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RHODIUM SPECIES
IN RADIOACTIVE WASTE SOLUTIONS

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RHODIUM SPECIES
IN RADIOACTIVE WASTE SOLUTION

INTRODUCTION

The predication of this report is that in considering highly-radioactive waste solutions, some fundamental knowledge of the species present would be helpful, although perhaps not essential, to the recovery of various constituents. The basic question directing the following work has been "what rhodium species exist in solutions?"

It is known that rhodium is present in low concentration (ca. 10^{-4} M) in alkaline waste solutions derived from the re-processing of nuclear reactor fuels.⁽¹⁾ Nitrate and nitrite are present in molar quantities. Other common anions include carbonate, sulfate, chloride, and assorted radiolysis products. The principal environment one may infer for rhodium in these solutions is, however, nitrogeneous. Therefore, the most reasonable experimental approach seems to be one involving simple solutions of rhodium and individual N-ligand anions.

RHODIUM CHEMISTRY

All evidence regarding the oxidation state of undissolved rhodium points to the fact that rhodium(III) is the most stable state. Unlike cobalt(III), which can be stabilized only in aqueous solutions by complexation, most rhodium dissolution procedures lead directly to rhodium(III).⁽²⁾ The stability of rhodium(III) is also reflected in oxidation potentials which have been determined⁽³⁾ and in the solubility of Rh_2O_3 . Rhodium(III) salts, primarily the chloride and oxide, have become available commercially. A full

range of rhodium(III) chloride complexes have been studied,⁽⁴⁾ and complexes with other common anions; e.g., cyano,⁽⁵⁾ thiocyanato,⁽⁶⁾ sulfato,⁽⁷⁾ hydroxo,⁽⁸⁾ and nitritoammine,⁽⁹⁾ have been reported. The complication of competing ligands in simple systems has been most conveniently avoided by converting rhodium(III) to the perchlorate,⁽¹⁰⁾ which is known to be a poor ligand. Controlled amounts of the ligand under study can then be added as desired. It has also been shown that the effective charge in such solutions of rhodium(III) species is plus three.⁽⁴⁾

RADIOLYSIS

Waste solutions produced in the reprocessing of nuclear reactor fuels are acidic and subject to high-intensity radiation fields. Acid wastes are neutralized with Na_2CO_3 and are then stored. Radiation levels remain high for long time periods (years). The effect of these fields on rhodium has not been carefully studied; but there seems to be little evidence indicating the production, or more properly, the stabilization of other oxidation states than rhodium(III). While rhodium(IV) and rhodium(V) exist, reported oxidation potentials⁽³⁾ would seem to indicate the reduction to rhodium(III) by one of a variety of constituents present, including nitrite.

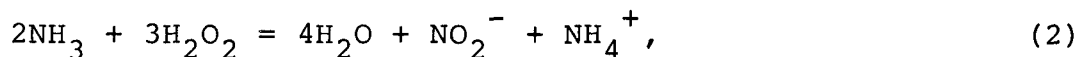
The radiolysis of nitrogen species, a subject of extensive study, has been recently reviewed.^(11, 12) One may consider the radiolysis products obtained beginning from the extremes of the N oxidation spectrum; i.e., NH_4^+ and NO_3^- . These ions represent the initial species in solution.

Although there has been substantial speculation and some disagreement regarding the mechanisms of the reactions, the primary radiolysis products of nitrate are generally agreed to be nitrite and oxygen. Also, the radiolysis intermediates of water ($\text{H}\cdot$ and $\text{HO}\cdot$) are involved.⁽¹³⁾ The net reaction is



There is a kinetic concentration effect which does not, however, alter the products obtained.

The radiolysis of ammonia, on the other hand, has been much less thoroughly investigated, but "in the presence of oxygen gives NO_2^- ."⁽¹²⁾ The overall reaction can be represented as



where hydrogen peroxide can be visualized as being produced either by the direct reaction of oxygen and water or by the combination of hydroxyl radicals ($\text{HO}\cdot$) obtained in the radiolysis of water. One can, therefore, anticipate the presence of virtually any oxidation state of nitrogen in trace concentrations. Major species, however, relate to equation (1), in which the thermodynamic equilibrium, normally displaced far to the left (NO_3^-), is now shifted relatively to the right by the high radiation field. In a 1.0 molar nitrate solution, one oxygen atom (concurrently one nitrite ion) is produced for every 100 eV of radiation energy absorbed.⁽¹¹⁾ One must therefore consider NO_2^- and NO_3^- as primary species.

ACIDITY

The assessment of potential ligands in solutions containing nitrate and nitrite ions centers on the latter.

Nitrate (NO_3^-), a weak conjugate base of the strong acid HNO_3 , represents a configuration in which all of the nitrogen orbitals are filled. Complex formation involving nitrate therefore must occur through an electron "depleted" oxygen orbital. Nitrate complexes consequently have been found to be of uniformly low stability, to exist primarily in aqueous

solutions of high nitrate concentration (e.g., $>5\text{M HNO}_3$),⁽¹⁴⁾ to dissociate in the presence of other stabilizing ligands, and to be generally insensitive to variations in acidity except when hydroxide is an effective ligand; i.e., at high pH.

Nitrite (NO_2^-), on the other hand, forms relatively stable complexes of at least two types--⁽¹⁵⁾ NITRO, in which the bonding is metal-nitrogen, and NITRITO, in which the bonding is metal-oxygen. The parent acid (HONO) is weak ($K_a = 5.0 \times 10^{-4}$)⁽¹⁶⁾ and is subject to disproportionation. One can write for nitrous acid systems:⁽¹⁷⁾



From free energy and standard potential tabulations,⁽³⁾ the calculated equilibrium constant for this reaction is 51, which is in good agreement with determinations made directly from concentration parameters.⁽¹⁸⁾ Nitrate solutions, therefore, are sensitive to acidity. Generally, one can infer that above pH 5, NO_2^- exists independently in solution; while below pH 5, HNO_2 , NO , and NO_3^- are predominant. The careful study of nitrous acid decomposition by Abel and co-workers,⁽¹⁸⁾ summarized by Bray,⁽¹⁹⁾ confirmed equation (3) and indicated the decomposition obeyed the following rate law:

$$d(\text{HNO}_2)/dt = k_1 [\text{HNO}_2]^4 / P_{\text{NO}}^2. \quad (4)$$

Therefore, even though the rate constant (k_1) is small, the formation of NO and NO_3^- is rapid because of the fourth power term, $[\text{HNO}_2]^4$.

Nitric oxide (NO) is soluble to the extent of about 10^{-3}M in aqueous solutions at room temperature and atmospheric pressure.⁽²⁰⁾ It may form the oxy-hyponitrite ion ($\text{N}_2\text{O}_3^{=}$) in reaction with water, but this ion has been found to be of limited stability in acidified aqueous solutions, probably

disproportionating to hyponitrite (N_2O_2^-) and nitrite (NO_2^-).⁽²¹⁾

Nitrite solutions and NO-saturated water solutions at the same pH give essentially indistinguishable spectra in an absorption band centering around 355 $\text{m}\mu$. As the pH decreases from 7 to 2, the band is resolved into a vibrational progression of at least six different frequencies from 325 to 385 $\text{m}\mu$.⁽²²⁾ Although $\text{NO}_{(\text{g})}$ shows only a broad band absorption in this area,⁽²³⁾ the resolution of the band into its component frequencies has been observed when NO was dissolved in hexane, benzene, methanol, ethanol, or isopropyl alcohol,⁽²⁴⁾ as well as water. Nitrate absorbs in a broad band at 302 $\text{m}\mu$.^(21, 25)

In the light of this information, it seems reasonable to consider acidified nitrite solutions as equilibrium mixtures containing primarily NO and NO_3^- . Some authors suggest the predominant species, particularly at high acidities, to be NO^+ .⁽²⁶⁾ The ability of NO to form NO^+ and NO^- has been established.^(15, 27, 28) It is not possible to distinguish, in some cases, between charged and uncharged ligands--particularly in complex compounds. However, the species NO^+ is probably favored by high acidity and low water activity (e.g., NO^+ in concentrated H_2SO_4 for organic nitrations). The form NO^- is probably favored by electron donors and reducing agents. Neither of these conditions appears to hold in the waste solutions or the cold simple solutions that have been examined for the uncomplexed molecular species. Concentrations have, therefore, been calculated in terms of molecular NO whether derived from the gas directly or by the decomposition of HNO_2 .

SUMMARY

Evidence here presented regarding rhodium species leads to the conclusion that in an aqueous acidic nitrate matrix

subject to high radiolysis, rhodium in low concentration forms the species $[\text{Rh}(\text{NO})_2]^{3+}$. Supporting information includes:

1. An adduct is formed which absorbs in the ultraviolet at 268 $m\mu$ in the absence of comparable absorption by solutions of Rh(III), NO_3^- , NO_2 , or N_2O , respectively.
2. The adduct is formed by direct reaction with $\text{NO}_{(g)}$ or acidified NO_2^- solutions ($3\text{HNO}_2 = 2\text{NO} + \text{NO}_3^- + \text{H}_3\text{O}^+$).
3. Mole ratio determination using either $\text{NO}_{(g)}$ or NO derived from NO_2^- yields a value Rh/NO of 1/2.
4. Ion exchange studies indicate only one species of substantial stability.
5. Charge determination indicates a value, +3, for a mononuclear species.
6. Products $\text{Rh}(\text{NO})_2(\text{OH})_3(\text{H}_2\text{O})$ and $[\text{Rh}(\text{NO})_2(\text{py})_4](\text{NO}_2)(\text{ClO}_4)$ have been isolated and identified by elemental analysis, infrared spectra, and mass spectrometry.
7. A tentative identification of $[\text{Rh}(\text{NO})_2]^{3+}$ has been made in radioactive waste solutions.

