

quacies in the theory used in interpreting light scattering data.¹⁵ The assumptions inherent in the treatment of the light scattering and centrifugation data are somewhat different. Centrifugation requires that the partial specific volumes of KCl and the tantalate be constant, and the solution density is assumed to be constant to facilitate computation. Both methods assume a monodisperse polymeric solute, and they both require that the degree of complexing by medium ions be constant, that the appropriate species activity coefficient products be constant, and both light scattering and schlieren centrifugations require that $\eta = Z'm'/2m_3 \ll 1$. The latter condition would appear to be somewhat more critical for the light scattering case, for the cross term in the activities, $(\partial \ln a_2/\partial m_3)$, is proportional to $\eta/(1 - \eta^2)$.¹⁶ At the highest concentrations in the light scattering and the schlieren centrifugations $\eta \approx 0.06$, while the largest value in the interference optics centrifugations was *ca.* 0.03. Since

(15) P. Stiger, *J. Phys. Chem.*, **64**, 242 (1960).(16) R. S. Tobias and S. Y. Tyree, *J. Am. Chem. Soc.*, **81**, 6385 (1959).

charge effects were rather small, it was necessary to centrifuge with rather high concentrations to obtain an estimate of Z' . The assumption of constancy of activity coefficients or more specifically that the derivatives of the activity coefficients with concentration vanish should be valid for the polymer noncross term at the concentrations encountered here, *i.e.*, $(\partial \ln \gamma_2/\partial m_2) \approx 0$. The other derivatives are not necessarily zero, and for KCl the change of activity coefficients with concentration does not generally reach a minimum until the molarity is *ca.* 2.5.¹⁷

When the studies of tantalate solutions were begun, it was thought that the light scattering measurements would provide the simplest means of determining the degree of polymerization. In practice, because of the difficulty in clarifying the solutions for light scattering, ultracentrifugation with interference optics proved to be the simplest method once a computer program was written to process the data.

(17) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth Scientific Publications, London, 1955, p. 479.

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Catalysis of Substitution Reactions of Rhodium(III) Complexes. The Reaction of Aquopentachlororhodate(III) Ion with Pyridine

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The observation of Delepine that alcohol facilitates the synthesis of certain rhodium(III) complexes was investigated. For the reaction between $K_2[Rh(H_2O)Cl_6]$ and pyridine (py) to yield *trans*- $[Rh(py)_4Cl_2]Cl$, it was found that the role of the alcohol is to generate catalytic amounts of a lower oxidation state of rhodium. It is assumed that this is Rh(I), and a two-electron bridged activated complex mechanism is proposed for the catalysis reaction.

Introduction

In 1929¹ and again in 1953,² Delepine reported a peculiar observation of a ligand exchange reaction for rhodium(III) which appeared to be catalyzed by alcohols. He had been synthesizing the chloropyridine complexes of rhodium(III) by the reaction of an aqueous solution of $Na_3[RhCl_6]$ with pyridine and isolating the products which were successively formed by the slow introduction of pyridine into the coordination sphere. Due to the insoluble nature of the tripyridine complex $[Rh(py)_3Cl_3]$, some difficulty was experienced in introducing a fourth molecule of pyridine. Delepine found that adding an excess of pyridine to a slurry of the insoluble complex and heating the mixture on a steam bath produced a considerable amount of the desired product in 10 hr. In order to increase the solubility of the nonionic intermediate, he added alcohol to a reaction

mixture and was surprised to observe that the reaction went immediately and quantitatively from $[RhCl_6]^{3-}$ to $[Rh(py)_4Cl_2]Cl$ at room temperature.

Delepine found that the alcoholic hydroxyl group was responsible for the increase in reaction rate. All primary alcohols had about the same activity, secondary alcohols were significantly less active, and tertiary alcohols were inactive. Ether, dioxane, and acetone were likewise without activity.

