COORDINATION COMPOUNDS

Reaction of Platinum(II) and Palladium(II) Nitrite Complexes with Potassium Bromide

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Abstract—The reaction of nitrite-bridged binuclear platinum and palladium complexes and KBr in aqueous solution is studied. It is shown that the Pt–O–N bridging bond dissociates during the reaction to yield two mono-nuclear complexes. Rate constants of the reaction at 15°C are determined.

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Works [1, 2] describe binuclear platinum(II) and palladium(II) complexes with nitrite bridges. These compounds were prepared by reacting nitrite complexes $[M(NO_2)_4]^{2-}$ or $M(A)_2(NO_2)_2$ (M = Pt, Pd; A = NH₃, NH₂CH₃-m, 1/2C₂H₄(NH₂)₂-en) with aqua compounds, for example,

$$\begin{bmatrix} nNO_{2} \\ nO_{2} \end{bmatrix} + \begin{bmatrix} H_{2}O \\ H_{2}O \end{bmatrix} (NO_{3})_{2} \longrightarrow$$

$$(1)$$

$$\longrightarrow \begin{bmatrix} nPd \\ NO_{2} \\ Pden \\ NO_{2} \end{bmatrix} (NO_{3})_{2} + 2H_{2}O,$$

$$K_{2}\begin{bmatrix} O_{2}N & NO_{2} \\ Pt \\ O_{2}N & NO_{2} \end{bmatrix} + \begin{bmatrix} H_{2}O \\ Pt(NH_{3})_{2} \end{bmatrix} (NO_{3})_{2} \longrightarrow$$

$$(2)$$

$$(2)$$

$$(2)$$

$$(2)$$

This work studies the reactions of nitro complexes with potassium bromide.

EXPERIMENTAL

The synthesis of platinum and palladium complexes with nitrite bridges is described in [1, 2].

 $[Pt(NH_3)_2(OH)_2]$ was prepared by reacting KOH with an aqueous solution of *cis*-diamminediaquaplatinum(II) in a ratio of 2 : 1 (mol/mol), followed by the separation of a $[Pt(NH_3)_2(OH)_2$ precipitate.

The bromide-ion concentration in solution was determined potentiometrically with an ANION-4100 pH-meter/conductometer using a bromide-selective

electrode with reference to an Ag/AgCl electrode. A calibration curve was plotted as the e.m.f. versus KBr concentration in standard solutions ($c = 1 \times 10^{-2}$, 1×10^{-3} , 1×10^{-4} , and 1×10^{-5} mol/L). Temperature was maintained constant with $\pm 0.5^{\circ}$ C oscillations using a thermostat.

The electrical conductivity in aqueous solutions was measured on an ANION-4100 pH-meter/conductometer using a primary conductometric converter (a four-electrode submersible cell). The cell constant was 1 cm^{-1} . The concentration of complexes in the solutions was 1×10^{-3} mol/L.

Instability constants were determined as follows. An aliquot of the complex was dissolved in 30 mL of distilled water and thermostated for 3 h at 25°C. The NO₂⁻ concentration in solutions was determined potentiometrically on an ANION-4100 pH-meter/conductometer using an NO₂⁻ ion-selective electrode with reference to a saturated Ag/AgCl electrode. The ion-selective electrode was calibrated against standard KNO₂ solutions ($c = 1 \times 10^{-2}$, 1×10^{-3} , 1×10^{-4} , and 1×10^{-5} mol/L).

The H⁺ concentration was determined potentiometrically with an ANION-4100 pH-meter/conductometer using a glass electrode with reference to an Ag/AgCl electrode.

In order to react $[NO_2(NH_3)_2PtNO_2Pt(NH_3)_2NO_2]NO_3$ with KBr, the complex (0.1 g) and KBr (0.01808 g) (1 : 1 mol/mol) were dissolved in water (40 mL). After 3 h, the solution was divided into two equal parts. To one part, a solution of K₂[PtCl₄] was poured. Precipitation was not observed, which verified the absence of a cationic complex in the solution. The second part was concentrated to dryness at room temperature. The dry residue was treated with a small amount of water, filtered, and then rinsed with distilled water, ethanol, and diethyl ether. The electrical conductivity of an aqueous solution of



Fig. 1. Substitution-reaction rate vs. KBr concentration at a fixed starting concentration of the complex equal to $c = 1 \times 10^{-3}$ mol/L.



