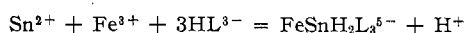citrate complex containing both Fe(III) and Sn(II) should be present in significant amounts. Dividing k by the estimated molar absorbance coefficient (ϵ 51; see Figure 2), the formation constant may be calculated for the mixed-metal complex. When the formation equilibrium is written in terms of uncomplexed metal ions

$$Sn^{2+} + Fe^{3+} + 3HL^{3-} = FeSnH_2L_3{}^{5-} + H^+$$

the formation constant equals 6.6×10^{24}.

In view of this relatively large equilibrium quotient,[7] it was confirmed experimentally that under conditions where the concentrations of citrate and Sn(II) far exceed the Fe(III) concentration, virtually all the iron was found in the mixed-metal complex. Under such conditions Beer's law, as shown in Figure 3, is obeyed when small increments of Fe(III) are added. Absorbance spectra recorded for these solutions indicate that a large absorption maximum is located at a wavelength shorter than 300 nm.

Mixed-Valence Iron(III)–Iron(II)–Citrate Complexes.—A linear relationship between interaction absorption and the concentration of mixed-valence
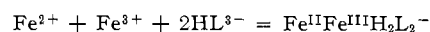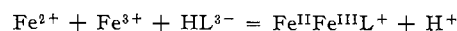
(7) One of the reviewers pointed out that the difference in magnitude of the formation constant determined in this work and the constant which follows (derived from literature data) may serve to illustrate the unusual stability of the mixed-metal complex: $K = [\text{FeL}^-][\text{Sn(HL)}_2{}^{4-}][\text{H}^+] / [\text{Fe}^{3+}][\text{Sn}^{2+}][\text{HL}^{3-}]^3 \approx 1.8 \times 10^{22}$.

complexes is shown in Figure 6. In this case the equation describing the line is

$$\frac{A_I}{[\text{Fe}^{2+}][\text{FeL}^-]} = k_1 + k_2 K_6 [\text{H}_2\text{L}^{2-}]$$

where intercept k_1 is the product of the molar absorbance coefficient and formation constant for one mixed-valence complex while slope $k_2 K_6$ contains an analogous product for the other complex. As may be seen, at very low H_2L^{2-} concentration the line curves toward the point of origin. Although experimental error in this region is greatest, there is a possibility that at low pH additional mixed-valence complexes may be found. Unfortunately, the molar absorbance coefficient for neither of the two mixed-valence complexes was available; consequently formation constants could not be calculated.

In terms of the uncomplexed metal ions the formation equilibria for the two mixed-valence complexes in the solutions studied are

$$\text{Fe}^{2+} + \text{Fe}^{3+} + \text{HL}^{3-} = \text{Fe}^{II}\text{Fe}^{III}\text{L}^+ + \text{H}^+$$

$$\text{Fe}^{2+} + \text{Fe}^{3+} + 2\text{HL}^{3-} = \text{Fe}^{II}\text{Fe}^{III}\text{H}_2\text{L}_2{}^-$$


Nitrosyl–Nitrite Interconversion in Ruthenium Complexes

BY JOHN B. GODWIN AND THOMAS J. MEYER*

The series of nitrosyl complexes $\text{Ru(AA)}_2(\text{NO})\text{X}^{3+}$ (AA = 2,2'-bipyridine, 1,10-phenanthroline; X = Cl⁻, Br⁻, NO₂⁻, pyridine) react with OH⁻ to give the corresponding nitro complexes $\text{Ru(AA)}_2(\text{NO}_2)\text{X}^+$, which have been isolated and characterized. For the equilibrium $\text{Ru(bipy)}_2(\text{NO})\text{Cl}^{2+} + 2\text{OH}^- = \text{Ru(bipy)}_2(\text{NO}_2)\text{Cl} + \text{H}_2\text{O}$, $K_1 = (1.6 \pm 0.4) \times 10^9 \ M^{-2}$ at 25.0° in 1.0 M NaCl. The nitro complexes can be reconverted into nitrosyl complexes by reactions with the Lewis acids BF₃, SnCl₄, or H⁺. The nitro–nitrosyl conversions are chemically reversible.