On the basis of weight, methanol was the most active catalyst. Delepine stated, however, that the promotion of the reaction by trace amounts of it was an artifact based on the tenfold difference in molecular weight of methanol and $Na_3[RhCl_6]$. In fact, it appeared that about 1 mole of alcohol had to be present for each mole of rhodium in order for the reaction to take place. No suggestion was offered for the role of the alcohol in the catalysis mechanism. This paper reports observations on this system which suggest that the alcohol generates a lower oxidation state of rhodium which is the catalyst.

(1) M. Delepine, *Bull. Soc. Chim. France*, **45**, 235 (1929).(2) M. Delepine, *Compt. rend.*, **236**, 559 (1953).

Experimental

(A) **Chemicals.**—All chemicals used were of reagent grade unless otherwise noted. Rhodium was in the form of sponge from Baker and Company. Pyridine was Fisher Scientific Company Spectranalyzed grade. A vapor chromatogram showed the 95% ethanol to be free from acetaldehyde. Demineralized water was used for quantitative kinetic runs. It was freshly boiled and saturated with nitrogen.

(B) **Synthesis.**—The method of Gutbier and Hutlinger³ was used to prepare $K_2[Rh(H_2O)Cl_5]$. Damp chlorine gas was passed over an intimate mixture of KCl and powdered Rh metal for 1 hr. at a temperature of about 550°. The resulting pink material was recrystallized twice from water containing a small amount of HCl.

The acetate $[Rh(CH_3CO_2)_2]_2$ was prepared by the method of Johnson, Hunt, and Neumann.⁴ Hydrous rhodium(III) oxide was refluxed in glacial acetic acid. After the solvent was removed, the residue was extracted with boiling acetone. The acetone solution was cooled in an ice bath and blue-green crystals of the product were obtained. Other rhodium compounds were also prepared by the methods described in the literature, and the specific references are given in the section on results.

(C) **Instruments.**—Visible and ultraviolet spectra and preliminary kinetic data were taken on a Beckman DK-2 spectrophotometer. Quantitative kinetic determinations were made on a Beckman DU spectrophotometer.

Vapor phase chromatography was done using 3-m. columns in a Wilkens Aerograph chromatograph. A column packing of Carbowax 20M on 60–80 mesh Chromosorb P firebrick support was used for mixtures of water and ethanol. Silicone oil 550 on the same support was used for mixtures of water and acetic acid.

(D) **Kinetics.**—Kinetic studies were made on reaction 1.

$$[Rh(H_2O)Cl_5]^{2-} + 4py \longrightarrow trans-[Rh(py)_4Cl_2]^+ + 3Cl^- \quad (1)$$

The reactions were carried out in a 1-cm. cell in the cell compartment of a spectrophotometer thermostated at $25 \pm 0.1^\circ$. The rates were measured by following the decrease in absorbancy of $[Rh(H_2O)Cl_5]^{2-}$ at 510 $m\mu$ (ϵ 110), and it is that rate constant to which the data reported here refer. All reactions were run with an excess of pyridine so that no significant decrease in its concentration occurred during the course of reaction.

The yellow reaction product was isolated as the 3-hydrate. *Anal.* Calcd. for $[Rh(py)_4Cl_2]Cl \cdot 3H_2O$: C, 41.4; H, 4.87; Rh, 17.8. Found: C, 41.6; H, 4.85; Rh, 17.7. The product was shown by conductivity measurements to be stable in water solution for times long compared to the kinetic studies. The complex is in the *trans* form.⁵

Results

(A) **Catalysis by Alcohol.**—In the absence of alcohol a moderately rapid reaction occurred between $[Rh(H_2O)Cl_5]^{2-}$ and pyridine. The first product of this reaction appeared to be $[Rh(py)_2Cl_4]^-$ which absorbs at 510 $m\mu$. This reacted slowly to form the insoluble $[Rh(py)_3Cl_3]$. The first-order rate constant for the disappearance of $[Rh(H_2O)Cl_5]^{2-}$ in 0.31 *M* pyridine was 0.63×10^{-3} sec.⁻¹.