Fig. 2. Substitution-reaction rate vs. the concentration of the complex at a fixed starting KBr concentration equal to $c = 1 \times 10^{-3}$ mol/L.

the thus-prepared precipitate was $21 \times 10^{-6} \Omega \text{ cm}^{-1}$. The reaction between [enPd(NO₂)₂Pden](NO₃)₂ and KBr (1 : 2 mol/mol) was conducted in the same way. The electrical conductivity of an aqueous solution of the thus-prepared precipitate was $28 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$.

To react $[(NH_3)_2Pt(NO_2)_2Pt(NO_2)_2]$ with KBr, to the complex (0.1 g) in water (40 mL), KBr (0.391 g) was added; the reagent ratio was 1 : 2 mol/mol. After 3 h, a solution of $[Pt(NH_3)_4]Cl_2$ was poured to the solution. A yellow precipitate (a) was observed. This precipitate was filtered, and the filtrate was concentrated to a minimum volume. The resulting yellow precipitate (b) was filtered and rinsed with distilled water, ethanol, and

diethyl ether. The elemental analysis of product (b) was carried out as described in [3].

For $[Pt_2(NH_3)_2(NO_2)_2Br_2]$ anal. calcd. (%): Pt, 57.69; NO₂, 13.61; Br, 23.67.

For $[Pt(NH_3)_2Br_2]$ anal. calcd. (%): Pt, 50.13; NO₂, 0; Br, 41.13.

Found (%): Pt, 50.45; NO₂, 0; Br, 41.40.

To react [Pden(NO₂)₂] or [Pt(mNO₂)₂] with KBr, the complex (0.010 g) was dissolved in a 0.3 M aqueous solution of NaNO₃ (50 mL). Then, 10 mL of potassium bromide solution ($c = 1 \times 10^{-2}$ mol/L) was added, and the e.m.f. was measured over time. The bromide-ion concentration did not change.

To plot the curves shown in Figs. 1 and 2, two sets of kinetic experiments were carried out at 15°C. In one set of experiments, the concentration of the complex was fixed ($c = 1 \times 10^{-3}$ mo/L), and the KBr concentration was varied ($c_1 = 1 \times 10^{-3}$ mol/L, $c_2 = 2 \times 10^{-3}$ mol/L, $c_3 = 3 \times 10^{-3}$ mol/L). These experiments were carried out as follows: [NO₂(NH₃)₂PtNO₂Pt(NH₃)₂NO₂]NO₃ (0.0329 g) was dissolved in a 0.3 M solution of NaNO₃ ($V_1 = 40$ mL, $V_2 = 35$ mL, $V_3 = 30$ mL), a KBr solution ($c = 1 \times 10^{-2}$ mo/L; $V_1 = 10$ mL, $V_2 = 15$ mL, $V_3 = 20$ mL) was added, and the e.m.f. was measured over time.

In the second set of experiments, the KBr concentration was fixed ($c = 1 \times 10^{-3}$ mol/L), and the concentration of the complex was varied ($c_1 = 0.5 \times 10^{-3}$ mol/L, $c_2 = 1 \times 10^{-3}$ mol/L, $c_3 = 2 \times 10^{-3}$ mol/L). These experiments were carried out as follows. [NO₂(NH₃)₂PtNO₂Pt(NH₃)₂NO₂]NO₃ ($m_1 = 0.01645$ g, $m_2 = 0.03290$ g, $m_3 = 0.06582$ g) was dissolved in a 0.3 M NaNO₃ solution (40 mL), a KBr solution (10 mL; $c = 1 \times 10^{-2}$ mol/L) was added, and the e.m.f. was measured over time.