Inferentially, one may therefore contend:

1. In acid wastes prior to neutralization, rhodium reacts with NO derived from NO_3^- radiolysis (i.e., NO_2^-) to form $[\text{Rh}(\text{NO})_2]^{3+}$.
2. The remainder of the Rh coordination sphere is filled with H_2O . Chloride possibly may be involved.
3. When the solutions are neutralized with Na_2CO_3 , rhodium forms an anion of the form $[\text{Rh}(\text{NO})_2(\text{CO}_3)_2]^-$.

These conclusions, in themselves, do not adequately account for the loading and elution characteristics of "real" rhodium species on anion exchange resins. They do, however, provide

a coherent conceptual pattern, based on factual information, with which to explore rhodium reactions in nitrate wastes.

EXPERIMENTAL

EQUIPMENT

Ultraviolet spectral measurements were made with a Beckman Model DK-2A spectrophotometer using 1 cm matched cells, while infrared measurements were made with a Beckman Model IR-10 using Nujol mulls. Trace (ppm range) rhodium analyses were performed using a Perkin-Elmer 303 Atomic Absorption unit on the 3435 Å rhodium line. Measurements of pH were made with a Beckman push button meter equipped with a Corning combination glass-calomel electrode No. 22 34132-30.

Infrared samples were mounted by standard procedures as pellets in KBr supplied by Harshaw Chemical Company, Cleveland, Ohio.

Mass spectra were obtained from an AEI MS/9 mass spectrometer operating at a 75 V electron beam. Samples were wet with ethanol and dried on the solid insertion probe, after which the probe was placed directly into the ion source.

Analyses for C, H, and N were obtained by Schwarzkopf Microanalytical Laboratory, Woodside, New York, except where noted.

CHEMICALS

All chemicals used were Baker and Adamson Reagent Grade unless otherwise specified.

Rhodium Chloride

(Fisher, purified) 6.802 g $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ were dissolved in 250.0 ml water. Ten ml aliquots were analyzed by precipitating

the sulfide, igniting to the oxide, and reducing to metal in hydrogen.⁽²⁹⁾

Yield: 11.60 ± 0.03 mg/ml

Calculated: 0.0133M

Found: 0.1127M

Rhodium Perchlorate

Ten ml aliquots of rhodium chloride solution were added to a Coors #3 crucible. The solution was twice fumed to about 2 ml total volume with 20 ml portions of 70 to 72% HClO₄.⁽¹⁰⁾ Dilution was made to appropriate volumes for the concentration desired.

Base titration of rhodium(III) solutions derived from rhodium perchlorate confirmed results reported in the literature^(30, 31, 32) on the conversion of the hexaquo complex to hydroxide adducts. No substantive evidence was found indicating hydroxide replacement below pH 3, although some minor aberrations in the curve were noted at pH 2. A differential plot failed to significantly define these areas from the background. Subsequent studies were performed below pH 3 to ensure the absence of hydroxide as a ligand.

Cerium Perchlorate

A standard solution of cerium(III) perchlorate was prepared by dissolving 3.7 g Ce(NO₃)₃·6H₂O in 250 ml H₂O and standardizing via a thiosulfate-iodine method after oxidation of Ce(III) to Ce(IV) by peroxydisulfate.⁽³³⁾

Calculated: 0.0465 ± 0.0002M

Appropriate dilution after fuming aliquots of the standard with HClO₄ yielded Ce(III) perchlorate solutions that were 0.0190M in Ce(III).

Potassium Nitrite

Two hundred and twenty-five grams of KNO_2 were dissolved in 500 ml H_2O and analyzed by a hydrazine-iodine method.⁽³⁴⁾

Calculated: 6.00M Found: 5.730 + 0.008M

Resins

Liquid tricapyrylyl monomethyl ammonium chloride (with some tridecyl contaminant)--"Aliquat 336"-- was supplied by General Mills, Inc., Chemical Division, Kankakee, Illinois. Quaternary amine resin XE-238 was supplied by Amberlite, Rohm and Haas, Philadelphia, Pennsylvania. Anion resin XAX-1316 was supplied by Ritter-Pfaudler Corporation, Ionac Chemical Division, Birmingham, New Jersey. Dowex 50WX2 was supplied by J. T. Baker Company, San Francisco, California.

SPECTRAL STUDIES, ULTRAVIOLETCharacterization And Rate Of Formation

Spectra were found to be conveniently identified in solutions containing 10^{-2} to 10^{-6} total mole content. In such solutions at approximately 10^{-4} M Rh(III) and 10^{-3} M NO, an adduct absorption band was observed at 268 $m\mu$ which did not appear in simple solutions of Rh(III), NO, or NO_2^- . The absorption appeared in solutions adjusted to pH values ranging from 1.5 to 10.5. Adjustment of pH was made after combination of the Rh and NO. When pH adjustments were above pH 7, no absorption band was observed. Development was slow but, once formed, appeared stable at basic pH. The band was slightly affected by pH, and a shoulder emerged on the strong NO electronic absorption at 205 $m\mu$ (Figure 1).

The rate of formation of the adduct was followed as a function of concentration parameters--rhodium(III), nitrite, and acidity. Data are summarized in Tables I through III.

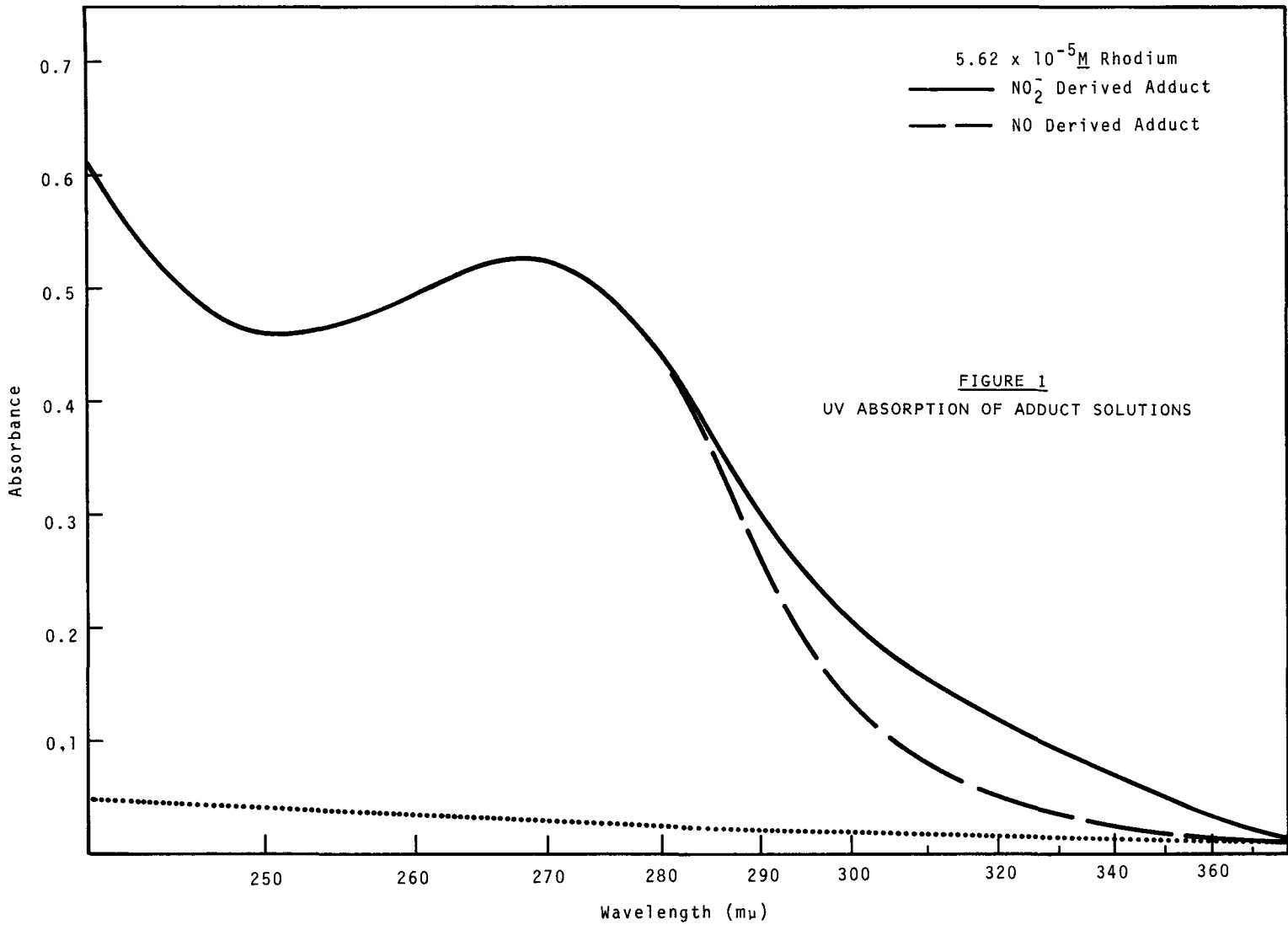


TABLE I
RATE DEPENDENCE ON RHODIUM

$[\text{NO}_2^-] = 3.38 \times 10^{-4} \text{ M}$ as potassium salt
 $\mu = 0.010$ as KClO_4
 $\text{pH} = 3$

Rh(III) M	Absorbance (A \propto Concentration Adduct) At				
	1 hr	5 hr	24 hr	29 hr	48 hr
0.283×10^{-4}	-0.01	-	0.11	0.11	0.15
0.565×10^{-4}	0.00	0.05	0.17	0.18	0.25
0.858×10^{-4}	0.01	0.07	0.22	0.26	0.32
1.13×10^{-4}	0.02	0.09	0.26	0.29	0.38
2.26×10^{-4}	0.06	0.16	0.42	0.47	0.52

Best fit: rate = $k[\text{Rh}]^{1/2}$

TABLE II
RATE DEPENDENCE ON NITRITE

$[\text{Rh(III)}] = 1.13 \times 10^{-4} \text{ M}$ as perchlorate salt
 $\mu = 0.010$ as KClO_4
 $\text{pH} = 3$