The addition of alcohol caused only a moderate increase in the rate of disappearance of $[Rh(H_2O)Cl_5]^{2-}$. The reaction, however, gave soluble *trans*- $[Rh(py)_4Cl_2]^+$ directly, with no intermediate complexes being formed. Hence, the catalysis primarily affects the

rate of formation of *trans*- $[Rh(py)_4Cl_2]^+$, rather than the disappearance of the starting material. The first product, $[Rh(py)_2Cl_4]^-$, of the uncatalyzed reaction was also found to go directly to the tetrapyridine complex in the presence of alcohol. All reactions were pseudo-first order. However, the systems were not convenient for detailed kinetic study.

In order to determine the fate of the alcohol, a reaction was carried out in aqueous solution using equimolar amounts of $K_2[Rh(H_2O)Cl_5]$ and ethanol, with pyridine in excess. When all the rhodium had reacted, the solution was acidified and the volatile material distilled. Vapor phase chromatography of the distillate revealed that no perceptible amount of alcohol had disappeared and that a trace of acetaldehyde had been formed.

The results suggested that the promotion of the reaction rate was due to catalysis, rather than to stoichiometric reaction with the alcohol, and that the acetaldehyde was produced by the reduction of a small amount of rhodium(III).

(B) **Effect of Reducing Agents and Reduced Forms of Rhodium.**—The fact that catalysis is due to traces of reduced rhodium was confirmed by adding traces of various reducing agents. Since acetaldehyde is a slightly better reducing agent than alcohol, it was chosen as a possible catalyst. It exhibited properties similar to alcohol, but gave somewhat more rapid pyridination reactions.

A few other reducing agents were also tested. Tin(II), $NaBH_4$, and hydrazine were most active. The approximate amount of reduced rhodium necessary to give a rapid reaction was determined from reactions catalyzed by these materials. When the amount of reduced rhodium was 0.5% of the total rhodium present, the reaction half-life at 25° was a few minutes. The rate was also several times faster than the fastest steps of the uncatalyzed reaction, at this level of catalyst.

Hypophosphorous acid, H_3PO_2 , which Dwyer used to produce what at first seemed to be rhodium(II) compounds,⁶ seemed to have some activity, although hardly more than alcohol. Cobalt(II) in the presence of pyridine did not increase the reaction rate.

A number of compounds which contained reduced rhodium were tested for catalytic activity. The rhodium(I) compounds tested were $[Rh(CO)_2Cl]_2$, $[Rh(CO)((C_6H_5)_3P)_2(Cl)]$, and $[Rh(CO)((C_6H_5)_3P)_2(SCN)]$. The first was a very powerful catalyst for the reaction. At a concentration of 2.10×10^{-5} *M*, with 0.31 *M* pyridine, the rate constant for the disappearance of $K_2[Rh(H_2O)Cl_5]$ was 2.0×10^{-3} sec.⁻¹. This number is used to estimate the amount of reduced rhodium in the catalysts in Table I. Solutions of $[Rh(CO)_2Cl]_2$ in acetone fairly rapidly lost their activity. The two other rhodium(I) compounds were inactive. These, however, were insoluble in water. Fine suspensions of them were made by dissolving the complexes in pyridine before adding them to the reaction. The compound

(3) A. Gutbier and A. Hutlinger, *Ber.*, **41**, 212 (1908).

(4) S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, **2**, 960 (1963).

(5) H.-H. Schmidtke, *Z. physik. Chem. (Frankfurt)*, **34**, 295 (1962).

(6) F. P. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. N. S. Wales*, **75**, 275 (1942); J. Lewis and R. S. Nyholm, *Chem. Ind. (London)*, 1386 (1960).