Introduction

We have reported the preparation of the series of nitrosyl complexes $\text{Ru(AA)}_2(\text{NO})\text{X}^{3+}$ (AA = 2,2'-bipyridine and 1,10-phenanthroline; X = Cl⁻, Br⁻, NO₂⁻, py).[1] The complexes act as a controlled source of nitrosonium ion (NO⁺) in that they react with hydroxide ion to give the corresponding nitro complexes[1] and with azide ion to liberate N_2 and N_2O.[2] Here we describe in detail the conversion of the nitrosyl complexes into nitro complexes, the measurement of the equilibrium constant for the reaction

$$\text{Ru(bipy)}_2(\text{NO})\text{Cl}^{2+} + 2\text{OH}^- = \text{Ru(bipy)}_2(\text{NO}_2)\text{Cl} + \text{H}_2\text{O}$$
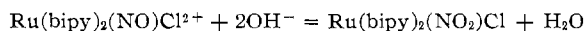
at 25° in 1 M NaCl, and the reconversion of coordinated nitrite into nitrosyl by reaction with either BF₃ or SnCl₄.

Experimental Section

Stannic chloride was distilled before use and boron trifluoride

(1) T. J. Meyer, J. B. Godwin, and N. Winterton, *Chem. Commun.*, 1872 (1970); J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 471 (1971).

(2) F. J. Miller and T. J. Meyer, *J. Amer. Chem. Soc.*, **93**, 1294 (1971).

was used as the gas. All other reagents were of reagent or analytical grade and used without further purification. The preparations of the ruthenium–nitrosyl complexes were reported earlier.[1] Infrared spectra were recorded on Perkin-Elmer 421 or Beckman Model IR12 spectrophotometers as KBr pellets. Ultraviolet–visible spectra were recorded on a Cary Model 14 spectrophotometer equipped with a thermostated constant-temperature cell block.

Preparations. 1. $\text{Ru(AA)}_2\text{NO}_2\text{X}\cdot\text{H}_2\text{O}$ (X = Cl, Br; AA = bipy, phen).—Two general procedures were used. A. One-tenth gram of the appropriate nitrosyl complex as its hexafluorophosphate salt, $[\text{Ru(AA)}_2(\text{NO})\text{X}](\text{PF}_6)_2$, was suspended in 5–10 ml of water and 1–2 ml of 2 M NaOH was added slowly with stirring. The suspended pale brown solid immediately began to turn red-brown and the solution color deepened. Stirring was continued for 15 min. The red-brown solid was then collected on a frit, washed twice with ice-cold water, twice with 1,2-dimethoxyethane, and several times with ether, and air-dried with suction.

B. One-tenth gram of the appropriate nitrosyl complex as its hexafluorophosphate salt was suspended in 25 ml of ethanol at 40–50° and 3 ml of 2 M aqueous sodium hydroxide was added slowly with vigorous stirring. The complex slowly dissolved and the solution turned deep red. After about 10 min a red-brown solid began to precipitate. Ether was added carefully

TABLE I

ANALYTICAL AND INFRARED DATA FOR THE NITRO COMPLEXES[a]

Compound	%C Calcd	%C Found	%H Calcd	%H Found	%N Calcd	%N Found	%F Calcd	%F Found	%halogen Calcd	%halogen Found	Nitrite bands ν_{as}	ν_s	δ_{ONO}	ρ_{w,NO_2}
Ru(bipy)₂(NO₂)Cl	48.48	48.41	3.23	3.46	14.14	13.84	...	...	7.07	6.96	1338 vs	1298 vs	813 s	610 w, b
Ru(phen)₂(NO₂)Cl·H₂O	53.33	53.15	2.96	3.18	12.96	12.50	...	...	6.45	6.63	1325 vs	1279 vs	815 s	605 w, b
Ru(bipy)₂(NO₂)Br·H₂O	44.53	45.01	2.96	3.11	12.99	12.85	...	...	14.84	14.65	1326 vs	1288 vs	815 s	605 w, b
Ru(phen)₂(NO₂)Br·H₂O	49.06	49.62	2.73	2.88	11.92	12.11	...	...	13.62	13.44	1327 vs	1285 vs	820 s	598 w, b
[Ru(bipy)₂(NO₂)(py)](PF₆)	42.02	41.88	2.94	3.09	11.76	11.61	15.97	15.80	...	...	1340 vs	1299 vs	812 s	610 w, b
[Ru(phen)₂(NO₂)(py)](PF₆)	46.46	46.35	3.06	3.18	11.22	11.31	15.26	15.38	...	...	1325 vs	1289 vs	811 s	610 w, b
Ru(bipy)₂(NO₂)₂·H₂O	47.52	46.88	3.16	3.16	16.53	16.25	...	...	...	...	1338 vs	1298 vs, 1309 vs	814 s	610 w, b
Ru(phen)₂(NO₂)₂·H₂O	52.08	51.56	2.89	3.07	15.18	15.18	...	...	...	...	1325 vs	1286 vs, 1304 vs	813 s	615 w, b