NO_2^- M	Absorbance (A \propto Concentration Adduct) At			
	6 hr	24 hr	48 hr	72 hr
0.845×10^{-4}	0.13	0.18	0.21	0.22
1.69×10^{-4}	0.11	0.20	0.24	0.27
2.54×10^{-4}	0.09	0.20	0.27	0.28
3.38×10^{-4}	0.06	0.21	0.27	0.28
4.23×10^{-4}	0.07	0.19	0.26	0.28

Rate independent of $[\text{NO}_2^-]$

TABLE III
RATE DEPENDENCE ON ACIDITY

$[\text{Rh(III)}] = 1.13 \times 10^{-4} \text{ M}$
 $[\text{NO}_2^-] = 3.38 \times 10^{-4} \text{ M}$ ($2.26 \times 10^{-4} \text{ M}$ in NO equivalency)
 $\mu = 0.01$ as KClO_4

Initial pH, H^+	Absorbance At				Final pH, H^+
	3/2 hr	18 hr	25 hr	42 hr	
4.75, 1.78×10^{-5}	0.028	0.075	0.094	0.138	4.22, 0.61×10^{-4}
4.25, 5.64×10^{-5}	0.034	0.330	0.419	0.574	3.80, 1.59×10^{-4}
3.90, 12.6×10^{-5}	0.082	0.625	0.723	0.860	3.15, 7.08×10^{-4}
3.25, 56.4×10^{-5}	0.106	0.485	0.592	0.692	2.70, 20.0×10^{-4}

Rate dependent on acidity but not via a simple coefficient

Formation was independent of nitrite concentration, dependent on the square root of rhodium concentration ($\text{Rh}^{1/2}$), and dependent on acidity but in a manner which could not be fit to a simple rate law.

Rhodium solutions containing a 10-fold molar excess of nitrate exhibited spectra essentially identical to nitrate solutions alone. The characteristic NO_3^- band at 302 $\text{m}\mu$, an absorption minimum at 270 $\text{m}\mu$, and the strong (off-scale) NO_3^- absorption centering at 205 $\text{m}\mu$ were observed.

Formula

The method of continuous variations⁽³⁵⁾ was employed. NO concentrations were calculated on the basis of the solubility of NO-saturated solutions⁽²⁰⁾ or from the equivalency: $3\text{HNO}_2 = 2\text{NO}$. Solutions were examined, varying from 10 to 70 mole percent rhodium in terms of the total constant metal ion-ligand concentrations. The pH was adjusted to 3.00. Potassium perchlorate (KClO_4) was added to maintain a constant ionic strength, $\mu = 0.010$. Development of the absorbing adduct was followed for a period of three days until constant absorbance readings indicated the attainment of equilibrium. Data are summarized in Figure 2 and indicate a species of the form $\text{Rh}(\text{NO})_2^{n+}$.

When the rhodium concentration was held constant and increasing amounts of ligand were added, an increase in absorbance was observed after constant equilibration time. The Rh(III) concentration was large enough to remain essentially constant in relation to the amount of rhodium incorporated into the adduct. For these conditions, one may write from the equilibrium constant:

$$\log [\text{complex}] = n \log [\text{ligand}] + \log [\text{metal ion}] + \log K_f^{(36)} \quad (5)$$

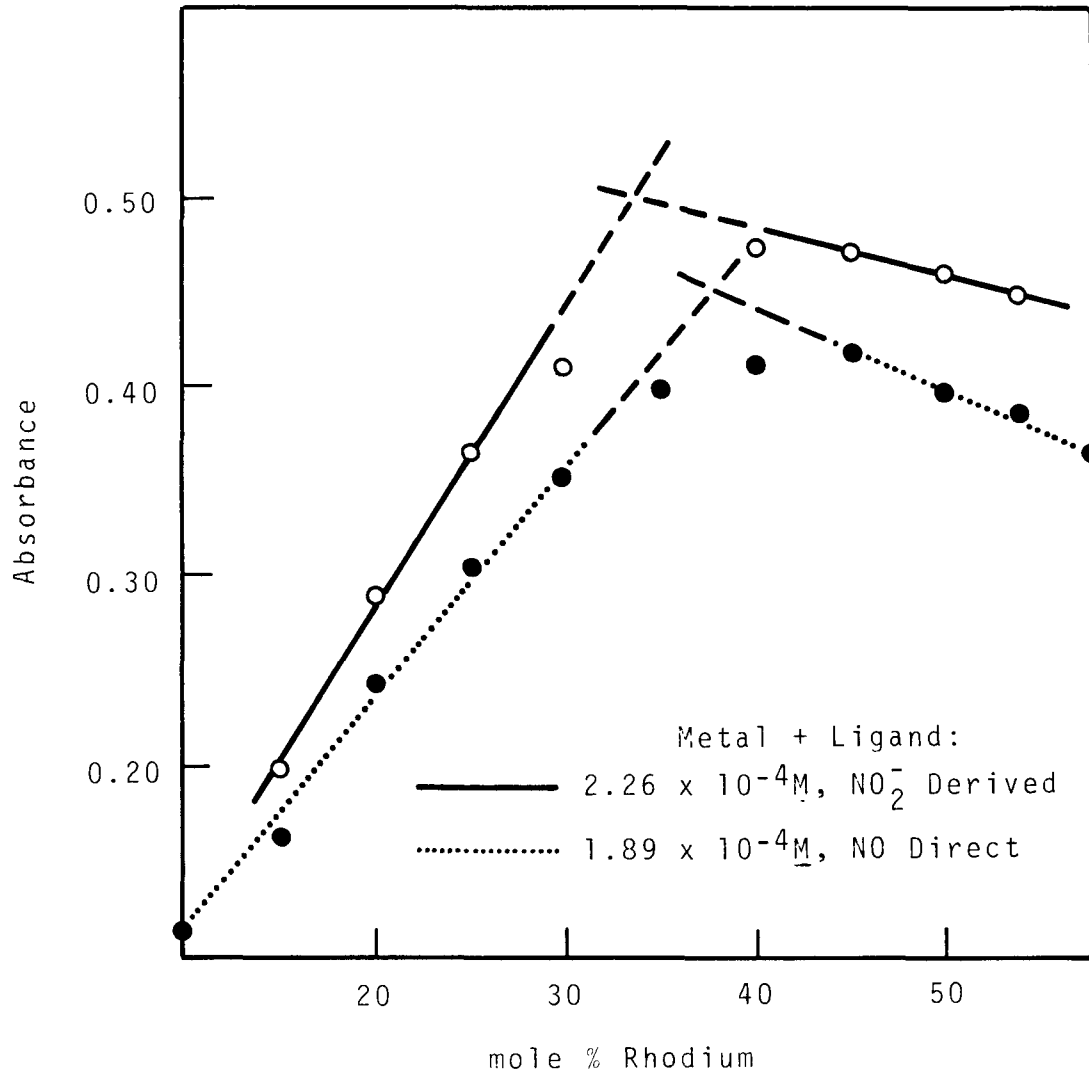


FIGURE 2
MOLE RATIO, METAL-TO-LIGAND

A plot of $\log [\text{complex}]$ versus $\log [\text{ligand}]$ indicated n , the ligand coefficient, to be between 1 and 2.

Extinction Coefficient

Solutions were prepared containing $1.13 \times 10^{-4} \text{ M Rh(III)}$ and saturated with $\text{NO}_{(g)}$, not excluding air. The pH was adjusted to 1.00 and maintained for three days. The corrected maximum absorbance was 1.00 ± 0.01 . The corrected maximum absorbance for similar solutions prepared with HNO_2 -derived NO was 1.02 ± 0.01 .

The molar extinction coefficient, E_m , at 268 $\text{m}\mu$ was calculated from the Beer-Bouguer Law $A = E_m bc$, using 1 cm quartz cells. The value calculated for E_m was 9.03×10^3 .

Stability Constant

For complexes of limited stability, several methods using spectrophotometric data were available to calculate an equilibrium constant. ^(36, 37)

Under conditions where the ligand incorporated in the complex is negligible or small with respect to the total ligand concentrations (Tables IV and V), and, where total incorporation of the metal ion into the complex is not complete, one can write: ⁽³⁸⁾

$$K_f = \frac{b^n A_d - d^n A_b}{b^n d^n (A_b - A_d)} = \frac{[\text{complex}]}{[\text{metal ion}][\text{ligand}]^n} \quad (6)$$

where n equals the ligand-to-metal ion ratio, b and d are different ligand concentrations, and A_b and A_d are absorbance values corresponding to b and d .

$$\begin{aligned} \text{Calculated: } K_f &= (3.3 \pm 0.4) \times 10^5, n = 2 \\ K_f &= (4.0 \pm 0.6) \times 10^2, n = 1 \end{aligned}$$

Rearranging Equation (5): ⁽³⁵⁾

$$\log K_f = \log [\text{complex}] - \log [\text{metal ion}] - n \log [\text{ligand}].$$

TABLE IV
SPECTROPHOTOMETRIC DATA

a. Nitric Oxide Excess

$\mu = 0.010$ (as KClO_4)
pH = 3

<u>Solution</u>	<u>Rh(III)</u> <u>M</u>	<u>NO</u> <u>M</u>	<u>Absorbance</u>
1	2.26×10^{-5}	2.26×10^{-3}	0.135
2	2.26×10^{-5}	2.37×10^{-3}	0.163
3	2.26×10^{-5}	4.49×10^{-3}	0.181
4	2.26×10^{-5}	5.61×10^{-3}	0.193
5	1.13×10^{-4}	2.26×10^{-3}	0.664
6	1.13×10^{-4}	3.37×10^{-3}	0.829
7	1.13×10^{-4}	4.49×10^{-3}	0.939

b. Rhodium(III) Excess

$\mu = 0.010$ (as KClO_4)
pH = 3

<u>Solution</u>	<u>Rh(III)</u> <u>M</u>	<u>NO</u> <u>M</u>	<u>Absorbance</u>
1	1.13×10^{-3}	0.56×10^{-4}	0.084
2	1.13×10^{-3}	1.13×10^{-4}	0.196
3	1.13×10^{-3}	1.69×10^{-4}	0.305
4	1.13×10^{-3}	2.26×10^{-4}	0.419
5	1.13×10^{-3}	2.82×10^{-4}	0.535