TABLE I^a
 RATES OF REACTION
 "Rh(II)"

$$[\text{Rh}(\text{H}_2\text{O})\text{Cl}_5]^{2-} + 4\text{py} \xrightarrow[25^\circ]{\text{"Rh(II)"}} \text{trans-}[\text{Rh}(\text{py})_4\text{Cl}_2]^+ + 3\text{Cl}^-$$

Catalyst concn., ^b <i>M</i>	Pyridine concn., <i>M</i>	Rate constant, ^c sec. ⁻¹	Concn. of added anion, <i>M</i>
6.00 × 10 ⁻⁴	0.31	6.32 × 10 ⁻³	...
6.00 × 10 ⁻⁴	0.31	5.10 × 10 ⁻³	...
3.00 × 10 ⁻⁴	0.31	3.15 × 10 ⁻³	...
1.50 × 10 ⁻⁴	0.31	1.36 × 10 ⁻³	...
0.725 × 10 ⁻⁴	0.31	0.54 × 10 ⁻³	...
0.725 × 10 ⁻⁴	0.31	0.48 × 10 ⁻³	...
2.90 × 10 ⁻⁴	0.744	1.64 × 10 ⁻³	...
2.90 × 10 ⁻⁴	0.572	1.66 × 10 ⁻³	...
2.90 × 10 ⁻⁴	1.240	1.68 × 10 ⁻³	...
2.90 × 10 ⁻⁴	0.372	1.48 × 10 ⁻³	...
2.90 × 10 ⁻⁴	0.31	8.42 × 10 ⁻³	...
2.90 × 10 ⁻⁴	0.31	8.21 × 10 ⁻³	...
2.90 × 10 ⁻⁴	0.31	5.12 × 10 ⁻³	0.0090, Cl ⁻
2.90 × 10 ⁻⁴	0.31	3.77 × 10 ⁻³	0.0181, Cl ⁻
2.90 × 10 ⁻⁴	0.31	3.16 × 10 ⁻³	0.0362, Cl ⁻
2.90 × 10 ⁻⁴	0.31	2.35 × 10 ⁻³	0.0724, Cl ⁻
2.90 × 10 ⁻⁴	0.31	2.3 × 10 ⁻³	0.0181, ClO ₄ ⁻
2.90 × 10 ⁻⁴	0.31	2.3 × 10 ⁻³	0.0181, NO ₃ ⁻
2.90 × 10 ⁻⁴	0.31	2.9 × 10 ⁻³	0.0090, NO ₃ ⁻
2.90 × 10 ⁻⁴	0.31	3.6 × 10 ⁻³	...

^a Comparisons of rate can be made only within each of the four groups of data. Each group of data is for the same catalyst solution. Different catalyst solutions prepared in the same way differ in activity. The concentration of $[\text{Rh}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ was 0.00724 *M* in all runs. ^b The catalyst concentration is the total concentration of rhodium, from the catalyst, of which only 10–20% is the low-valent, catalytic form. ^c Most of the values reported are averages of duplicate runs which agree to better than 10%.

designated⁷ as $[\text{Rh}(\text{bipy})_2]\text{ClO}_4 \cdot 3\text{H}_2\text{O}$ was catalytically active although when tested it was somewhat decomposed.

Among the compounds of supposedly rhodium(II) were the preparations⁸ reported as $[\text{Rh}(\text{py})_6]\text{Cl}_2$ and $[\text{Rh}(\text{py})_6]\text{Cl}$. These compounds were inactive, and the latter gave an analysis for $[\text{Rh}(\text{py})_4\text{Cl}_2]\text{Cl} \cdot 3\text{H}_2\text{O}$. The dimer $[\text{Rh}(\text{CH}_3\text{CO}_2)_2]_2$ was also inactive. When added to the reaction mixture it immediately precipitated as the insoluble pyridine adduct, $[\text{Rh}(\text{CH}_3\text{CO}_2)_2\text{py}]_2$. Partly decomposed $[\text{Rh}(\text{bipy})_2\text{Cl}]_2(\text{ClO}_4)_2$ ⁷ exhibited some activity.

(C) **Reaction Kinetics.**—The pyridination reaction (1) was investigated at 25° using a catalyst made by the reaction of aqueous chlororhodate solution with hydrazine at room temperature for several days. Aliquots of the catalyst were pipetted into aqueous solutions of pyridine and chlororhodate, and the reaction was followed as described above. This catalyst solution gave reproducible results for a series of kinetic runs taken within several hours of each other. However, solutions made up in the same way did not always have exactly the same activity, since the reaction between hydrazine and rhodium was very slow and the catalyst solutions were decomposed by air. The kinetic data derived in this way are reported in Table I.