The subsequent kinetic experiments were conducted at the starting concentration of the complex equal to $c = 1 \times 10^{-3}$ mol/L and the KBr concentration equal to $c = 2 \times 10^{-3}$ mol/L for complexes with two nitrite bridges (for complexes with one nitrite bridge, $c = 1 \times 10^{-3}$ mol/L). A sample of the complex was dissolved in 40 mL (45 mL) of an NaNO₃ solution (c = 0.3 mol/L), then 10 mL (5 mL) of a KBr solution ($c = 1 \times 10^{-2}$ mol/L) was added, and the e.m.f. was measured over time.

The rate constants calculated from the equation for a second-order reaction within one experiment remain virtually constant.

The table displays the experimental data for the reaction of complexes with potassium bromide at 15°C.

RESULTS AND DISCUSSION

In the consideration of the mechanism of formation of binuclear complexes with nitrite bridges and their reactions with various reagents, one should keep in mind that hydroxo complexes always exist in solutions of acidic aqua compounds, for example,

$$[Pt(NH_3)_2(H_2O)_2]^{2^+} \longrightarrow H^+ + [Pt(NH_3)_2H_2O(OH)]^+,$$

$$[Pt(NH_3)_2H_2O(OH)]^+ \longrightarrow H^+ + [Pt(NH_3)_2(OH)_2].$$
(3)

Thus, nitrite bridges can theoretically form as a result of the substitution of the oxygen atoms of the nitro groups (1) for water molecules in the aqua complexes or (2) for hydroxo groups in equation products.

In the same way, hydroxo complexes existing in solution can enter the reaction when nitro complexes are reacted with various reagents. To evaluate the possibility for the reaction to follow the second route, nitro complexes were reacted with hydroxo compounds:

$$[Pt(NO_2)_4]^{2-} + [Pt(NH_3)_2(OH)_2] \longrightarrow$$

$$\longrightarrow [(NO_2)_2Pt(NO_2)_2Pt(NH_3)_2]^0 + 2OH^-.$$
(4)

The results of pH measurements and the nonappearance of a precipitate of a binuclear complex show that the binuclear complex does not form via substitution for hydroxo groups.

Therefore, in the solutions produced by the reaction between nitro complexes and aqua compounds, unreacted mononuclear hydroxo complex should exist together with the binuclear complex.

The potentiometric titration of the solution of the hydroxo complex $[Pt(NH_3)_2(OH)_2]$ with a KBr solution showed that Br⁻ ions cannot substitute for hydroxo groups.

Thus, in a solution containing both aqua and hydroxo complexes, only aqua complexes can react with $[M(NO_2)_4]^{2-}$ or $M(A)_2(NO_2)_2$ and with KBr.

An argument in favor of this scenario is the fact that the yield of the binuclear complex produced by reaction (2) increases as the solution is acidified, as a result of the displacement of the reaction equilibrium to the left.

Binuclear platinum and palladium complexes with nitrite bridges are stable in aqueous solutions; i.e., M–ONO bonds are not broken by water molecules. This conclusion is supported by the potentiometrically determined instability constants of the complex. For $[(NO_2)_2Pt(NO_2)_2Pt(NH_3)_2]^0$, $k_4(NO_2) = 3.30 \times 10^{-7}$; for $[(NH_3)_2Pt(NO_2)_2Pt(NH_3)_2](NO_3)_2$, $k_2(NO_2) = 1.69 \times 10^{-9}$.

We studied the reaction of binuclear complexes with potassium bromide in aqueous solutions.

Initially, we suggested that the reaction would follow one of the following two routes: Rate constants for the reactions of binuclear platinum(II) and palladium(II) complexes with KBr at $15^\circ C$