[a] Infrared data in KBr pellets ±3 cm⁻¹. Key: vs, very strong; s, strong; w, weak; b, broad.

in order to complete precipitation. The solution was filtered, and the red-brown solid on the frit was washed twice with cold ethanol and several times with ether and air-dried. The solid was recrystallized from a 1:1 mixture of acetonitrile–methanol by slowly adding ether in excess.

Using either procedure the products were obtained in 60–70% yield.

2. **[Ru(AA)₂(NO₂)(py)]PF₆** (py = Pyridine).—One-tenth gram of [Ru(AA)₂(NO)(py)](PF₆)₃ was added to 30 ml of water. The solution was heated to 50–60° with vigorous stirring until the solid had completely dissolved (10–15 min), and then 2 ml of 2 M sodium hydroxide was added slowly dropwise. The solution changed color rapidly from yellow to red. Excess aqueous ammonium hexafluorophosphate was added and the deep red-orange solid was collected on a frit, washed several times with water, and air-dried with suction. After recrystallization twice from acetone–ether, the salts were obtained in 60–70% yield.

3. **Ru(AA)₂(NO₂)₂·H₂O.**—The dinitro complexes can be prepared by either procedure A or B in part 1 above but are most easily prepared by adding excess sodium nitrite to hot solutions of Ru(AA)₂(OH)₂Cl⁺ as described earlier.[1]

Reactions with BF₃ and SnCl₄.—Suspensions of 40–60 mg of the nitro complex, either Ru(bipy)₂NO₂Cl or Ru(bipy)₂(NO₂)₂, were made in 20–30 ml of dichloromethane containing tetra-*n*-butylammonium hexafluorophosphate in 5–10-fold excess. A few drops of stannic chloride was added to the solution in a dry glove bag. The solution was immediately decolorized and the suspended solid changed from deep red-brown to very pale brown after a few minutes. The solids were collected, washed several times with dichloromethane and ether, and air-dried. Infrared spectra of the solids were identical with those for known samples of [Ru(bipy)₂(NO)Cl](PF₆)₂ and [Ru(bipy)₂(NO)NO₂](PF₆)₂. The same results were obtained by bubbling boron trifluoride through the dichloromethane suspensions.

Results

A. The Nitro Complexes.—Analytical and infrared data for the series of nitro complexes are given in Table I. The positions of the nitrite bands indicate clearly that nitrite is nitrogen rather than oxygen bound.[3] The complexes are presumably cis since the analogous nitrosyl complexes are also apparently cis.[1]

B. Equilibrium and Stoichiometry Measurements. —The bipyridine– and phenanthroline–nitrosyl complexes are converted into nitro complexes in solution by the addition of hydroxide ion

$$Ru(bipy)_2(NO)Cl^{2+} + 2OH^- \rightarrow Ru(bipy)_2(NO_2)Cl + H_2O \quad (1)$$
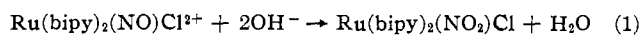
The nitro complexes are in turn reconverted into nitrosyl complexes in acidic solutions

$$Ru(bipy)_2(NO_2)Cl + 2H^+ \longrightarrow Ru(bipy)_2(NO)Cl^{2+} + H_2O \quad (2)$$

That the nitrosyl–nitrite conversion for Ru(bipy)₂(NO)Cl²⁺ is chemically reversible is indicated in Figure 1.