TABLE V
FORMATION CONSTANT CALCULATIONS

a. Direct From Spectrophotometric Data ⁽³⁸⁾

$$K_f = \frac{b^n A_d - d^n A_b}{b^n d^n (A_b - A_d)}$$

Rh(III)	<u>b</u> M	<u>d</u> M	<u>A_b</u>	<u>A_d</u>	<u>K_f (n = 2)</u>	<u>K_f (n = 1)</u>
2.26 x 10 ⁻⁵	3.37 x 10 ⁻³	2.26 x 10 ⁻³	0.163	0.135	4.35 x 10 ⁵	4.15 x 10 ²
	4.49 x 10 ⁻³	3.37 x 10 ⁻³	0.181	0.163	2.99 x 10 ⁵	4.48 x 10 ²
	5.61 x 10 ⁻³	4.49 x 10 ⁻³	0.193	0.181	3.18 x 10 ⁵	4.98 x 10 ²
	4.49 x 10 ⁻³	2.26 x 10 ⁻³	0.181	0.135	3.88 x 10 ⁵	4.27 x 10 ²
	5.61 x 10 ⁻³	2.26 x 10 ⁻³	0.193	0.135	3.53 x 10 ⁵	4.41 x 10 ²
1.13 x 10 ⁻⁴	5.61 x 10 ⁻³	3.37 x 10 ⁻³	0.183	0.163	2.74 x 10 ⁵	4.65 x 10 ²
	3.37 x 10 ⁻³	2.26 x 10 ⁻³	0.829	0.664	3.45 x 10 ⁵	2.94 x 10 ²
	4.49 x 10 ⁻³	3.37 x 10 ⁻³	0.939	0.829	2.93 x 10 ⁵	3.37 x 10 ²
	4.49 x 10 ⁻³	2.26 x 10 ⁻³	0.939	0.664	3.03 x 10 ⁵	3.08 x 10 ²
				(3.3 ± 0.4) x 10 ⁵	(4.0 ± 0.6) x 10 ²	

b. From Evaluation Of Equilibrium Constant Parameters ⁽³⁶⁾

$$\log K_f = \log [\text{complex}] - \log [\text{Rh}] - n \log [\text{NO}]$$

$$\text{Initial Rh(III)} = 2.25 \times 10^{-5} \text{M}, \epsilon_m = \text{molar absorbance index} = 9.0 \times 10^3$$

<u>Complex</u>	<u>Rh(III) Residual</u>	<u>NO</u>	<u>K_f (n = 2)</u>	<u>K_f (n = 1)</u>
2.14 x 10 ⁻⁵	0.11 x 10 ⁻⁵	5.61 x 10 ⁻³	6.2 x 10 ⁵	3.5 x 10 ³
2.01 x 10 ⁻⁵	0.24 x 10 ⁻⁵	4.49 x 10 ⁻³	4.2 x 10 ⁵	1.9 x 10 ³
1.80 x 10 ⁻⁵	0.45 x 10 ⁻⁵	3.37 x 10 ⁻³	3.4 x 10 ⁵	1.2 x 10 ³
1.50 x 10 ⁻⁵	0.75 x 10 ⁻⁵	2.25 x 10 ⁻³	4.0 x 10 ⁵	0.9 x 10 ³
			(4.4 ± 0.8) x 10 ⁵	(1.9 ± 0.8) x 10 ³

An equilibrium constant can also be calculated if the extinction coefficient of the complex is determined. By this means, the concentration of the complex can be calculated and the other constituent concentrations can be evaluated by difference (Tables IV and V, pages 15 and 16).

$$\begin{aligned} \text{Calculated: } K_f &= (4.4 \pm 0.8) \times 10^5, n = 2 \\ K_f &= (1.9 \pm 0.8) \times 10^3, n = 1 \end{aligned}$$

RESIN STUDIES

Stability

Dowex 50WX2 (capacity 5.876 meq/dry g) was found to steadily increase the acidity of solutions of HClO_4 with which it was in contact when HClO_4 concentrations exceeded ca. 0.2M. The effect was not pronounced until acidities of 0.5M or higher were attained. Equilibration studies were therefore carried out in solutions of approximately 0.1M HClO_4 corresponding to an acidity of pH 1. The effect was attributed to perchlorate oxidation of the quaternary amine exchange sites and was confirmed by an observed decrease in capacity.

Elution

Solutions of rhodium(III) equilibrated with NO were, in turn, equilibrated with Dowex 50WX2. Typically, 1.00 ml of 0.01127M Rh(III) solution saturated with NO for 24 hr was added to 2 g resin. The acidity was adjusted to approximately pH 1 and, after 5 to 10 min of stirring, the mixture was transferred to a column containing acidities: pH 7, pH 3, pH 1, 1M H^+ , or 2M H^+ . Solutions were monitored spectrophotometrically for the adduct absorbing at 268 $\text{m}\mu$.

Elution at acidities below pH 1 (pH 3 and pH 7) gave normal distribution curves indicating about 25% retention; i.e., 75% of the product eluted directed in fractions corresponding

to column volume displacement. At higher acidities, essentially all the product was eluted, apparently without adsorption. The distribution showed less tailing at the highest values. No significant change in the absorption spectra was observed in any of the fractions collected that could not be attributed to acidity effects. The displacement of the adduct (unadsorbed) occurred ahead of the neutral eluting solutions and only in the small tailing fraction was there a significant blurring of the absorption peak into a shoulder comparable to those obtained on pH adjustment above 3. Significantly, when these fractions were adjusted to pH 1, a normal peak resulted.

After acid elution in several cases, the column was eluted further with either Ce(III) perchlorate or Th(IV) perchlorate. No additional elution of the 268 m μ adduct was observed, nor were other species indicated. A single Rh-NO species was therefore assumed.

Charge/Species And Charge/Species Rh Atom

The method of Cady and Connick⁽³⁹⁾ as modified by Wolsey, Reynolds, and Kleinberg⁽⁴⁾ was used. In a typical experiment, 25 ml of $1.13 \times 10^{-3} \text{M}$ Rh(III)-NO saturated solution was added to an exact amount of Dowex 50WX2 resin (ca. 0.2 g) and a small amount of known acid added to establish the desired acidity level and volume. The mixture was stirred for 4 to 6 hr and two 1-ml aliquots were withdrawn for the analysis of acidity and rhodium levels, respectively, in the equilibrated solution. A 10-ml aliquot of H₂O was added to the solution. Another 4 to 6 hr of stirring was performed and two aliquots were withdrawn for analysis. One calculation could be made from each pair of equilibrations to evaluate species charge. Data are summarized in Table VI and indicate a value of plus three.

Rhodium solutions derived from contact with Dowex 50WX2

TABLE VI
CHARGE/SPECIES

	<u>Series/ Equilibration</u>	<u>Total Rh (mmole)</u>	<u>Equilibrium Volume</u>	<u>Final H⁺ (M)</u>	<u>Residual Rh (M)</u>	<u>Residual Rh (mmole)</u>	<u>Adsorbed Rh (mmole)</u>	<u>Charge/ Species</u>
I	1	0.0282	35	0.705	3.18×10^{-5}	0.0011	0.0271	2.7
	2	0.0281	37	0.609	2.22×10^{-5}	0.0008	0.0002	
	3	0.0281	39	0.538	1.59×10^{-5}	0.0006	0.0002	
		Resin: 0.2152 g Dowex 50WX2, 1.265 meq capacity - O ₂ excluded						
II	1	0.0282	35	0.705	2.89×10^{-5}	0.0010	0.0272	2.4
	2	0.0281	37	0.606	2.11×10^{-5}	0.0008	0.0001	
	3	0.0281	39	0.535	1.41×10^{-5}	0.0006	0.0002	
		Resin: 0.2329 g Dowex 50WX2, 1.369 meq capacity - O ₂ excluded						
III	1	0.0282	35	0.703	3.09×10^{-5}	0.0011	0.0271	3.0
	2	0.0281	37	0.612	2.12×10^{-5}	0.0008	0.0002	
		Resin: 0.2154 g Dowex 50WX2, 1.266 meq capacity - O ₂ excluded						
IV	1	0.0113	34	0.191	2.00×10^{-5}	0.0007	0.0106	2.2
	2	0.0113	41	0.146	1.12×10^{-5}	0.0005	0.0002	
	3	0.0112	43	0.129	0.81×10^{-5}	0.0003	0.0001	
		Resin: 0.2 2 g Dowex 50WX2, 1.229 meq capacity - O ₂ excluded						
V	1	0.0158	30	0.198	2.74×10^{-5}	0.0008	0.0150	0.2
	2	0.0158	37	0.150	2.58×10^{-5}	0.0009	-	
	3	0.0157	39	0.131	2.11×10^{-5}	0.0008	-	
		Resin: 0.2561 g Dowex 50WX2, 1.505 meq capacity - O ₂ <u>not</u> excluded						

resin were contacted with Dowex 50WX2 to insure the presence of a single species. The solution was analyzed to assure the adsorption of rhodium. The resin was separated from the solution and placed in a column above a small amount of H⁺-form Dowex 50WX2. Elution was begun with a Ce(III) solution of known acidity, and the two eluate fractions of highest rhodium content were used to calculate charge/species/Rh atom.

The rhodium band preceding the Ce(III) front was sharp. Cerium(III) is quantitatively adsorbed by Dowex 50W.⁽³⁹⁾ Rhodium solutions of 4.52×10^{-2} M and 4.52×10^{-3} M were used in the initial equilibrations with NO. Resin capacity exceeded rhodium adsorbed in all cases by roughly 10:1. Data are summarized in Table VII and indicate a mononuclear rhodium species of +3 charge.