Complex	<i>k</i> , L/(mol s)
$\begin{bmatrix} NH_3 & NO_2 & m \\ Pt & Pt \\ NH_3 & NO_2 & m \end{bmatrix} (NO_3)_2$	2.8
$\begin{bmatrix} NO_2 & NH_3 \\ enPd & Pt \\ NO_2 & NH_3 \end{bmatrix} (NO_3)_2$	2.0
$\begin{bmatrix} NO_2 \\ enPd & Pden \\ NO_2 \end{bmatrix} (NO_3)_2$	16
$\begin{bmatrix} NH_{3} & NH_{3} \\ NO_{2}-Pt-NO_{2}-Pt-NO_{2} \\ NH_{3} & NH_{3} \end{bmatrix} NO_{3}$	8.5
$\begin{bmatrix} NH_3 & NH_3 \\ NO_2 - Pd - NO_2 - Pt - NO_2 \\ NH_3 & NH_3 \end{bmatrix} NO_3$	7.6
$\begin{bmatrix} NH_3 & NH_3 \\ NO_2 - Pt - NO_2 - Pt - Cl \\ NH_3 & NH_3 \end{bmatrix} NO_3$	5.0
$\begin{bmatrix} NH_3 & NH_3 \\ Cl-Pt-NO_2-Pt-Cl \\ NH_3 & NH_3 \end{bmatrix}$	4.5
$\begin{bmatrix} NH_3 & NH_3 \\ Cl - Pd - NO_2 - Pt - Cl \\ NH_3 & NH_3 \end{bmatrix} NO_3$	5.2

(1) bromide bridges substitute for nitrite ones to yield a binuclear complex,

$$\begin{bmatrix} A & A \\ NO_2 - Pt - NO_2 - Pt - NO_2 \\ A & A \end{bmatrix}^+ + Br^-$$

$$\longrightarrow \begin{bmatrix} A & A \\ NO_2 - Pt - Br - Pt - NO_2 \\ A & A \end{bmatrix}^+ + NO_2^-;$$
(5)

(2) the Pt–O–N bond dissociates to yield two mononuclear complexes,

$$\begin{bmatrix} A & A \\ NO_2 - Pt - NO_2 - Pt - NO_2 \end{bmatrix}^+ + Br^-$$

$$\longrightarrow \begin{bmatrix} A & A \\ NO_2 - Pt - NO_2 \\ A \end{bmatrix}^0 + \begin{bmatrix} A \\ Br - Pt - NO_2 \\ A \end{bmatrix}^0.$$
(6)

Special experiments verified the second reaction route (scheme 6). This indicates that the Pt–Br bond is stronger than the Pt–O–N bond is weaker than the Pt–NO₂ bond.

An argument in favor of the incapability of Br⁻ ions to substitute for the nitro groups coordinated to the central atom through their nitrogens is the nonoccurrence of reaction between KBr and mononuclear complexes $[Pden(NO_2)_2]$ and $[Pt(mNO_2)_2]$.

Potentiometric titration of solutions of complexes with a KBr solution using a bromide-selective electrode was employed to study the kinetics of reaction (6) at 15°C.

The first experiments were carried out at various starting concentrations of the complex and bromide ions. These experiments showed that, for equal starting concentrations of the complexes, the reaction rate is proportional to the KBr concentration, and for fixed starting bromide ion concentrations, the reaction rate is proportional to the concentration of the complex (Figs. 1, 2).

The plots in Figs. 1 and 2 show that the substitutionreaction rate is proportional to the concentrations of both reagents. Therefore, to calculate rate constants k in further experiments, we used an equation for secondorder reactions with equivalent concentrations of the reagents,

$$k = \frac{c_0 - c}{\tau c_0 c},$$

where c_0 is the starting Br⁻ concentration and *c* is the Br⁻ concentration at moment τ .

The table displays the experimental data on the reactions of complexes with potassium bromide at 15°C. In view of the fact that in the binuclear complex $[enPd(NO_2)_2Pden](NO_3)_2$, the Pd–ON bond is broken during the reaction and in the other complexes, the Pt–ON bonds are broken, we derive the following inference from the constants determined:

(1) the Pt–ON bond is far stronger than the Pd–ON bond;

(2) the nature of the second coordination center virtually does not influence the reaction rate; and

(3) the dissociation rate of the Pt–ON bond under the impact of Br[–] ions is affected by the nature of the *trans*-positioned ligand, increasing in the order NO–Pt–A < NO–Pt–Cl < NO–Pt–NO₂.

Comparing the rate constants that we determined here with the kinetic parameters previously determined for other binuclear complexes [4, 5], we find that nitrite complexes combine thermodynamic instability with kinetic lability.

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