dichlorodiammine palladium(II) with excess ammonia.

(A) **(Reaction I).**—

$$[\mathrm{Pd(NH_3)_2Cl_2}] + \mathrm{NH_3} \rightleftarrows [\mathrm{Pd(NH_3)_3Cl}]^+ + \mathrm{NH_3} \rightleftarrows [\mathrm{Pd(NH_3)_4}]^{++} \quad \text{(I)}$$

In the presence of excess ammonia, the equilibrium is shifted toward the formation of the $[\mathrm{Pd(NH_3)_4}]^{++}$ ion. Upon standing in the desiccator over concentrated sulfuric acid, the concentration of ammonia decreases and the equilibrium is slowly forced to favor the formation of the $[\mathrm{Pd(NH_3)_3Cl}]^+$ ion.

(B) **(Reaction II).**—The chlorotriammine palladium(II) ion then undergoes the following equilibrium reactions (Reaction II) by *trans* elimination.



$$\left[\begin{array}{ccc} \mathrm{NH_3} & & \mathrm{Cl} \\ & \mathrm{Pd} & \\ \mathrm{NH_3} & & \mathrm{NH_3} \end{array}\right]^+ + \mathrm{NO_2}^- \rightleftarrows$$

ii

$$\left[\begin{array}{ccc} \mathrm{NH_3} & & \mathrm{Cl} \\ & \mathrm{Pd} & \\ \mathrm{NO_2} & & \mathrm{NH_3} \end{array}\right] + \mathrm{NO_2}^- \rightleftarrows \left[\begin{array}{ccc} \mathrm{NO_2} & & \mathrm{Cl} \\ & \mathrm{Pd} & \\ \mathrm{NO_2} & & \mathrm{NH_3} \end{array}\right]^- \quad \text{(II)}$$

iv v

The excess nitrite ion now reacts by *trans* elimination with the chlorotriamine palladium (II) cation to give compounds (iv) and (v). The non-electrolyte $[\mathrm{Pd(NH_3)_2(NO_2)Cl}]$ is soluble in the presence of excess nitrite ion to give the chlorodinitroammine palladium(II) ion. The following experimental data can be cited as evidence for the postulated reaction mechanism.

(a) **Change in *p*H.**—The *p*H increases slowly after the addition of the solution containing nitrite ion to the ammoniacal solution of $[\mathrm{Pd(NH_3)_2Cl_2}]$. Replacement of coördinated ammonia molecules by nitrite ions should produce an increase in *p*H.

The *p*H studies also favor the above postulate. The total decrease in *p*H during the period of crystallization of the *cis*-dinitrodiammine palladium(II) amounts to several *p*H units, indicating that the coördinated ammonia molecules become more labile as the *p*H decreases and are, therefore, displaced by the nitrite ion as in compounds (iv) and (v). However, the final *p*H above 9 indicates that the ammonia is present in excess over the stoichiometric amount throughout the reaction.

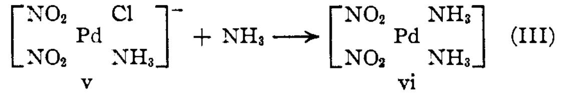
(b) **Effect of Chloride Ion.**—The reaction occurring when the *cis*- or *trans*-dinitrodiammine palladium(II) is substituted for the dichlorodiammine compound as a starting material seems to indicate that the chlorotriammine palladium(II) complex reacts with the nitrite ion. Under these conditions, only the *trans*-dinitrodiammine palladium(II) complex crystallizes from the solution according to the reaction

$$\left[\begin{array}{c} \mathrm{Pd(NH_3)_2(NO_2)_2} \\ \textit{cis}\text{ or }\textit{trans} \end{array}\right] + \mathrm{NH_3} \rightleftarrows [\mathrm{Pd(NH_3)_3NO_2}]^+ + \mathrm{NO_2}^- \rightleftarrows \left[\begin{array}{c} \mathrm{Pd(NH_3)_2(NO_2)_2} \\ \textit{trans} \end{array}\right]$$

However, if chloride ions are introduced into the reaction mixture, the *cis*-dinitrodiammine palladium(II) isomer precipitates out followed by the *trans* isomer. This seems to indicate that the $[\mathrm{Pd(NH_3)_3Cl}]^+$ plays an essential role in Reaction I and initiates the reaction with the nitrite ion to give the *cis* isomer.