In spectrum A the solution contains Ru(bipy)₂(NO)Cl²⁺, in B a sufficient excess of sodium hydroxide
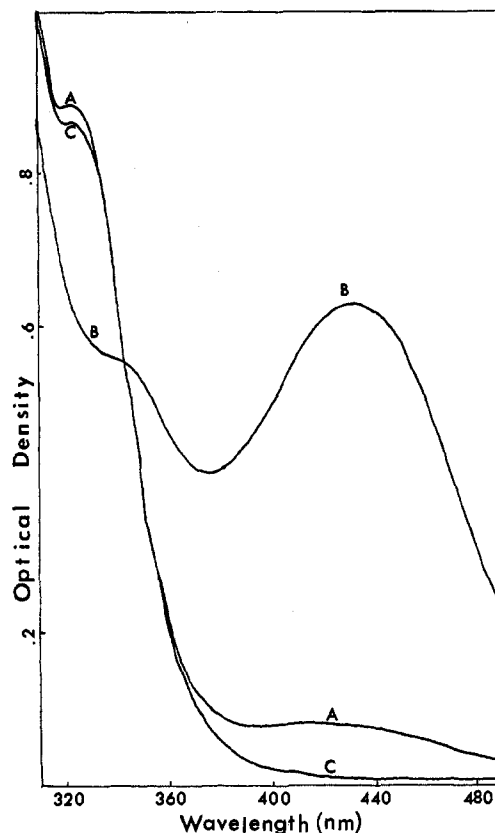
(3) K. Nakamoto, J. Fujita, and H. Murato, *J. Amer. Chem. Soc.*, **80**, 4817 (1958).

Figure 1.—Solution spectra (in 1.0 M NaCl) in 2-cm cells: (A) [Ru(bipy)₂(NO)Cl²⁺] = 4.08 × 10⁻⁵ M, partial conversion to Ru(bipy)₂(NO₂)Cl; (B) solution A made 1.28 × 10⁻⁴ M in OH⁻, giving Ru(bipy)₂(NO₂)Cl; (C) solution B to which 1 drop of concentrated HCl has been added, giving back Ru(bipy)₂(NO)Cl²⁺.

has been added so that the nitrosyl complex has been completely converted into Ru(bipy)₂(NO₂)Cl, and in C the solution has been reacidified to give back Ru(bipy)₂(NO)Cl²⁺. Spectrum B corresponds closely to the spectrum of a known, analyzed sample of Ru(bipy)₂(NO₂)Cl in the same medium. The interconversion between nitro and nitrosyl forms was similarly shown to be reversible for the other bipyridine complexes.

The stoichiometry of reaction 1 was verified by the spectrophotometric titration of solutions of Ru(bipy)₂(NO)Cl²⁺ (10⁻⁴–10⁻⁵ M) by hydroxide ion. The optical density at the maximum for Ru(bipy)₂(NO₂)Cl (432 nm) increases steadily as OH⁻ is added. A well-defined break in the titration occurs at [OH⁻]_added/[Ru(bipy)₂(NO)Cl²⁺]_initial = 2.0, and the addition of further amounts of OH⁻ has no effect on the spectrum. The well-defined isosbestic point at 342 nm (see Figure

1, at 340 nm in water) demonstrates that only the nitrosyl and nitro complexes are present in appreciable concentration during the titration. Even in the dilute solutions used, the reactions between $Ru(bipy)_2(NO)Cl^{2+}$ and OH^- were complete within 1 min.

Attempts were also made to determine the stoichiometry of reaction 2 by spectrophotometrically titrating solutions of $Ru(bipy)_2(NO_2)Cl$ ($10^{-4}-10^{-5}$ M) with HCl. Within experimental error the stoichiometry of reaction 2 was verified. However in the dilute solutions used, the nitro–nitrosyl conversion took several hours and some decomposition of the solutions was observed. In all cases an isosbestic point was observed at 340 nm and no absorption bands other than those attributable to either $Ru(bipy)_2(NO)Cl^{2+}$ or $Ru(bipy)_2(NO_2)Cl$ appeared in the spectra.