TABLE VII
MULTIPLICITY: CHARGE PER Rh(III) ATOM^(4, 39)

Elutrient (Initial)		Eluate (Final)		Charge/ Rh(III) Atom
Ce(III) M	H ⁺ M	Rh(III) M	H ⁺ M	
1.90×10^{-3}	0.1050	1.7×10^{-3}	0.1051	3.3
1.90×10^{-3}	0.1050	2.0×10^{-3}	0.1052	2.7
1.90×10^{-2}	0.1171	1.95×10^{-2}	0.1172	2.9
1.90×10^{-2}	0.1171	1.81×10^{-2}	0.1175	3.3
1.90×10^{-2}	0.1171	1.79×10^{-2}	0.1185	3.1
1.90×10^{-2}	0.1171	1.92×10^{-2}	0.1180	

$$\text{Charge/Rh atom} = \frac{(\text{H}^+)_{\text{i}} + 3(\text{Ce}^{3+})_{\text{i}} - (\text{H}^+)_{\text{f}}}{(\text{Rh})_{\text{f}}}$$

PRECIPITATION STUDIESHydroxide

A 2:1 molar ratio of hydroxide to rhodium was found in base (KOH) titrated solutions which had been derived from the direct reaction of NO and Rh(III) (Figure 3). Fresh solutions became cloudy at \sim pH 5. The dull, white precipitate was isolated and analyzed for rhodium and nitrogen.

<u>Found</u>		<u>Calculated For Rh(NO)₂(OH)₃H₂O</u>
44.4	Rh	44.40
12.03	N	12.07

The filtrate retained a substantial absorption at 268 μ as did solutions derived by dissolving the precipitate in 1M HClO₄. It was estimated that about half of the adduct had been carried by the precipitate.

Infrared absorptions were observed in the solid at 1620 cm^{-1} (W, broad), 1390 cm^{-1} (S), 1315 cm^{-1} (W), 1115 cm^{-1} (W), 825 cm^{-1} (S), 630 cm^{-1} (M), and 390 cm^{-1} (S), as well as a very strong, broad band at 3000 to 3500 cm^{-1} attributable to the OH, H₂O moiety (Figure 4, page 23). A similar product was isolated from acidified solutions prepared with Rh and NO₂⁻. The absorptions occurred within the limits shown in Figure 4, with the solid line indicating the product analyzed.

When parent solutions were aged 4 to 8 days after the Rh-NO reaction, the solutions became substantially more yellow, and titration with base produced no precipitate. The acidity of such solutions seemed to equilibrate at \sim pH 2. This reaction did not produce marked changes in the 268 μ peak or the titration curve. The absorption maximum appeared constant although less well resolved from the 200 μ nitrogen-oxygen absorption when adjusted to pH values above 3.

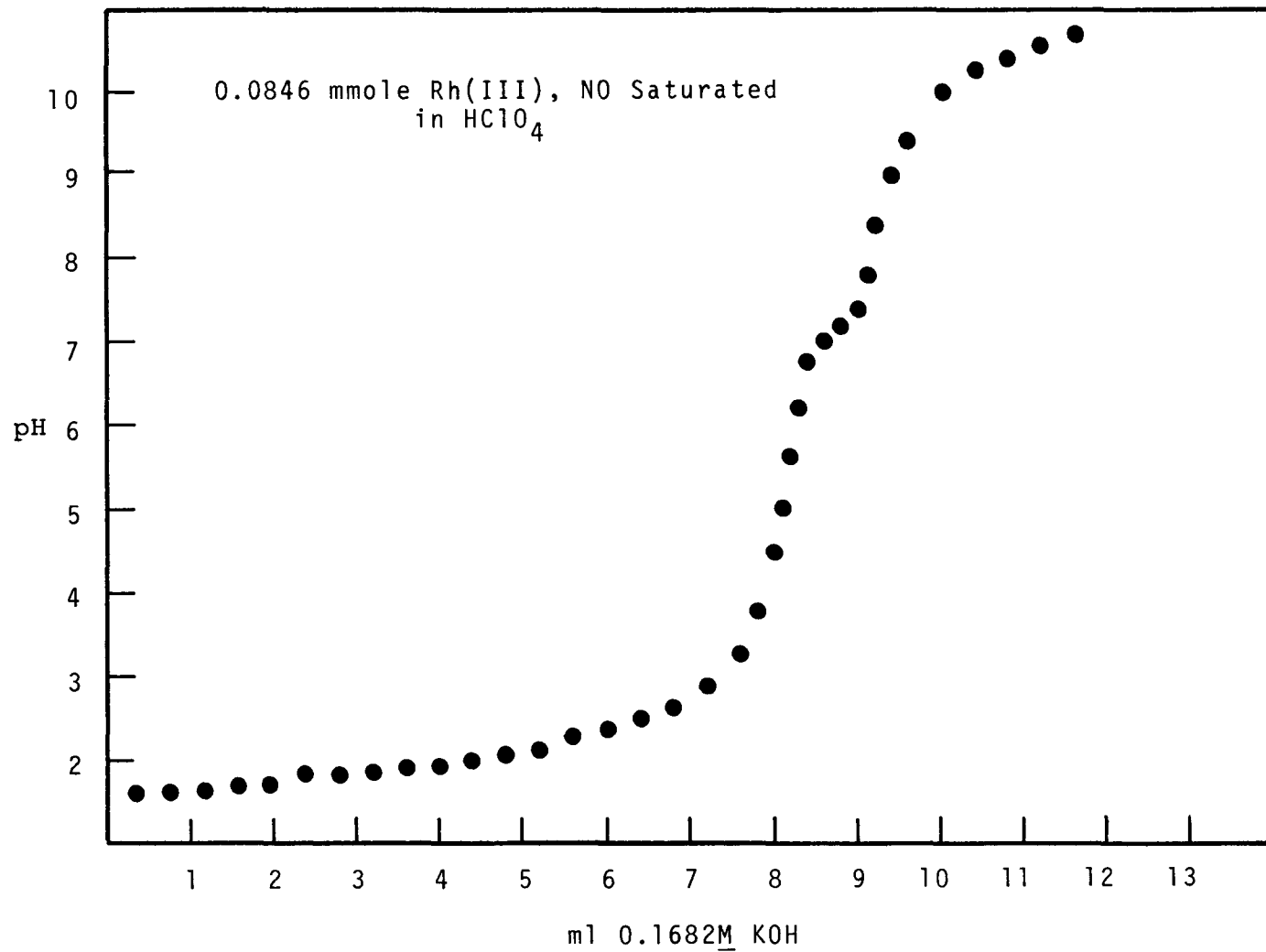


FIGURE 3
TITRATION OF ADDUCT SOLUTION

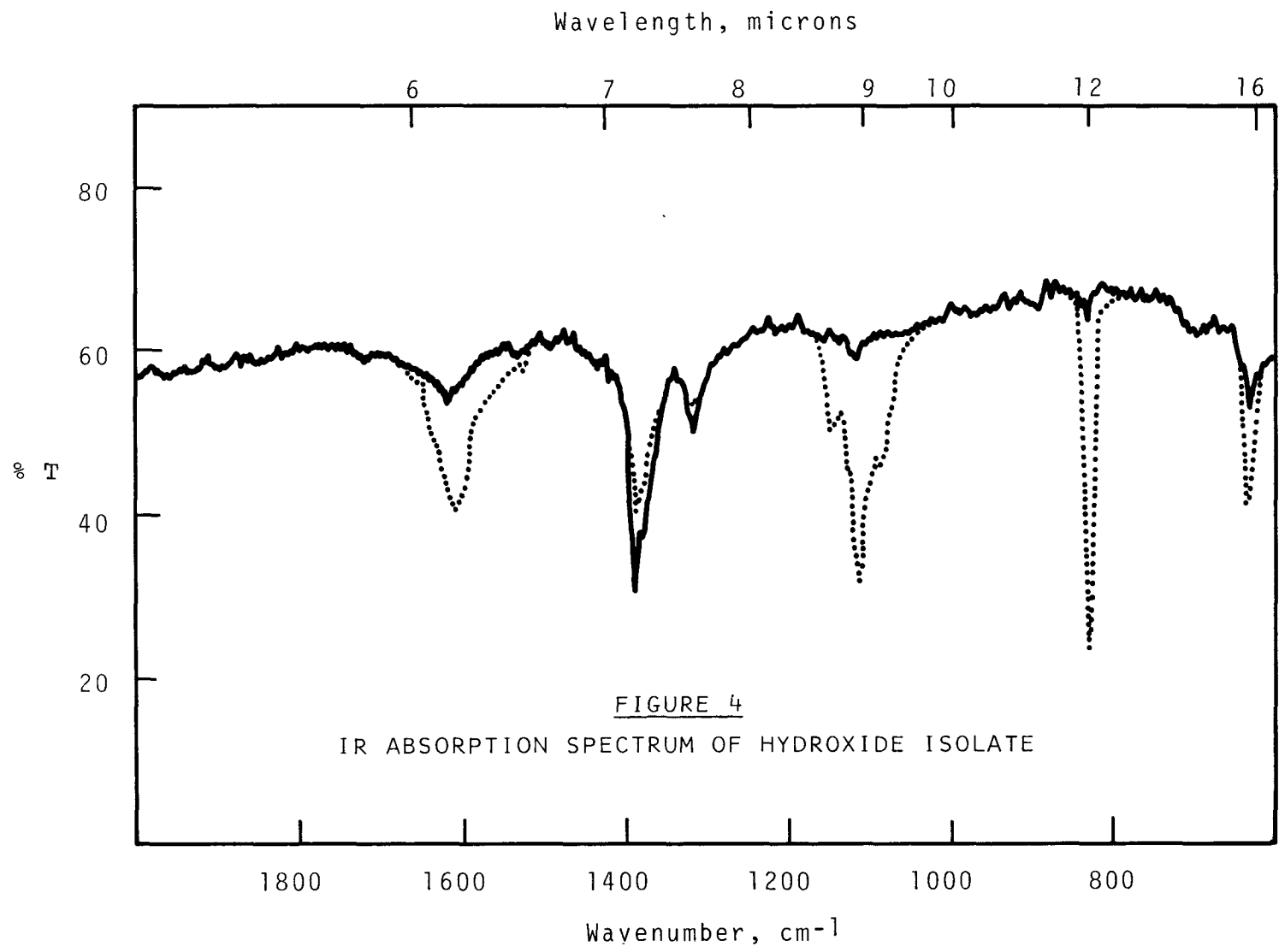


FIGURE 4
IR ABSORPTION SPECTRUM OF HYDROXIDE ISOLATE

Pyridyl Complexes

Quantities of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ varying from 0.1 to 1.0 g were weighed, dissolved in a minimum of water, and converted to perchlorate solutions by twice fuming to a volume of 1 to 2 ml with HClO_4 . The remaining solution was diluted to approximately 10 ml and saturated with nitric oxide for 72 hr after the solutions had been purged for 2 hr with argon. The yellow color became appreciably lighter with time. Transfer was made to a 50 ml volumetric flask that had been argon-flushed.