(c) **Failure of the Non-electrolyte $[\mathrm{Pd(NH_3)_2(NO_2)Cl}]$ to Precipitate.**—From solubility considerations, it would be expected that the compound $[\mathrm{Pd(NH_3)_2(NO_2)Cl}]$ should precipitate from the reaction mixture. Failure to obtain this non-electrolyte seems to indicate that the *trans*-$[\mathrm{Pd(NH_3)_2(NO_2)Cl}]$ is more soluble in excess nitrite ion than either *cis*- or *trans*-$[\mathrm{Pd(NH_3)_2(NO_2)_2}]$. In the reaction between the *cis*- or *trans*-dinitrodiammine palladium(II) complex, ammonia and sodium nitrite only, the *trans* dinitro isomer is obtained. The presence of the chloride ion in the coördination sphere thus seems to prevent the precipitation of the non-electrolyte, $[\mathrm{Pd(NH_3)_2(NO_2)Cl}]$. Introduction of another nitro group into the complex leads then to the formation of the dinitrochloroammine palladium(II) anion.

(C) **(Reaction III).**—In Reaction III the coördinated chloride is displaced by ammonia, which is still present in rather large excess, by *trans* elimination.



$$\left[\begin{array}{ccc} \mathrm{NO_2} & & \mathrm{Cl} \\ & \mathrm{Pd} & \\ \mathrm{NO_2} & & \mathrm{NH_3} \end{array}\right]^- + \mathrm{NH_3} \longrightarrow \left[\begin{array}{ccc} \mathrm{NO_2} & & \mathrm{NH_3} \\ & \mathrm{Pd} & \\ \mathrm{NO_2} & & \mathrm{NH_3} \end{array}\right] \quad \text{(III)}$$

v vi

The *trans* effect of the stronger coördinating and more electronegative nitro group should increase the lability of the chloride ion and increase its tendency for displacement. Under these conditions the solubility product of the *cis*-dinitrodiammine palladium(II) is exceeded and the complex precipitates out of solution.

The important step in the mechanism of *cis* formation seems to be the introduction of three electronegative groups into the molecule which then reacts with the excess ammonia present to give the *cis* isomer. This is verified by the reaction between potassium nitropalladite and ammonia in which the *cis*-dinitrodiammine palladium(II) isomer is formed.

$$[\mathrm{Pd(NO_2)_4}]^- + \mathrm{NH_3} \rightleftarrows [\mathrm{Pd(NH_3)(NO_2)_3}]^- + \mathrm{NH_3} \longrightarrow \textit{cis}\text{-}[\mathrm{Pd(NH_3)_2(NO_2)_2}]$$

In the reaction of *cis*- or *trans*-dinitrodiammine palladium(II) with ammonia and sodium nitrite, the third electronegative group never enters the coördination sphere, since the *trans*-$[\mathrm{Pd(NH_3)_2(NO_2)_2}]$ precipitates from the reaction mixture. However, the presence of a chloride ion in the coördination sphere *trans* to a nitro group makes this non-electrolyte react with the nitrite ion to give the dinitrochloroammine palladium(II) anion. The dinitrochloroammine palladium(II) anion may then react in two possible ways to form the *cis* dinitro isomer.

$$[\mathrm{Pd(NH_3)(NO_2)_2Cl}]^- + \mathrm{NO_2}^- \rightleftarrows [\mathrm{Pd(NH_3)(NO_2)_3}]^- + \mathrm{NH_3} \rightleftarrows \textit{cis}\text{-}[\mathrm{Pd(NH_3)_2(NO_2)_2}] \quad \text{(a)}$$

$$[\mathrm{Pd(NH_3)(NO_2)_2Cl}]^- + \mathrm{NH_3} \rightleftarrows \textit{cis}\text{-}[\mathrm{Pd(NH_3)_2(NO_2)_2}] \quad \text{(b)}$$

The latter reaction is favored because it is believed that the chloro group would be more readily eliminated than the nitro group in the presence of ammonia. This is in agreement with the observations of Tschernaiev.[17]

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[17] I. I. Tschernaiev, *Ann. inst. platine*, **6**, 23 (1928).

(D) (Reaction IV).—However, the *cis*-dinitrodiammine palladium(II) isomer is rather soluble and the *cis* complex in solution can undergo further reaction (Reaction IV) in the presence of the excess of ammonia and nitrite ion.

$$[Pd(NH_3)_2(NO_2)_2] + NH_3 \rightleftharpoons [Pd(NH_3)_3(NO_2)]^+ + NO_2^- \rightleftharpoons [Pd(NH_3)_2(NO_2)_2] \quad (IV)$$

Again *trans* elimination occurs in the formation of the *trans*-dinitrodiammine palladium(II) from the nitrotriammine palladium(II) cation. The following experimental data favor the above reaction mechanism.

(a) *p*H Studies.—From Table I, solutions 1-A, 2-A and 3-A, it can be seen that when the *p*H drops below 9.7 the *trans*-dinitrodiammine isomer is formed. If it is assumed that a large amount of the *cis* isomer (vi) is formed, an appreciable amount of the *cis* isomer will remain in solution, since it has been shown to be more soluble than the *trans* compound. The *cis* isomer in solution will be in equilibrium with (vii) and as the *p*H decreases the tendency for the replacement of the coördinated ammonia by nitrite ions will increase. This replacement occurs by regular *trans* elimination and the less soluble *trans*-dinitrodiammine isomer precipitates.