Acidic solutions of $Ru(bipy)_2(NO)Cl^{2+}$ and basic or neutral solutions of $Ru(bipy)_2(NO_2)Cl$ are stable even in the presence of light and air for at least 3 hr. $Ru(bipy)_2(NO)Cl^+$ is slowly converted into $Ru(bipy)_2(NO_2)Cl$ in neutral solution. Relevant molar extinction coefficients for the two complexes in the concentration range $10^{-4}-10^{-5}$ M are as follows: $Ru(bipy)_2(NO)Cl^{2+}$ (325 nm (sh)), ϵ 11,200 $\pm$ 300 (water), ϵ 10,600 $\pm$ 300 (1.0 M NaCl); $Ru(bipy)_2(NO_2)Cl$ (432 nm), ϵ 7500 $\pm$ 200 (water or 1.0 M NaCl).

The equilibrium constant K_1 for the reaction

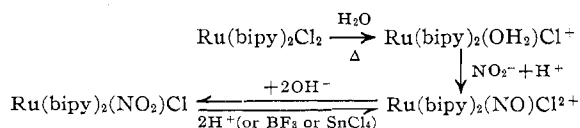$$Ru(bipy)_2(NO)Cl^{2+} + 2OH^- = Ru(bipy)_2(NO_2)Cl + H_2O$$
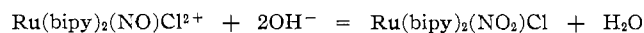
was also measured spectrophotometrically at 25.0 $\pm$ 0.2° in 1.0 M sodium chloride. In solutions containing appreciable amounts of both nitrosyl and nitro complexes, the concentration of the latter can be determined spectrophotometrically at 432 nm (ϵ 7500) since the optical density contributed by the nitrosyl complex is negligible at that wavelength. Using the known stoichiometry of the reaction and the observed concentration of $Ru(bipy)_2(NO_2)Cl$, then $[OH^-]$, $[Ru(bipy)_2(NO)Cl^{2+}]$, and K_1 can be calculated. The calculated values for K_1 at 298°K for five experiments gave 1.2, 1.9, 1.7, 2.0, and 1.4 $\times$ 10^9 M^{-2} which yields an average value of

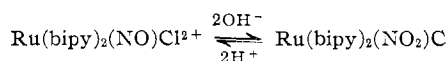$$K_1 = \frac{[Ru(bipy)_2(NO_2)Cl]}{[Ru(bipy)_2(NO)Cl^{2+}][OH^-]^2} = (1.6 \pm 0.4) \times 10^9 \, M^{-2}$$

Discussion

The series of reactions leading to the ruthenium nitrite complexes is illustrated below for the chloronitrobipyridine complex

$$Ru(bipy)_2Cl_2 \xrightarrow[\Delta]{H_2O} Ru(bipy)_2(OH_2)Cl^+$$

$$\downarrow NO_2^- + H^+$$

$$Ru(bipy)_2(NO_2)Cl \underset{2H^+(or\ BF_3\ or\ SnCl_4)}{\overset{+2OH^-}{\rightleftarrows}} Ru(bipy)_2(NO)Cl^{2+}$$
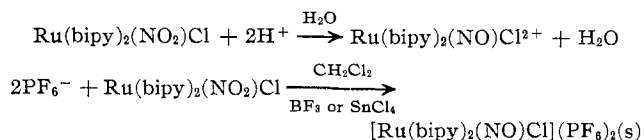
The reactions represent a useful if indirect route to the series of cis[1] nitro complexes which has the advantage of synthetic control at each step.

