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The Catalytic Species in the Labilization of Rhodium(III) Complexes by Reducing Agents or Hydride-Producing Compounds

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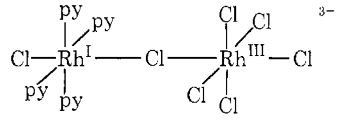
Several kinetic aspects of the catalyzed reaction $RhCl_6^{3-} + 4py \rightarrow [Rh(py)_4Cl_2]^+ + 4Cl^-$ (py = pyridine) have been examined in an effort to distinguish between the two proposed mechanisms for the reaction, one involving a rhodium(I) intermediate and the other a hydridorhodium(III) complex. Catalysts containing rhodium(I) compounds are found to be more active than those containing reducing (and/or hydride-producing) reagents such as sodium borohydride, ethanol, or molecular hydrogen. Hydrido complexes of rhodium(III) show little or no catalytic activity. It is found that the reactive rhodium(I) compounds do not turn into hydride complexes under the conditions of the pyridination reaction. The primary kinetic isotope effect required by the hydride-catalyst mechanism does not occur, but instead a small solvent isotope effect consistent with a rhodium(I) catalyst is found. The addition of *o*-phenanthroline inhibits the pyridination reaction, and this is interpreted in terms of its action as a scavenger for catalytic rhodium(I).

Introduction

The conversion of potassium hexachlororhodate(III), $K_3[RhCl_6]$, into dichlorotetrapyridinerhodium(III) chloride, $[Rh(py)_4Cl_2]Cl$ (py = pyridine), is a lengthy process. The substitution proceeds in steps, and before the product is obtained, trichlorotripyridinerhodium(III), $[Rh(py)_3Cl_3]$, precipitates as a tar. In 1929,[1] Delepine found that the addition of a little alcohol to the reaction mixture caused the conversion to occur immediately. From the quantity of alcohol involved, it was not clear whether promotion was due to catalysis or to stoichiometric reaction of the rhodium complex with the alcohol.[2] This method was occasionally found to be convenient in preparing rhodium complexes.[3,4]

Because it is a congener of much studied cobalt, rhodium has been investigated a good deal more intensively in the past decade. Interest in the promotion of pyridination by alcohol led to a kinetic study[5] which established that several reducing agents (including acetaldehyde, borohydride ion, hydrazine, and dichlorotetracarbonyldirhodium(I)) were capable of increasing the reaction rate. Some of these materials were active in small enough quantities to indicate that catalysis was occurring. From these facts and the nature of the reaction kinetics, a mechanism was proposed which was analogous to the labilization of platinum(IV) compounds by platinum(II).[6] Reducing agents were thought to produce rhodium(I), which, being labile,[7] rapidly surrounded itself with pyridine ligands. The planar rhodium(I) complex then formed a bridged intermediate (through its axial position) with an inert rhodium(III) ion and also coordinated a sixth ligand giving an intermediate, perhaps



Finally, the two rhodium atoms exchanged oxidation states, giving the product and a new molecule of rhodium(I) catalyst.

Another investigation had established that the action of borohydride ion on rhodium compounds produced hydrido complexes.[8] On this basis, an alternative mechanism was suggested in which the rhodium did not change its oxidation state. Successive rapid substitutions of coordinated chloride ligands by hydride ions were followed by rapid substitutions of hydride ligands by pyridine molecules.[9,10] Wilkinson and co-workers[10] also found that molecular hydrogen catalyzed pyridination reactions. They studied the polarographic reduction of solutions of rhodium(III) complexes and found that the reduction is a two-electron process. It was not possible, however, to decide whether the reduction product was rhodium(I) or a hydridorhodium(III) complex.[11] Recently, the rhodium(I) intermediate has been used to explain some substitutions by hydrazine in bis(ethylenediamine)-rhodium(III) complexes, although the data did not necessarily preclude a rhodium(III) hydride intermediate.[12]

It is of interest to determine which of these two mechanisms is responsible for the catalysis of rhodium(III) substitution. The reaction is of great utility[9] in devising synthetic routes among the inert and robust complexes of rhodium. It is also a potentially valuable technique in the synthesis of inert forms of other elements.

Although the dependence of the substitution rate on the concentrations of the reactants has been worked

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[8] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 3594 (1963).