From 5 to 25 ml aliquots of the Rh-NO equilibrated solution were refluxed for 2 hr with 5 ml each of pyridine and ethanol. Oxygen was not excluded, but 0.2 g of 10% zinc amalgam was added in contact with the solution. The solution became more brownish in color and a white solid separated after about 1/2 hr. More solid could be obtained by reducing the solution volume under vacuum after reflux but some $[\text{pyH}^+\text{ClO}_4^-]$, precipitating as well, required removal by recrystallization. The solid had a low H_2O solubility (ca. 10^{-4} moles/liter) but was recrystallized readily in 50 vol % pyridine/ H_2O . Recovery was approximately 40% on recrystallization.

For $[\text{Rh}(\text{NO})_2(\text{py})_4]^{2+}(\text{NO}_2^-)(\text{ClO}_4^-)$:

	Rh	C	H	N
Calculated	16.48	38.46	3.23	15.70
Found	16.4 (as residue)	38.67	3.46	15.23

The UV spectrum of aqueous solutions in contact with the solid showed a band at about 260 $\text{m}\mu$ with some minor fine structure.

Infrared absorptions observed for the solid were:

3460 (B), 3100 (B), 1615 (S), 1496 (W), 1456 (S), 1420 (B, S), 1390 (W), 1362 (W), 1328 (S), 1277 (W), 1225 (M), 1165 (W),

1100 (B, S), 1071 (Sh, S), 1052 (W), 1021 (M), 830 (S), 780 (Sh), 765 (S), 702 (S), 622 (S), 462 (M). See Figure 5.

Mass spectral values observed for the solid were:

154.16, 157.30, (165), (166), 167.087, (168), 200.067, 201.111, 231.193.

Masses in parentheses were not determined exactly. Particularly strong low m/e values were 26 through 32, 49 through 54, and 79.

In comparable experiments, a 5-fold excess of NaNO_2 (relative to Rh) was added directly to diluted Rh(III) perchlorate solutions and allowed to stand for 72 hr in contact with air before transfer to a 50-ml volumetric flask. Five ml aliquots were refluxed with an equal volume of pyridine and ethanol, respectively. A white solid formed and was recrystallized from 50 vol % pyridine/ H_2O . Recovery was approximately 30% on recrystallization.

For $[\text{Rh}(\text{NO})(\text{py})_4(\text{NO}_2^-)]^{2+}(\text{NO}_2^-)(\text{ClO}_4^-)$:

	Rh	C	H	N
Calculated	16.07	37.50	3.15	15.30
Found	16.2 (as residue)	38.07	3.50	15.32 (by Kjeldahl)

Examination of aqueous solutions of the compound exhibited a broad band absorption at 264 $\text{m}\mu$ with minor fine structure and a weak, broad band at 350 $\text{m}\mu$.

Infrared absorptions by the solid included:

3450 (B), 3140 (W), 3070 (W), 1612 (S), 1580 (W), 1496 (M), 1460 (Sh), 1425 (B, S), 1348 (M), 1318 (M), 1222 (S), 1161 (M), 1100 (B, S), 1075 (Sh, S), 1050 (W), 1020 (M), 870 (W), 832-827 (S, doublet), 762 (S), 700 (S), 644 (W), 624 (M), 458 (M). See Figure 6.

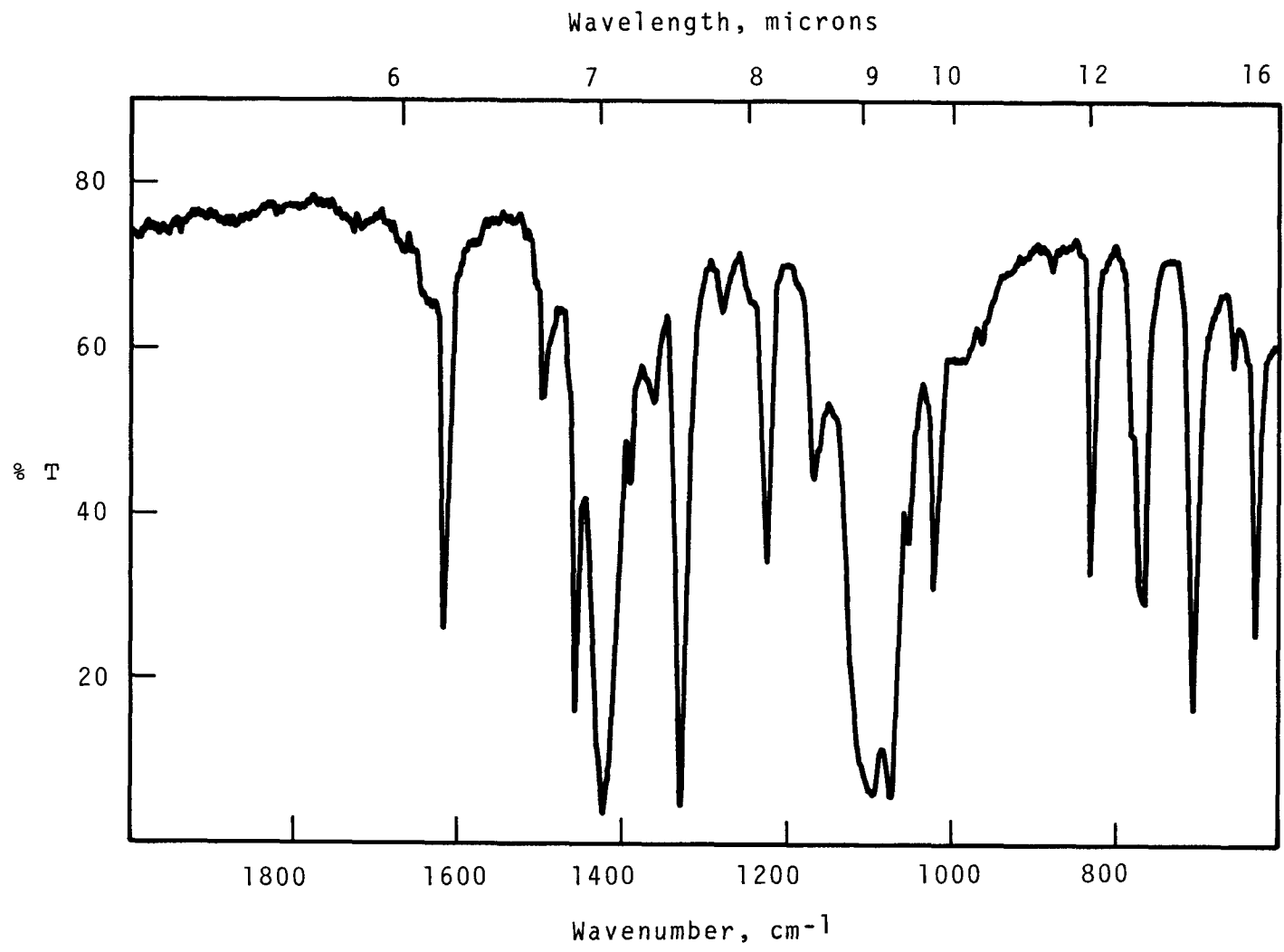


FIGURE 5
IR SPECTRUM $[\text{Rh}(\text{NO})_2(\text{py})_4][\text{NO}_2][\text{ClO}_4]$