The formation of the *trans* isomer from the tetrammine by the action of sodium nitrite and formic acid (see preparations) can be explained by the increase in lability of the coördinated ammonia molecules in acid solution. The *p*H seems to exert a dual effect. It is a measure of the ammonia concentration and it affects the lability of the ammonia groups in the coördination sphere. The latter effect probably becomes of major importance in solutions of low *p*H.

(b) Temperature Studies.—Since the *cis*-dinitrodiammine isomer would be expected to be more insoluble at lower temperatures, an increase in its yield would be expected. Similarly, since the solubility of the *trans* isomer would also be decreased, the total per cent. yield should be higher. An examination of Table I, solutions 3-E and 4-E, shows that this is the case. The fact that at 40° no *cis* isomer formed, can also be explained by the greater solubility of the *cis* form. The soluble *cis* isomer forms the *trans* compound which precipitates by the *trans* elimination mechanism.

(c) Dilution Studies.—The effect of dilution can also be explained by a consideration of the greater solubility of the *cis* isomer. In dilute solutions the concentration of the *cis* isomer is much smaller and it will not precipitate. The reaction will therefore proceed as in step IV to form the *trans* isomer.

(d) Ammonium Nitrite Studies.—The same mechanism can be used to explain the formation of the *cis* isomer at relatively low *p*H values (8–9) when ammonium nitrite is substituted for sodium nitrite. The concentration of ammonia will be maintained fairly high by the presence of a large excess of the ammonium salt. Thus even at lower *p*H values the concentration of ammonia will favor the formation of the *cis* isomer.

(e) Reaction between $K_2Pd(NO_2)_4$ and NH_3.—If $K_2Pd(NO_2)_4$ is treated with ammonia in the cold, the *cis*-dinitrodiammine palladium(II) isomer is obtained in significant yield, followed by the formation of the *trans* isomer. This would seem to indicate that the *cis* isomer is formed first even at room temperatures and that it then rearranges to form the more insoluble *trans*-dinitrodiammine palladium(II) isomer by the mechanism postulated in Reaction IV.

(5) Mechanism Study of the Reaction between $K_2Pd(NO_2)_4$ and NH_3.—This investigation was made in a manner analogous to that described in the preceding section. Potassium nitropalladite was treated with ammonia and the initial *p*H and the *p*H, as successive crops of crystals were obtained, was measured. Results are given in Table II. Solutions were 1-A through 4-A. These were run at room temperatures and in accord with Mann's work.[6] Only the *trans* isomer was obtained. Solutions 1-B and 2-B were run at low temperatures (10–12°), and under these conditions it was found possible to obtain appreciable yields of the *cis* isomer. The tests described in an earlier section were used to differentiate between the *cis* and *trans* isomers.

TABLE II

STUDY OF REACTION BETWEEN POTASSIUM NITROPALLADITE AND AMMONIA

Soln. no.	Total % *cis*	Total % *trans*	Total % yield	Time at reacn. hr.	*p*H at transition	Remarks
1-A	-0-	27.3	27.3	191	..	25 ml. H_2O 25°
2-A	-0-	27.3	27.3	191	..	25 ml. H_2O 25°
3-A	-0-	34.3	34.3	121	..	20 ml. H_2O (Mann's cond.)
4-A	-0-	31.8	31.8	121	..	15 ml. H_2O 25°
1-B	22.9	13.6	36.5	210	9.86	Mann's cond. temp. 10–12°[a]
2-B	20.5	16.0	36.5	210	9.81	Mann's cond. temp. 10–12°[a]

[a] See Table I.

Discussion

Reaction between $K_2Pd(NO_2)_4$ and NH_3.—A postulated reaction mechanism is given below for the reaction between potassium nitropalladite and ammonia.

$$K_2Pd(NO_2)_4 + NH_3 \rightleftharpoons [Pd(NH_3)(NO_2)_3]^- + NH_3 \rightleftharpoons \underset{cis}{[Pd(NH_3)_2(NO_2)_2]} \quad (I)$$

$$\underset{cis}{[Pd(NH_3)_2(NO_2)_2]} + NH_3 \rightleftharpoons [Pd(NH_3)_3(NO_2)]^+ NO_2^- \rightleftharpoons \underset{trans}{[Pd(NH_3)_2(NO_2)_2]} \quad (II)$$

Table II, solutions 1-A through 4-A, shows that at room temperature only the *trans* isomer is obtained. This can be explained by the greater solubility of the *cis* isomer in solutions of lower ionic strength. The mechanism of *trans* formation from the *cis*-dinitrodiammine palladium(II) isomer in solution has been discussed previously. The increased solubility of the *cis* form is also shown to a lesser degree by the *trans* isomer. A decrease in the percentage yield would then be expected under the above conditions, which is verified by the experimental results. At lower temperatures (10–12°) an appreciable yield of the *cis* isomer was obtained, because of the decreased solubility of the *cis* form. Table II, solutions 1-B and 2-B, shows that at low temperatures both *cis* and *trans* isomers are formed. It becomes obvious that under the above conditions the presence of the chloride ion is not necessary for the formation of the *cis* isomer.