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[11] R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, 4107 (1965).

[12] D. J. Baker and R. D. Gillard, *Chem. Commun.*, 520 (1967).

out for one of these catalyzed reactions,[5] the results do not unambiguously point to one mechanism rather than the other. One of the main differences between the mechanisms is the nature of the two catalytic chain carriers proposed, and this paper reports the results of a number of experiments designed to distinguish between them.

Experimental Section

Chemicals.—Potassium hexachlororhodate(III) was prepared by the method of Anderson and Basolo.[13] The crude material was extracted into 6 *M* hydrochloric acid. Concentration of the filtrate on the steam bath gave a precipitate of dark red needles. The salt was dried at 170° to constant weight. Some of it was dissolved in water and reduced with a slight excess of sodium borohydride. After standing for 1 hr, the black precipitate was filtered out and ignited with a Meker burner to give rhodium metal. The chloride in the filtrate was determined by titration with mercuric nitrate, using a nitroprusside indicator. *Anal.* Calcd for K_3RhCl_6: Rh, 23.8; Cl, 49.1. Found: Rh, 24.0; Cl, 49.1. The product of the catalyzed pyridination of $RhCl_6^{3-}$ ion was $[Rh(py)_4Cl_2]Cl$. Some of the product was collected, recrystallized from boiling water containing a few drops of hydrochloric acid, and ignited to give rhodium metal. *Anal.* Calcd for $[Rh(py)_4Cl_2]Cl$: Rh, 19.6. Found: Rh, 19.6. Dichlorotetracarbonyldirhodium(I), $[Rh(CO)_2Cl]_2$, was obtained by the method of Heiber[14] and purified by recrystallization in hexane (mp 125–126°, lit.[15] 124–125°).

2,4-Pentanedionatodicarbonylrhodium(I), $[Rh(CO)_2acac]$, was prepared from the previous compound by treatment with 2,4-pentanedione and barium carbonate (mp 154°, lit.[16] 155°). Dihydrotetrapyridinerhodium(III) hexachlorophosphate, $[Rh(py)_4H_2]PCl_6$, and hydridopentaamminerhodium(III) chloride, $[Rh(NH_3)_5H]Cl_2$, were prepared by the methods of Wilkinson.[8,17] The hydride stretching frequency of the latter indicated that it had been partly hydrolyzed to the hydridoaquotetraamminerhodium(III) chloride, $[Rh(NH_3)_4(H_2O)H]Cl_2$.[17]

The following were distilled under nitrogen before use in kinetic runs: water, deuterium oxide, pyridine (refluxed with zinc dust), 3-pentanone (refluxed with lithium aluminum hydride), and diglyme (refluxed with sodium borohydride).

Catalysts.—The catalysts were added to the reaction in various ways. Alcohol was pipetted into the aqueous pyridine solution before the dissolution of the K_3RhCl_6. The rhodium(I) compounds were dissolved in 3-pentanone, and the sodium borohydride was dissolved in diglyme; they were then pipetted into freshly made hexachlororhodate solutions. These catalysts were quite sensitive to air and had to be handled carefully under nitrogen. Occasional erratic results were judged to be due to oxygen contamination. The $[Rh(py)_4H_2]PCl_6$ catalyst was prepared as an acetone solution, and $[Rh(NH_3)_5H]Cl_2$ was dissolved in water. Hydrogen was introduced at the lower concentration as an aliquot of hydrogen-saturated water. At the higher concentration, the reaction solution was saturated with hydrogen before the potassium hexachlororhodate was added.

Kinetic Runs.—The rates of pyridination of hexachlororhodate ion were measured on a Beckman DU spectrophotometer at 510 mμ. The hexachlororhodate, along with some sodium chloride, was dissolved in aqueous pyridine. An aliquot of freshly prepared catalyst was then added, and some of the solution was pipetted into a cuvette and placed in the thermostated (25.0 ± 0.02°) sample chamber of the spectrophotometer. The rate constants for the disappearance of the hexachlororhodate were calculated from standard first-order plots of log $(A - A_\infty)$ *vs.* time. The reactions were first order in hexachlororhodate and catalyst concentrations. The reaction rates were insensitive to the concentration of pyridine, so long as it was in considerable excess. They were, however, sensitive to ionic strength,[5] and the purpose of sodium chloride was to minimize the over-all change in the ionic strength of the reaction mixture as the pyridination progressed. It was not practicable to correct for the fairly slow rates of the competing aquation and uncatalyzed pyridination reactions. Their products also absorbed at 510 mμ and underwent pyridination as well, so the rate of disappearance of the 510-mμ absorption was not much affected by the competing reactions. The disappearance of hexachlororhodate ion in the presence of *o*-phenanthroline was measured on a Cary Model 14 spectrophotometer.