The complexes exist in the nitro form in aqueous solutions containing hydroxide ion and in the nitrosyl form in acidic solutions. Conversion between the two forms
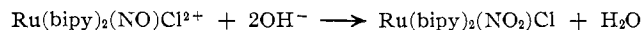
$$Ru(bipy)_2(NO)Cl^{2+} \underset{2H^+}{\overset{2OH^-}{\rightleftharpoons}} Ru(bipy)_2(NO_2)C$$

is reversible. Formally, reactions like

$$Ru(bipy)_2(NO_2)Cl + 2H^+ \xrightarrow{H_2O} Ru(bipy)_2(NO)Cl^{2+} + H_2O$$

$$2PF_6^- + Ru(bipy)_2(NO_2)Cl \xrightarrow[BF_3\ or\ SnCl_4]{CH_2Cl_2}$$

$$[Ru(bipy)_2(NO)Cl](PF_6)_2(s)$$

involve oxide ion (O^{2-}) transfer from coordinated nitrite to the Lewis acids H^+, BF_3, and $SnCl_4$. The reaction with H^+ is analogous to the conversion of free nitrite ion into NO^+

$$NO_2^- \xrightarrow{H^+} HNO_2 \xrightarrow{H^+} H_2NO_2^+ \, (NO^+ \cdot H_2O)$$
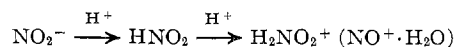
By the same formalism conversion from nitrosyl to nitrite

$$Ru(bipy)_2(NO)Cl^{2+} + 2OH^- \longrightarrow Ru(bipy)_2(NO_2)Cl + H_2O$$

occurs by oxide ion donation to coordinated NO^+. The nitrosyl complexes react with bases other than OH^-, but the products of reaction depend specifically on the base used as in reactions with NO^+ itself,[4] for example

$$Ru(bipy)_2(NO)Cl^{2+} + H_2O + N_3^- \longrightarrow$$

$$Ru(bipy)_2(OH_2)Cl^+ + N_2 + N_2O^2$$
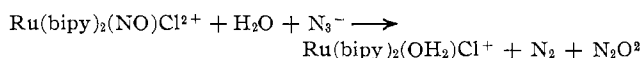
Reversible conversion between nitrosyl and nitro forms has also been found for nitroprusside ion, $Fe(CN)_5NO^{2-}$,[5] and its ruthenium analog.[6] From kinetic data the reaction between $Fe(CN)_5NO^{2-}$ and OH^- occurs stepwise[7,8] as in

$$Fe(CN)_5NO^{2-} + OH^- \longrightarrow Fe(CN)_5NO_2H^{3-}$$

$$Fe(CN)_5NO_2H^{3-} + OH^- \longrightarrow Fe(CN)_5NO_2^{4-} + H_2O$$
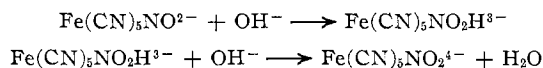
We have obtained no spectrophotometric evidence for the existence of $Ru(bipy)_2(NO_2H)Cl^+$ either by acidification of solutions of $Ru(bipy)_2(NO_2)Cl$ or by adding OH^- to solutions of $Ru(bipy)_2(NO)Cl^{2+}$.

When basic solutions of $Fe(CN)_5(NO_2)^{4-}$ are acidified, the intermediate $Fe(CN)_5(NO_2H)^{3-}$ has been said to form rapidly.[7-9] Our failure to observe the analogous intermediate $Ru(bpiy)_2(NO_2H)Cl^+$ upon careful acidification of solutions of $Ru(bipy)_2(NO_2)Cl$ may indicate either that the neutral ruthenium complex has a much lower affinity for H^+ or that the protonated intermediate in the nitroprusside system may be $Fe(CN)_4(CNH)(NO_2)^{3-}$ rather than $Fe(CN)_5(NO_2H)^{3-}$.

For the overall equilibrium

$$Fe(CN)_5NO^{2-} + 2OH^- = Fe(CN)_5NO_2^{4-} + H_2O$$
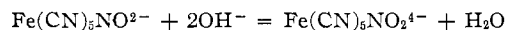
at 25.0° in 1 M NaCl, Swinehart and Rock[10] have found $K_1 = (1.5 \pm 0.3) \times 10^6$. Under identical conditions for

$$Ru(bipy)_2(NO)Cl^{2+} + 2OH^- = Ru(bipy)_2(NO_2)Cl + H_2O$$
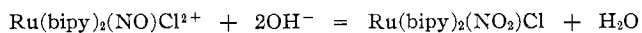
we find $K_1 = (1.6 \pm 0.4) \times 10^9$ M^{-2}. Clearly the nitrosyl coordinated to the ruthenium has the higher affinity for OH^- and it should behave chemically more nearly like NO^+. Qualitative observations on the relative reactivities of the two complexes also support this conclusion.[4]