(7) B. Martin and G. M. Waind, *Proc. Chem. Soc.*, 169 (1958); *J. Inorg. Nucl. Chem.*, **23**, 207 (1961); R. G. Gillard and G. Wilkinson, *J. Chem. Soc.*, 3594 (1963).

Groups of data listed together are from the same catalyst within a short period of time. Concentration of catalytic rhodium as listed in the table simply refers to the concentration of rhodium added from the standard catalyst. The amount in the reduced form is estimated from rates with a $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ catalyst to be 10–20% of this.

The reaction was first order in the concentration of $[\text{Rh}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$, and the disappearance of this ion was taken to be a measure of the rate of reaction. This rate is equal to the rate of formation of $[\text{Rh}(\text{py})_4\text{Cl}_2]$ in these catalyzed reactions. The first-order rate constant decreased slightly during the course of the reaction. This was found to be due to the increase in ionic strength. The rate constant varied less when an inert electrolyte was added initially. The reaction was also first order with respect to the catalyst, and zero order in pyridine, so long as pyridine was kept in considerable excess.

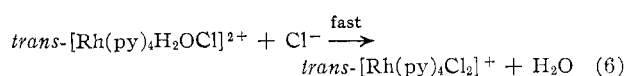
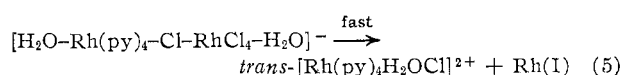
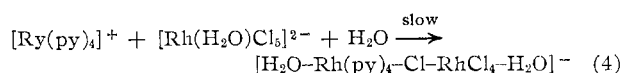
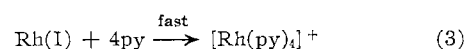
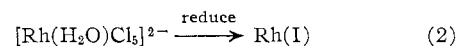
Added chloride ion had an inhibitory effect. That this was not due to a reaction between chloride and rhodium was indicated by a similar inhibition caused by nitrate and perchlorate ions, which are less likely to associate with the rhodium complex. Although the catalyst used in Cl⁻ runs happened to be more active than that in NO₃⁻ runs, the relative amount of inhibition was about the same.

Attempts to stabilize and isolate the reduced form of rhodium have thus far been unsuccessful. Its identification by electroanalytical and magnetic techniques has also failed. A mixture of tris(1,10-phenanthroline)rhodium complexes was isolated from a solution of reduced rhodium. The total analysis gave the average composition $[\text{Rh}(\text{phen})_3]_{1.2.60}$. The diamagnetism of this material suggests that the reduced rhodium was in the +1 state.

Discussion

The problem posed by Delepine's observation is fairly well solved. The role of the alcohol in the pyridination reaction is to reduce a small amount of rhodium. Chatt and Shaw⁸ have observed that RhCl_3 can be reduced by alcohol to the +1 state in the presence of KOH and ligands which stabilize that oxidation state.

The bulk of the evidence accumulated to date is consistent with the mechanism shown below.



(8) J. Chatt and B. L. Shaw, *Chem. Ind. (London)*, 931 (1960); 290 (1961).

A chain mechanism involving rhodium(II) cannot, however, be disregarded, assuming that rhodium(II) complexes are labile. The reason for preferring rhodium(I) as the catalytic species is, first, that $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, which must rapidly yield $[\text{Rh}(\text{py})_4]^+$, is a powerful catalyst for the reaction. The fact that the other Rh(I) compounds tested did not catalyze the reaction is probably explained not only by their insolubility, but also by the strong stabilizing influence of the phosphine ligands in the complexes. In the presence of pyridine, the reaction to form $[\text{Rh}(\text{py})_4]^+$ does not proceed to any significant extent.⁹ The second reason is that the +1 oxidation state of rhodium is well established. Few compounds of rhodium(II) have been prepared to date, and none of them is monomeric. The third reason involves the stoichiometry and configuration of the product. Since rhodium(I) forms planar complexes,