Spectra.—Nuclear magnetic resonance spectra were recorded on a Varian Associates HA-100 spectrometer. Solutions (5%) of $[Rh(CO)_2Cl]_2$ and $[Rh(CO)_2acac]$ were prepared in water–pyridine solvents. The solutions rapidly turned dark brown, and, in the case of the chloride, a gas (probably carbon monoxide) was evolved, but no precipitate was evident. The spectra were scanned to about τ 40. Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer.

Results and Discussion

Catalyst Activity.—Table I lists the first-order rate constants for several catalysts. The relative activity of the catalysts, k_2, was calculated by dividing k_1 by the concentration of the catalytic species. In the cases of $[Rh(CO)_2Cl]_2$ and sodium borohydride, k_2 is shown to be a true second-order rate constant.

TABLE I

RATE CONSTANTS FOR THE PYRIDINATION OF HEXACHLORORHODATE[a]

Promoter	10^6[Catalyst], *M*	$10^4 k_1$, sec^{-1}	$10^{-2} k_2$,[b] l./mole sec
$[Rh(CO)_2Cl]_2$	2.78[c]	4.6	1.7
	3.71	6.2	1.7
	5.21	10.6	2.0
	7.42	13.8	1.9
$[Rh(CO)_2acac]$	6.98	14.0	2.0
$[Rh(py)_4H_2]PCl_6$	4.95	~0[d]	
$[Rh(NH_3)_5H]Cl_2$	37.9	4.3	0.11
$NaBH_4$	6.60[e]	2.8	0.44
	9.17	4.0	0.44
	13.2	5.7	0.42
	18.3	7.1	0.39
C_2H_5OH	17,000	64	0.0038
H_2	8.5	~0[d]	
	850	21.2	0.025

[a] $[K_3RhCl_6] = 5.56 \times 10^{-3}$ *M*, $[C_5H_5N] = 0.310$ *M*, [NaCl] $= 4.29 \times 10^{-2}$ *M*. [b] $k_2 = k_1$/[catalyst]. [c] Reported as [Rh(I)]. [d] No faster than the aquation reaction. [e] Reported as $[H^-]$.

It can be seen from the rate constants that the two rhodium(I) compounds were better catalysts than either the reducing (or hydride-producing) reagents or the hydridorhodium(III) compounds. This was the expected behavior pattern if rhodium(I) were the real catalyst for the reaction and the other promoters were reducing some of hexachlororhodate ion in the solution. One would expect that if a hydride were responsible for the catalysis, the rhodium(I) compounds would be among the less active catalysts. The fact that the two rhodium(I) catalysts had the same catalytic activity is explicable in terms of quantitative

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conversion of each into the chain carrier, $[Rh(py)_4]^+$. This is not surprising in view of the labile nature of rhodium(I) and the excess of pyridine in the reaction mixture. The conclusion is consistent with the independence of the reaction rate on the concentration of pyridine.[5]

Formation of Hydrides by Rhodium(I) Compounds.—Wilkinson has synthesized a number of hydrido complexes of rhodium(III).[8] The proton magnetic resonances of the hydrido ligand fell in the range τ 25–35. In an effort to find whether the rhodium(I) catalysts were turning into hydridorhodium(III) compounds under the conditions of pyridination, strong solutions of them were made in water–pyridine solvents. Neither of the solutions exhibited resonances beyond τ 10. These compounds were strong promoters of the pyridination reaction. If the catalytic material in the reaction was a hydridorhodium(III) complex, the rhodium(I) compounds should be readily converted into it. It might be argued that the rhodium(I) complexes were merely producing hydride ions, but this would not account for their effectiveness as catalysts, since they are more active than hydride ions.