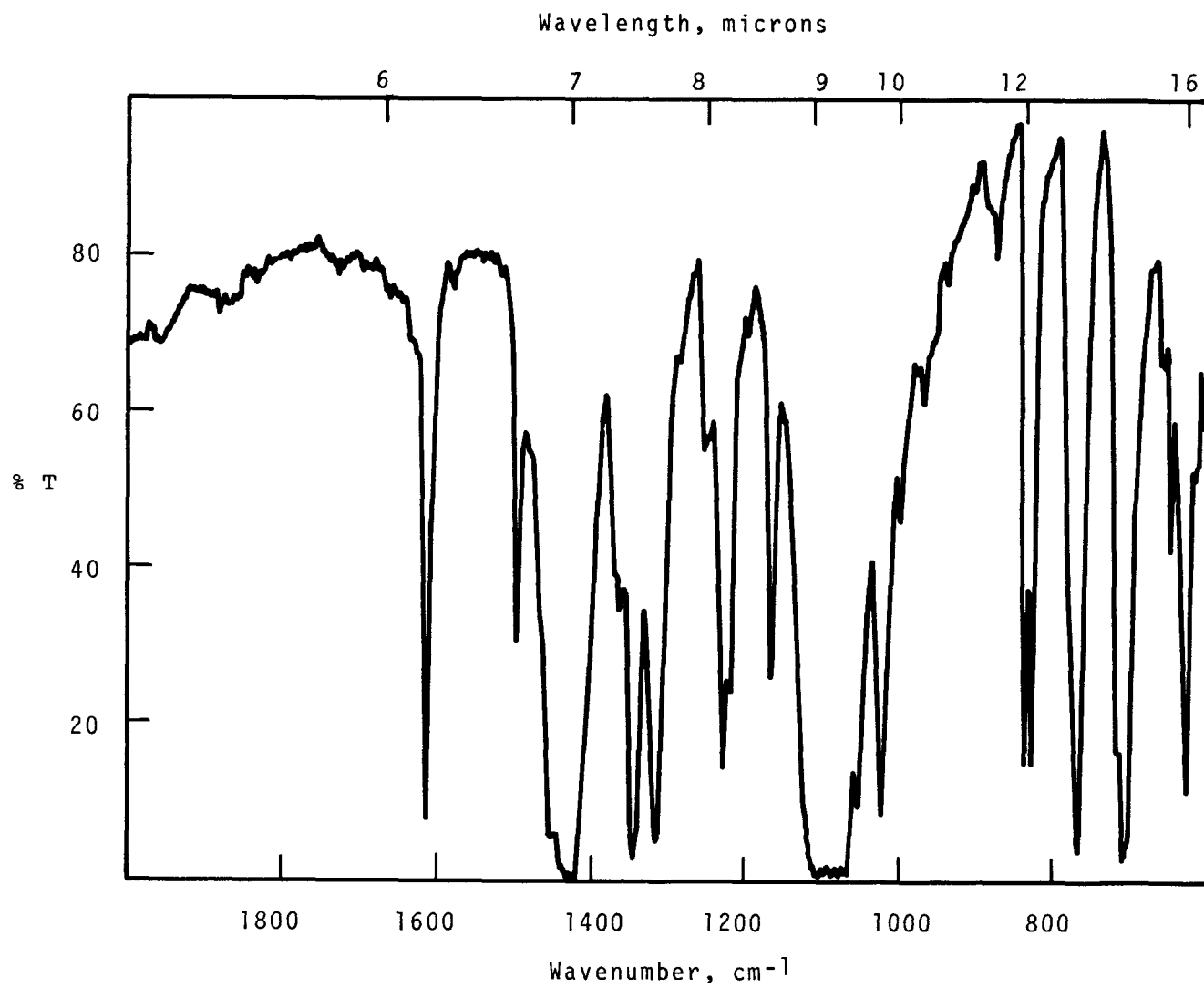


FIGURE 6
IR SPECTRUM $[\text{Rh}(\text{NO})(\text{py})_4(\text{NO}_2)][\text{NO}_2][\text{ClO}_4]$

Mass spectrometer peaks observed include:

154.162, (157), (200), (201), (317), (318), 320.129, (321).

Treatment of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ solutions directly with pyridine/ethanol reflux yielded a known yellow crystalline product: $\text{trans-}[\text{Rh}(\text{py})_4(\text{Cl})_2]^+(\text{Cl}^-)$, ^(40, 41) whose infrared spectrum of

3400 (Vb, S), 2160 (B, W), 1600 (M), 1480 (W), 1454 (S), 1210 (M), 1155 (W), 1070 (M), 1020 (W), 770 (B, M), 698 (M), is in agreement with literature values.

Other Reagents

Attempts to precipitate a rhodium species of the form $[\text{Rh}(\text{NO})_2]^{3+}$ with sodium salts of p-toluenesulfonate, diphenyl dithiocarbamate, dithiooxalate, and phenylarsonate were unsuccessful. Sodium salts of tetraphenylborate and tetrafluoroborate were not available.

SPECIES IDENTIFICATION IN RADIOACTIVE WASTE SOLUTION

Numerous anion exchange resins have been monitored as absorbants of rhodium from radioactive waste solutions. In an attempt to identify rhodium solution species, four anion exchangers were chosen--Dowex 1X2, Amberlite XE-238, Ionac XAX-1316, and "Aliquat 336." In each case a quantity of anion exchanger of known capacity was contacted with a fixed quantity of the waste solution for 10 min to 2 hr. In all cases except those in which Aliquat 336 was used, the absorbate was eluted with one or more of the reagents 1% HClO_4 , 4% NaOH , 15% HCl , 10% NH_4SCN , 5% sodium citrate, 5% sodium oxalate, 5% sodium tartarate, 5% sodium acetate, 5% sodium formate, 4% KI , and 5% NH_4Cl .

Elution with the specified reagents led to two observations: (1) elution was reasonably efficient and yielded solutions with very strong UV absorbancies at 305 $\text{m}\mu$ (NO_3^-) and 355 $\text{m}\mu$

(NO₂⁻), completely masking absorptions around 270 m μ (Dowex 1X2), XE-238); or (2) elution was inefficient as evidenced by low absorption at 305 and 355 m μ , and showed no 270 m μ peak. In either instance, the result was inconclusive.

Aliquat 336, a liquid quaternary amine, was used in a procedure derived from previous studies.⁽⁴²⁾ Twenty percent Aliquat 336 in CCl₄ was contacted with the waste solution for 2 hr and, after 100-fold dilution, was monitored spectrophotometrically directly against CCl₄ since it was shown that Aliquat 336, as supplied, did not significantly absorb at these dilutions. A strong peak was observed in the wavelength range 264 to 274 m μ as well as a peak centered at 355 m μ , normally associated with nitrite. Variation of the absorbance peak occurred with conditions, but no coherent pattern of association was developed. The equilibrated Aliquat 336 solution contained large quantities of rhodium, as indicated by atomic absorption analysis.

Stripping of Aliquat 336 with nitrate or nitrite solutions was avoided in order to maintain a clear spectral field in which to observe rhodium species absorption. Elution with 1% HClO₄ and 15% HCl did elute substantial rhodium, as indicated by analysis of the aqueous solution. The aqueous solution indicated a strong absorption at about 285 m μ , as well as remnants of the nitrite absorption series centering around 355 m μ . Stripping of Aliquat 336 with the other eluents mentioned previously did not remove significant quantities of rhodium.

Rhodium-nitric oxide equilibrated solutions (pH = 1, initial), which showed a strong 268 m μ absorption, were equilibrated with 15% HCl and saturated NH₄Cl solutions for 25 hr at 25 °C. The absorption peak had shifted to 278 m μ and 275 m μ , respectively, by the end of that time; and did not shift significantly thereafter.

DISCUSSION

The rhodium solution adduct absorbing at 268 $m\mu$ may be assigned the formula $[\text{Rh}(\text{NO})_2]^{3+}$ on the basis of the experimental work to date. Tentative identification of a species of this type has been made in radioactive waste solutions. Spectral studies, rate studies, resin equilibration studies including calculation of species charge, the isolation products, infrared spectra, and mass spectral assignments all tend to confirm the assignment.

NITRITE DECOMPOSITION

The kinetics of nitrous acid decomposition has been the subject of a careful study by Abel and coworkers,^(17, 18) and has been summarized by Bray.⁽¹⁹⁾ Even though the rate constant (K_1) is small, the decomposition of HNO_2 occurs relatively rapidly in solutions whose acidity approximates or exceeds the ionization constant of HNO_2 (5.0×10^{-4} @ 25 °C) because of the fourth power term, $(\text{HNO}_2)^4$. That the adduct is formed independently of nitrite concentration can be accounted for by envisioning a rate of HNO_2 decomposition more rapid than the rate of adduct formation. The fact that HNO_2 concentration does not affect the formation of the adduct and that the adduct does not form in basic nitrite solutions confirms NO as the ligand. The adduct also forms directly with $\text{NO}_{(g)}$.

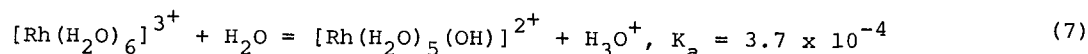
SPECTRAL EVIDENCE

Data to support the formula assignment (Figure 2, page 13) and calculation of the formation constant (Tables IV and V, pages 15 and 16) seem internally consistent when the assignment $[\text{Rh}(\text{NO})_2]^{3+}$ is made. Calculations from the derived constant show that in 0.1M solutions of the complex, 4% is dissociated; in 0.01M solutions, 19%; in 0.001M solutions, 91%.

Therefore, a large ligand excess is required at low rhodium concentrations to account for the incorporation of rhodium in the complex. This condition is met in radioactive waste solutions where NO_3^- and NO_2^- are in molar concentration or higher. (1)

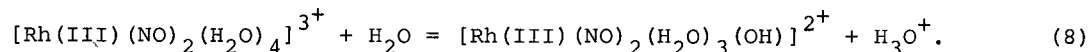
TITRATION DATA

The fact that only two moles of base are observed to add per mole of Rh when Rh-NO solutions are titrated is unexpected. Forrester and Ayres⁽⁴³⁾ observed that for solutions of Rh(III) perchlorate, a three-mole base reaction with $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ proceeds via two steps, the first of which can be represented by the proton transfer:

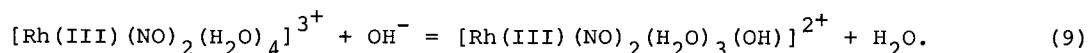


In the second step, two moles of hydroxide are "added" to give neutral $\text{Rh}(\text{OH})_3(\text{H}_2\text{O})_3$.