(9) L. Vallarino, *J. Chem. Soc.*, 2287 (1957).

the *trans* product is a necessary consequence of the proposed mechanism, while rhodium(II) might give either the *cis* or *trans* product. The same reasoning explains why rhodium will not pick up a fifth pyridine ligand even though the reaction is run at a fairly high concentration of pyridine: rhodium(I) is very unlikely to associate with more than four pyridines. It is also of interest to note that this mechanism for the Rh(I) catalysis of Rh(III) reactions is strictly analogous to the mechanism for Pt(II) catalysis of reactions of Pt(IV) complexes.¹⁰ Finally, the magnetic evidence cited above suggests the presence of rhodium(I) in the reduced solutions.

Acknowledgments.—This research was supported by the U. S. Atomic Energy Commission under contract No. AT(11-1)-1087.

(10) F. Basolo, M. L. Morris, and R. G. Pearson, *Discussions Faraday Soc.*, 29, 80 (1960).

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Polarographic Evaluation of the Formation Constants of Aquo-Copper(II) Complexes in Acetone

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Formation constants for the four aquo-copper(II) complexes $\text{Cu}(\text{H}_2\text{O})_3^{+2}$, $\text{Cu}(\text{H}_2\text{O})_2^{+2}$, $\text{Cu}(\text{H}_2\text{O})_3^{+2}$, and $\text{Cu}(\text{H}_2\text{O})_4^{+2}$ in acetone have been evaluated. Log k values are 1.75, 1.50, 1.00, and 0.75 in 0.1 M LiClO_4 solution and 1.75, 1.25, 0.80, and 0.65 in 0.1 M $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ solution.

Because even the most careful purification of an organic solvent leaves a surprisingly large amount of water in the solvent, *e.g.*, a solvent which is 99.98% pure, *i.e.*, 0.02% in water, is 0.01 M in water, one of the most important problems with regard to the interpretation of experimental results on studies dealing with the nature and behavior of inorganic ions in nonaqueous media is the effect of residual water. In a previous communication,¹ we presented information, in the form of formation constants for the aquo-copper(II) complexes, on the preferential solvation of copper(II) ion by residual water molecules in nitromethane and ethanol. Because these two solvents exhibit opposite extremes of behavior with regard to compatibility with water, we have evaluated the formation constants of aquo-copper(II) complexes in acetone, a solvent whose compatibility with water is between those of nitromethane and ethanol. This information should provide a better understanding of the magnitude of the effect of residual water on the behavior of metal ions in nonaqueous solutions than that which is possible from the results of the previous study alone.

Experimental

Reagent grade acetone was treated with potassium permanganate, dried over anhydrous potassium carbonate, and distilled from phosphorus pentoxide. All other pertinent experimental information has been presented elsewhere.^{1,2}

Results

The temporary constants in Table I were obtained by graphical evaluation of plots of $E_{1/2}\text{Cu(II)/Cu(I)}$ vs. $-\log [\text{H}_2\text{O}]$ (Fig. 1). Because the limiting slopes of the curves at high water concentrations (0.1–1 M) were *ca.* 0.24, only four constants were obtainable. These constants were refined by the method of successive approximations. The refined values are presented in Table II. A detailed discussion of the treatment of the experimental data was presented previously.¹

TABLE I
TEMPORARY FORMATION CONSTANTS FOR THE AQUO-COPPER(II)
COMPLEXES IN ACETONE

0.1 M LiClO_4	0.1 M $(\text{C}_2\text{H}_5)_4\text{NClO}_4$
$\log k_1 = 1.89$	$\log k_1 = 1.96$
$\log k_2 = 1.52$	$\log k_2 = 1.37$
$\log k_3 = 1.05$	$\log k_3 = 0.84$
$\log k_4 = 0.64$	$\log k_4 = 0.33$

(1) R. C. Larson and R. T. Iwamoto, *Inorg. Chem.*, 1, 316 (1962).

(2) I. V. Nelson and R. T. Iwamoto, *ibid.*, 1, 151 (1962).