Kinetic Isotope Effect.—The catalysis mechanism involving hydride substitution would seem to require a large change in rate when the hydride catalyst was changed to deuteride. Promotion of the reaction by this mechanism depends on the speed of making or breaking a hydrogen-to-metal bond in the rate-determining step. That speed must be greater than the speed of making the metal-to-pyridine bond or of breaking the metal-to-chloride bond (whichever is the rate-determining step of the uncatalyzed reaction). When $[Rh(CO)_2Cl]_2$ was used as the catalyst, any hydrido complex which was formed would have to extract its proton from the water. Whether this was a hydride or a deuteride complex would then depend on whether the solvent was H_2O or D_2O. For this catalyst, the ratio of the rate constants, k_{H_2O}/k_{D_2O}, was 0.87 ± 0.07. This value is in the range expected for a solvent isotope effect and is quite small to be associated with making or breaking a hydrogen bond. With ethanol as the catalyst (which would exist in D_2O solution as C_2H_5OD), k_{H_2O}/k_{D_2O} was 1.35 ± 0.08. Once more, the result is consistent with a change in the properties of the solvent. The author suggests that the reason for the increase in rate constant ratio from 0.87 to 1.35 might be that ethanol is a better reducing agent in H_2O than in D_2O.

Substitution by *o*-Phenanthroline.—A perplexing synthesis of a rhodium(III) compound using reducing (or hydride-producing) catalysts was that of dichlorobis(*o*-phenanthroline)rhodium(III) chloride, $[Rh(phen)_2Cl_2]Cl$.[9] The mechanism involving a rhodium(I) intermediate would probably require a *trans* configuration for the compound. This is, in fact, the geometry assigned by Wilkinson, although the assignment is disputed.[18] On the other hand, there are other reasons to think that the *cis* geometry is more probable. *o*-Phenanthroline ligands in *trans* positions experience mutual repulsions by the protons at the 2 and 9 positions. Examination of molecular models suggested that the Rh–N bond distance would have to be of the order of 2.8 A for a 1.2-A van der Waals radius of hydrogen. This is abnormally long (*cf.* 2.23 A in $[Rh(NH_3)_5Cl]Cl_2$).[19] The unfavorable energetic situation of a *trans*-bis(*o*-phenanthroline) complex has been observed for a compound in which the *o*-phenanthrolines are made to assume this geometry. Livingstone[20] prepared $[Pd(phen)_2](ClO_4)_2$, which has planar geometry (see below), and, with such strong ligands, should be thermodynamically stable and probably kinetically inert to substitution. Treatment of the compound with aqueous chloride, however, gave an immediate precipitate of $[Pd(phen)Cl_2]$. This lability probably is the result of steric repulsion between the ligands. The author is in the preliminary stages of an X-ray crystallographic determination of the $[Pd(phen)_2](ClO_4)_2$ structure (space group I2/c, a = 14.48 A, b = 11.02 A, c = 14.79 A, β = 95.56°, four molecules per unit cell). The palladium does have planar coordination, and the phenanthrolines appear to be somewhat bowed about their twofold axes by the steric strain. In view of these facts, it would seem that diacidobis(*o*-phenanthroline) complexes would be in a more favorable energetic situation in a *cis* configuration.

The puzzle of having a *cis* geometry seemingly precluded by the mechanism and *trans* by the energetics was resolved when an attempt was made to catalyze the substitution of *o*-phenanthroline. Under the same conditions that pyridination readily took place, using alcohol or $[Rh(CO)_2Cl]_2$ as a catalyst, *o*-phenanthroline did not react with hexachlororhodate ion at any appreciable speed. The rate of disappearance of the ion was the same whether *o*-phenanthroline was there or not. It was concluded that in both cases the reaction was one of aquation of the rhodium, although the strong absorption of the phenanthroline in solution made it impossible to determine spectroscopically whether any *o*-phenanthroline was coordinated.