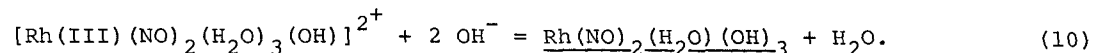
A species of the type $[\text{Rh}(\text{NO})_2(\text{H}_2\text{O})_4]^{3+}$ would have a higher acidity than $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ because of the nucleophilicity of NO, therefore the reaction



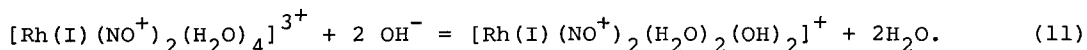
should be represented by a relatively large constant. The abstraction of an initial proton, therefore, may occur indistinguishably from the excess acid in the system, reflected by titration to the first inflection (Figure 3, page 22) as in the following:



The second inflection would thus correspond to the abstraction of two additional protons and the formation of a neutral species



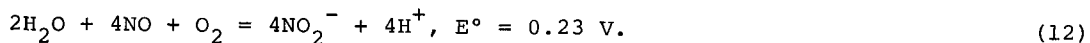
One might also anticipate a substantial decrease in the acidity of an aquated species, $[\text{Rh}(\text{I})(\text{NO}^+)_2(\text{H}_2\text{O})_4]^{3+}$, as opposed to $[\text{Rh}(\text{III})(\text{NO}^\circ)_2(\text{H}_2\text{O})_4]^{3+}$, due to the delocalization of charge. Only two protons might be abstracted in simple aqueous titration because of the decreased species acidity, but a soluble species would again need to be accounted for, as shown by



The most logical inference from these data is that the formation of a species $[\text{Rh}(\text{III})(\text{NO})_2]^{3+}$ occurs initially and that this species can be precipitated by the addition of base. On standing, however, conversion of the ligand to NO^+ either internally or by external oxidation results in soluble hydroxylate species under the prevailing conditions. This inference, confirmed by the weak IR absorption band at 1610 cm^{-1} , can be attributed to complexed neutral NO .^(15, 28) Wilkinson and co-workers⁽⁴⁴⁾ assign NO^+ stretch frequencies in metal ion complexes to the range 1580 to 1980 cm^{-1} , and NO^- stretch frequencies in metal ion complexes to the range 1045 to 1250 cm^{-1} .

CHARGE/SPECIES

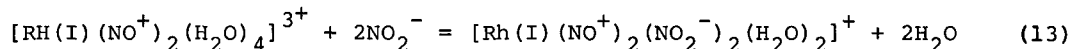
The oxidation of NO does not yield free NO^+ in solutions of relatively low acidity, although it is well known that this ion can exist in concentrated H_2SO_4 . A more likely product under the relevant conditions than $[\text{N}(\text{III})\text{O}]^+$ is $[\text{N}(\text{III})\text{O}_2]^-$.



Accepting this argument, one can account for the variation in charge/species determinations observed (Table VI, page 19).

The oxidation of NO within the ligand field may be thought to give rise to NO^+ , but the oxidation of free NO yields anionic species. If the resultant anions subsequently enter the

coordination sphere of rhodium, the charge/species observed will be reduced.



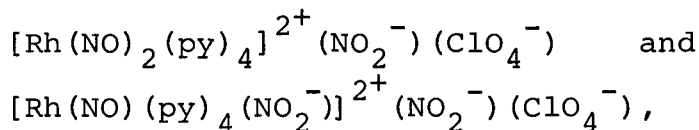
This result is consistent with the fact that equilibration with oxygen reduces the charge/species observed in Rh-NO saturated solutions. The plausibility of this explanation is enhanced by the absorption at 825 cm^{-1} observed in the hydroxide isolate which can be assigned to NO_2^- .⁽⁴⁵⁾

The determination of charge/species/Rh atom indicates the Rh-NO adduct to be mononuclear. The ligand, therefore, does not act as a bridging group as with some nitrite complexes,⁽⁴⁶⁾ and the assigned formula $[\text{Rh}(\text{NO})_2]^{3+}$ is correct.

PYRIDYL COMPLEXES; INFRARED AND MASS SPECTRA

The isolation of a complex in which pyridine fills the remaining coordination positions of $[\text{Rh}(\text{NO})_2]^{3+}$ is subject to some hazards which direct precipitation by heavy anions does not entail. The fact that an $[\text{Rh}(\text{NO})_2]^{3+}$ -anion precipitate was not obtained directly is attributable to both concentration and stability effects. Rhodium in the solutions from which isolation was attempted was 10^{-3} molar, and the instability of thio-substituted derivatives of the compound types used is notorious. With higher Rh concentrations and reagents of the tetra-R boron type, isolations should be possible.

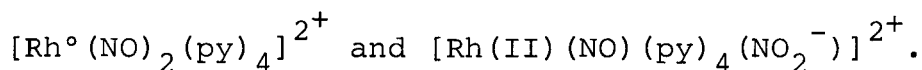
Isolation procedures involving pyridine substitution have been used successfully with Rh complexes, however.^(40, 47) Of the isolated compounds corresponding to element analysis of



confirmatory evidence in terms of both IR (Figures 5 and 6, pages 26 and 27) and mass spectral data are available. In

both compounds, the sharp absorption band at 1615 cm^{-1} can be attributed to the N-O stretch. Furthermore, the fact that this absorption lies above 1500 cm^{-1} strongly suggests nitric oxide to be in the nitrosyl form, NO^+ .⁽⁴⁴⁾ A characteristic NO_2^- absorption occurring at 830 cm^{-1} is split in the case of the second compound. It has been suggested that the splitting of this NO_2^- peak can be caused by asymmetry in the ligand field⁽⁴¹⁾ in nitrite complexes; e.g., in dinitro cis--rather than trans--complexes. From previous studies,^(40, 47) one anticipates trans- $[\text{Rh}(\text{NO})_2(\text{py})_4]^{2+}$; but in trans- $[\text{Rh}(\text{NO})(\text{py})_4(\text{NO}_2)]^{2+}$, asymmetry is introduced by virtue of the disparity of the trans-groups, NO^+ and NO_2^- .

The rhodium oxidation states implied by these data are, therefore:



Since a small amount of amalgamated zinc was present during the isolation of the first product, $[\text{Rh}(\text{NO})_2(\text{py})_4]^{2+}$, a lower oxidation state of rhodium perhaps can be expected. The delocalization of charge represented by $[\text{Rh}(\text{II})(\text{NO}^+)]^{3+}$ compared with $[\text{Rh}(\text{III})(\text{NO}^\circ)]^{3+}$ may be consequential in the difficulties encountered in isolating a heavy anion salt. Studies on the titration and precipitation of dinitrosyl rhodium hydroxides can be rationalized in this way. Data are insufficient to be definitive, however.

Data from mass spectroscopy are perhaps less convincing, but do support the assignments made. Strong m/e values are observed at 30 (NO), 46 (NO_2), and 79 (pyridine). In addition, the fragmentation pattern of pyridine, including strong peaks at 27 (HCN) and 52 (pyridine-HCN),⁽⁴⁸⁾ is generally observed. The presence of the assigned primary ligands can, therefore, be accounted for. At higher values, mass correspondences are

not exact, as for instance, 167.087 found and 166.91 calculated for $[\text{Rh}(\text{OH})_2\text{NO}]^+$. There appears to be mass defect of about 0.2 amu per peak observed. Although differences between higher masses also roughly correspond to the expected presence of fragments; e.g., $231.93 - 201.111 = 30.078$ ($\text{NO} = 29.998$), the mass defects are larger than the expected experimental error would seem to predict. There seems no other coherent way to account for mass peaks observed, however. Fragments tentatively identified in this way from mass differences include O^+ , CN^+ , and CO^+ . Rhodium species which have whole mass number correspondences to m/e values obtained include $[\text{RhO}(\text{NO})(\text{ClO})]^+ - 200$, $[\text{RhO}(\text{NO})(\text{CN})_2]^+ - 201$, $[\text{RhO}(\text{NO})_2(\text{CN})_2]^+ - 231$, $[\text{Rh}(\text{py})_2(\text{NO})_2]^+ - 321$. Accepting these assignments, the evidence for the composition of the isolated products is confirmed.

RHODIUM IN RADIOACTIVE WASTE SOLUTIONS

Attempts to identify $[\text{Rh}(\text{NO})_2]^{3+}$ in radioactive waste solutions have been inferentially successful. Solid anion exchange resins (Dowex 1X2, Amberlite XE-238) adsorb rhodium from the waste solutions but also adsorb large quantities of nitrate and nitrite which exhibit strong UV absorptions in the eluate solutions. In high concentration, these components effectively mask any rhodium present. Ionac XAX-1316, on the other hand, known to adsorb no Rh from basic radioactive waste solutions,⁽¹⁾ will adsorb practically no nitrate or nitrite either, hence Ionac XAX-1316 cannot be used as a separative identification device.

Aliquat 336 in suitable concentration in CCl_4 extracts rhodium, a fact confirmed by atomic absorption analysis. A strong 264 to 274 $\text{m}\mu$ maximum is observed which usually occurs at the lower wavelengths in solutions. When batch-eluted with 15% HCl or 10% HClO_4 , the peak diminishes and an absorption band at 285 $\text{m}\mu$ appears in the aqueous phase. The band is nearly identical with that obtained when known $[\text{Rh}(\text{NO})_2]^{3+}$

solutions are equilibrated with chloride except for a 7 to 10 m μ shift of maximum. It, therefore, seems reasonable to suggest that the species isolated from radioactive waste solutions is a dinitrosylchloro complex of internal form $\text{Rh}(\text{NO})_2\text{Cl}_n \cdots$, where n is probably 1 or 2. "Real" solutions are subject to much more rigorous equilibration conditions; e.g., heat and time, than the synthetic solutions prepared. The shift observed in absorption peak in synthetic solution is suggestive, however.

The chloride content of waste solutions, while probably not high,⁽¹⁾ is nonetheless likely to be 100-fold higher than the rhodium concentration present. Therefore, the formation of a nitrosylchloro species is not precluded. Although the chloride in this study may have been derived from Aliquat 336 itself (tricaprylylmonomethyl ammonium chloride), the fact that both HCl and HClO_4 elute a comparable product suggests the species to be pre-formed and that significant quantities of additional chloride at high chloride concentrations are not complexed. A study of the anion adsorption characteristics of "real" rhodium species, therefore, might begin with the use of HClO_4 in this separation step. A successful elution step in which $(\text{Rh}(\text{NO})_2(\text{H}_2\text{O})_4)^{3+}$ can be eluted directly has not been found.

No evidence was found for rhodium- N_2 complexes even when solutions were flushed with nitrogen rather than argon. Metal ion-ligand conditions similar to those reported for the formation of some molecular nitrogen complexes^(32, 49-51) were used, but no evidence for ligand N_2 was found in these systems.

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