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Summary

1. The reactions between $[Pd(NH_3)_2Cl_2]$, ammonia and sodium nitrite in aqueous solution were investigated with respect to the effect of variations in temperature, concentration of palladium, nitrite ion, ammonia and chloride ion.

2. Cold concentrated palladium solutions containing chloride ion favor the formation of the *cis*-dinitrodiammine palladium(II) isomer.

3. The *cis*-dinitrodiammine isomer in solution slowly reacts in a stepwise manner with ammonia and nitrite ion to form the *trans* isomer.

4. The ammonia and nitrite ion concentrations have relatively little effect upon the product formed.

5. The effect of *p*H may be of minor importance, low *p*H values favoring *trans* formation.

6. Small yields of the *cis* isomer were obtained in the cold by the action of ammonia upon the nitropalladite.

7. A mechanism is postulated which can explain all of the observed phenomena only if *trans* elimination is assumed.

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Hydrogen Exchange between Cracking Catalyst and the Butanes[1]

BY S. G. HINDIN, G. A. MILLS AND A. G. OBLAD

It is now established that oxide cracking catalysts are "acidic" in nature and that the "acidity" is responsible for the activity of this group of catalysts.[2a,b] The polarized complex (carbonium ion) theories, which have been successful in correlating the mechanisms of acid catalysis, have also been successful in explaining the chemistry of catalytic cracking in a general way.[2b,3] However, more detailed information on the nature of the catalyst–hydrocarbon complexes and the mechanisms of hydrogen transfer reactions is needed to establish the specific reaction of the catalyst with hydrocarbons. A study of the exchange reactions occurring between the cracking catalyst and hydrocarbon molecules offers such opportunity since it has been shown that cracking catalysts promote hydrogen exchange between water and hydrocarbons at temperatures far below those at which cracking occurs.[3,4]

A general study was made of the hydrogen exchange reactions of a typical silica–alumina cracking catalyst with various hydrocarbon classes. The results confirmed the general findings of Hansford[3] concerning the relative temperatures required for the exchange. In order to measure the factors critical to the exchange, a more detailed study was made with *n*-butane and isobutane. The C_4 paraffins were chosen because, of the paraffins which contain hydrogen atoms linked to primary, secondary, and tertiary carbon atoms, the butanes have the lowest molecular weight and are, therefore, the least complicated for analysis. Furthermore, it is necessary that any complete theory deal adequately with the generally unreactive paraffin molecule. Two effects were looked for: one, to ascertain the effect of structure of the paraffin on reactivity and, two, to determine the effect of other reagents, water, olefin and air on the exchange.

The general experimental procedure was either to contact the paraffin with a silica–alumina cracking catalyst that had been enriched with deuterium or to contact the silica–alumina cracking catalyst containing hydrogen with the monodeuterated hydrocarbon. The reaction time and temperature were chosen on the basis of preliminary work as one hour at 150°. After reaction, the hydrocarbon was removed and analyzed by means of a mass spectrometer. The effect of other agents was followed by incorporating them into the reaction mixture.

Experimental

Preparation of Reagents.—Isobutane, research grade, from Phillips Petroleum Co., was treated with anhydrous aluminum bromide at 0° to remove possible traces of olefins. Individual samples, 11.2 cc. (S.T.P.), were sealed into break-seal ampules under high vacuum conditions and used as needed. Normal butane, research grade, from Phillips Petroleum Co., was used without further purification.

Two monodeuterated isobutanes were prepared, one in which the deuterium was attached to a primary carbon atom, and the other in which it was attached to the tertiary carbon atom. They were prepared by means of the Grignard reaction. Solvent used in the preparation was removed by low-temperature distillation of the hydrocarbon in a Podbielniak column. Since preliminary work had indicated that little exchange was found at 50°, the hydrocarbons were further treated to remove possible olefin contaminants by passage through a bed of silica–alumina catalyst maintained at that temperature. The 2-methylpropane-2-*d* was further treated by passage through 98% sulfuric acid.

The deuterated silica–alumina cracking catalyst was prepared in the following manner: 50 g. of a standard synthetic silica–12.5 wt. % alumina cracking catalyst (Houdry

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