It was further discovered that phenanthroline is an inhibitor of catalyzed pyridination. The rate of the reaction in the absence of *o*-phenanthroline ($[K_3RhCl_6] = 5.56 \times 10^{-4}\ M$, $[C_5H_5N] = 0.310\ M$, $[NaCl] = 4.29 \times 10^{-2}\ M$, and $[Rh_2(CO)_4Cl_2] = 2.39 \times 10^{-6}\ M$) was 3.9 times as fast as in 0.015 M *o*-phenanthroline solution. With 0.218 M ethanol as the catalyst, the inhibition factor was 2.4. The product was identified spectroscopically as $[Rh(py)_4Cl_2]^+$ ion. It was difficult to see how the hydride mechanism for catalysis could be used to account for the inhibition. If rhodium(I) was the catalyst, however, the product and the decrease in rate were easily explained. *o*-Phenanthroline reacts rapidly with rhodium(I). If the complex formed cannot be oxidized by hexachlororhodate ion to a rhodium(III) compound, the *o*-phen-

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anthroline is effectively removing some of the catalyst from the reaction chain. Pyridine competes with *o*-phenanthroline for the rhodium(I), and to whatever extent it forms complexes with the labile metal, the catalyzed pyridination is carried on. The slower rate is the result of the decreased effective catalyst concentration. The smaller inhibition of the alcohol catalyst compared with $[Rh(CO)_2Cl]_2$ can also be accounted for. As *o*-phenanthroline removed rhodium(I), the excess alcohol was able to produce more while, with the $[Rh(CO)_2Cl]_2$ catalyst, only a fixed amount of rhodium(I) was available.

The question still remained about the synthesis of $[Rh(phen)_2Cl_2]Cl$. Closer scrutiny of the procedure indicated that the catalyst, hydrazinium chloride, was added in sufficient quantity to reduce more than half of the rhodium present. Furthermore, the reaction was carried out in boiling 50% ethanol. It may have been that the chain mechanism, with rhodiums exchanging oxidation states, did not occur. Instead, all of the rhodium was reduced, underwent ligand exchange, and was reoxidized by the reducing and oxidizing agents present in the reaction mixture.

Conclusion

The author feels that many of the data presented in this paper are inconsistent with the catalytic species in the pyridination of hexachlororhodate ion being a hydride. On the other hand, nothing presented here or elsewhere is inconsistent with the catalyst being a rhodium(I) complex. The reagents which have been shown to produce hydrido complexes have previously been used in such large quantities that the small amounts of reduced rhodium needed to bring about catalysis could easily have been formed. When the amounts of the promoters are reduced to a minimum, it is found that rhodium(I) compounds are more active than hydride ion. Since rhodium(I) does not form hydrido complexes under the reaction conditions, it seems necessary to conclude that it is the primary catalytic agent.

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Stereochemistry of Oxidative Addition Reactions of Iridium(I) Complexes[1,2]

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A study has been made of the stereochemistry of the oxidative addition reactions of halogens, hydrogen halides, alkyl halides, and acetyl halides with *trans*-$[IrCl(CO)((C_6H_5)_2PCH_3)_2]$. The stereochemistry of the resulting octahedral complexes has been assigned by a combination of nmr and far-infrared spectroscopy. Evidence supporting a kinetically controlled *trans* addition is reported. Reactions with mercuric chloride and perfluoroalkyl iodides are also described.

Oxidative addition reactions involving four- and five-coordinate d^8 complexes is a subject of considerable current interest.[4–6] Impetus is given to this research by the number of homogeneous catalysts which are d^8 complexes and whose mode of action involves oxidative addition and its reverse, reductive elimination.[4] To understand the detailed mechanisms by which such homogeneous catalysts act requires a knowledge of the stereochemical course of these reactions. The two-stage oxidative addition of five-coordinate d^8 complexes has been shown to be *cis*.[4] Herein is described our investigation of the stereochemistry of oxidative additions involving planar four-coordinate complexes.

When this project was begun, the only definitive stereochemical information concerning oxidative additions with four-coordinate complexes were the results of Basolo[7] on platinum(II) amine complexes and Vaska's[8] addition of oxygen to *trans*-halogenocarbonylbis(triphenylphosphine)iridium(I) (1, X = Cl). Reaction of chlorine with the platinum(II) complexes afforded octahedral products in which the chlorine atoms were *trans*;[7] however, it is not clear that this configuration results from kinetic or thermodynamic control. *cis* addition is clearly indicated in the formation of $[IrX(CO)((C_6H_5)_3P)_2O_2]$. The apparent *cis* elimination of chlorine from tetrachlorobis(tri-*n*-

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(2) Abstracted from the Ph.D. dissertation of C. T. Sears, University of North Carolina, 1966.

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