(4) T. J. Meyer, unpublished observations.
(5) L. Cambi and L. Szego, *Gazz. Chim. Ital.*, **58**, 71 (1928).
(6) E. J. Barans and A. Müller, *Chem. Ber.*, **102**, 3915 (1969).
(7) J. Mašek and J. Dempír, *Inorg. Chim. Acta*, **2**, 443 (1968).
(8) J. Mašek and H. Wendt, *ibid.*, **3**, 455 (1969).
(9) J. Dempír and J. Mašek, *ibid.*, **2**, 402 (1968).
(10) J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, **5**, 573 (1966).

Hydrolysis of Coordinated Cyanate Ion.   A Comparison of the Isocyanatopentaammine Complexes of Ruthenium(III) and of Rhodium(III)

BY PETER C. FORD

A kinetic study of the acid-catalyzed hydrolysis of coordinated cyanate ion to coordinated ammonia plus carbon dioxide has been carried out for the complex ions $Ru(NH_3)_5(NCO)^{2+}$ and $Rh(NH_3)_5(NCO)^{2+}$. In dilute acid, the hydrolysis of each complex displayed a simple second-order rate law: $d[M(NH_3)_5(NCO)^{2+}]/dt = k_2[M(NH_3)_5(NCO)^{2+}][H^+]$ with $k_2 = 0.62 \pm 0.02\ M^{-1}\ sec^{-1}$ for M = Rh(III) ($\Delta H^{\ddagger} = 10.9$ kcal/mol, $\Delta S^{\ddagger} = -23$ eu) and with $k_2 = 0.059 \pm 0.001\ M^{-1}\ sec^{-1}$ for M = Ru(III) ($\Delta H^{\ddagger} = 12.2$ kcal/mol, $\Delta S^{\ddagger} = -23$ eu) at 25.0°.   At higher acid concentrations (>0.1 M), hydrolysis of the rhodium(III) complex displays more complicated spectrophotometric kinetics owing to the relative stability of a reaction intermediate $Rh(NH_3)_5(NH_2CO_2H)^{3+}$ which can be isolated as a solid salt and characterized spectroscopically. This species decomposes in the solid form and in aqueous solution to give CO_2 plus $Rh(NH_3)_6^{3+}$. In aqueous solution, the decomposition follows the rate law $d[Rh(NH_3)_5(NH_2CO_2H)^{3+}]/dt = (k_0 + k_{-1}[H^+]^{-1})[Rh(NH_3)_5(NH_2CO_2H)^{3+}]$ with $k_3 = 2.1 \times 10^{-3}$ sec^{-1} and $k_{-1} = 0.96 \times 10^{-3}\ M\ sec^{-1}$ at 25°.   These data and reactivity differences between the ruthenium(III) and rhodium-(III) complexes are interpreted in terms of the probable hydrolysis mechanism.

Introduction

Reactions of ligands coordinated to transition metals have been a topic of considerable interest in recent years.[1] These studies have taken the form of comparisons of reaction characteristics of coordinated *vs.* uncoordinated (free) ligands and comparisons of different metal ion coordination sites with ligand reactions. Relatively few studies (outside organometallic systems) have compared ligand reactivity between analogous complexes where the only difference is a single nuclear charge or a single d-orbital electron. Comparisons of such compound pairs have been made[2] for properties and some reactions of organonitrile ligands in the isoelectronic complex ions $Ru(NH_3)_5(RCN)^{2+}$ and $Rh(NH_3)_5(RCN)^{3+}$ (both low-spin $4d^6$) where the principal difference is a single metal atom nuclear charge and have been made for some ammine complexes of Ru(II) and Ru(III) where the difference is one 4d electron and consequently a +1 difference in ionic charge.[3] In the present study are compared the reactivity of coordinated cyanate ion in the analogous complexes $Ru(NH_3)_5(NCO)^{2+}$ (low-spin $4d^5$) and $Rh(NH_3)_5(NCO)^{2+}$ (low-spin $4d^6$) having the same electrostatic charge but electronic configurations differing by one d-orbital electron.

The principal reaction with which this study is concerned is the acid-catalyzed hydrolysis of coordinated cyanate ion to carbon dioxide plus coordinated ammonia (eq 1).   Balahura and Jordan[4] have reported a similar

$$M(NH_3)_5(NCO)^{2+} + H_3O^+ \longrightarrow$$
$$M(NH_3)_6^{3+} + CO_2 \quad (M = Rh(III) \text{ or } Ru(III)) \quad (1)$$
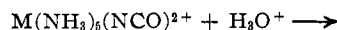
study of the analogous cobalt(III) complex (eq 1, M = Co(III)) where they demonstrated that the reaction rate is first order in acid concentration.   A similar acid-catalyzed pathway has been reported for the hydrolysis of cyanic acid (HNCO) to CO_2 plus NH_4^+.

Experimental Section

Materials.—Chloropentaammineruthenium(III) chloride, [Ru-$(NH_3)_5Cl]Cl_2$, was prepared by published methods from ruthenium trichloride (Engelhard Industries).[3a]   Chloropentaamminerhodium(III) chloride, [Rh(NH_3)_5Cl]Cl_2, was prepared by the method of Johnson and Basolo[5] from rhodium trichloride (Engelhard Industries).   Aquopentaamminerhodium(III) perchlorate, $[Rh(NH_3)_5H_2O][ClO_4]_3$, was prepared using the method of Foust[2] by refluxing aqueous $[Rh(NH_3)_5Cl]Cl_2$ 2 hr in the presence of stoichiometric silver(I) perchlorate (Ag(I):Rh(III) = 3).   Filtration of the hot reaction solution followed by addition of sodium perchlorate leads to a nearly quantitative yield of solid $[Rh(NH_3)_5H_2O][ClO_4]_3$.   Sodium cyanate (Sargent), urea (Mallinckrodt), and Spectrograde *N,N*-dimethylacetamide (Aldrich) were obtained from commercial sources and used without further purification.

Syntheses. $[Ru(NH_3)_5(NCO)]Br_2$.—$[Ru(NH_3)_5Cl]Cl_2$ (0.27 g, 0.93 mmol) was digested in a 5-ml silver trifluoroacetate solution (prepared by dissolving Ag_2O (0.20 g, 0.86 mmol) in sufficient aqueous trifluoroacetic acid).   The resulting solution was filtered to remove silver chloride and deaerated by entraining with argon in a small separatory funnel.   The Ru(III) of this solution was then reduced by adding granular zinc amalgam (0.5 g) and agitating the solution with a stream of purified argon.   After sufficient time (about 10 min) to effect complete reduction to Ru(II), the solution was neutralized with sodium bicarbonate, solid sodium cyanate (0.5 g, 7.7 mmol) was added to it with agitation, and the resulting mixture was immediately filtered.   The filtrate solution was then exposed to air to allow slow oxidation to Ru(III).   Subsequent addition of sodium bromide solution gave a dark yellow precipitate which was recrystallized from hot water to give 0.21 g (0.54 mmol, 58% yield) of [Ru(NH_3)_5-

(1) For an extensive review see M. M. Jones, "Ligand Reactivity and Catalysis," Academic Press, New York, N. Y., 1968.

(2) R. D. Foust, Jr., and P. C. Ford, presented at the Pacific Conference for Chemistry and Spectroscopy, San Francisco, Calif., Oct 1970; to be submitted for publication.

(3) (a) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970); (b) R. E. Clarke and P. C. Ford, *ibid.*, **9**, 495 (1970); (c) P. C. Ford, R. D. Foust, Jr., and R. E. Clarke, *ibid.*, **9**, 1933 (1970).

(4) R. J. Balahura and R. B. Jordan, *ibid.*, **9**, 1567 (1970).

(5) S. A. Johnson and F. Basolo, *ibid.*, **1**, 925 (1962).