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The Thermodynamic and Kinetic Stabilities of Some Tetra-μ-Carboxylatodirhodium(II) Adducts

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The stability constants and forward and reverse rate constants have been determined for adduct formation reactions involving tetra-μ-acetato, tetra-μ-propionate and tetrakis-μ-methoxyacetatodirhodium-(II) with the ligands pyridine, picolinic acid, niacin and isonicotinic acid. The experimentally observed stability trend is isonicotinic acid > pyridine ≃ niacin ≫ picolinic acid. It appears that the π-bonding ability of the ligands determines the order of stability of these adducts. The variation of the stabilities of the adducts formed from different tetra-μ-carboxylatodirhodium(II) complexes and a given ligand is related to an inductive effect as well as the lipophylic nature of the carboxylate side chain. The more hydropholic character of the propionate species apparently exerts a desolvating effect at the two axial positions resulting in a more rapid ligand exchange.

Introduction

Tetra-μ-carboxylatodirhodium(II) complexes (Figure 1) offer a unique and interesting system for the investigation of ligand exchange reactions in solution. The four bridging carboxylate ions occupying the equitorial position on the two rhodium(II) cations are kinetically inert. This is in contrast to the rapid ligand exchange which occurs at the two axial positions. The exchange process is usually accompanied by a color change when, as in aqueous solution, the two axially bonded waters are replaced by different non-oxygen donor atoms. For example, when one or both the axial water molecules are replaced by a ligand containing a nitrogen donor atom, the color of the complex changes from blue to pink. Making use of this property one can monitor directly the concentrations and rate of change in the concentration of the rhodium(II) complexes by utilizing spectrophotometric techniques. It should also be pointed out that these systems are unique in that the tetra-μ-carboxylatodirhodium(II) complexes are neutral species and that the ligands involved in the exchange process can only function as monodentates. This simplifies the mechanistic interpretation of the rate studies since the measured rate constant, k_f, does not involve the uncertainties introduced by the large calculated ion pair constant, K_o, that is present in measured rate constants involving substitution reactions of charged species.

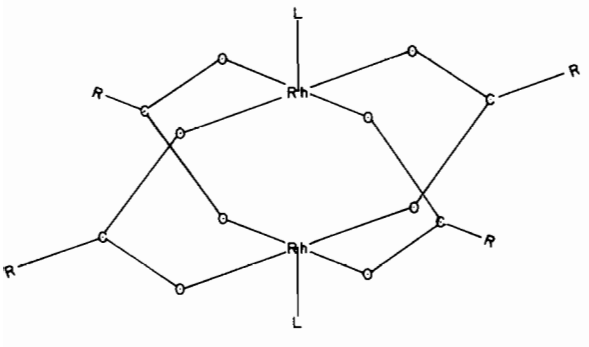

Figure 1. The structure of tetra-μ-carboxylatodirhodium(II) complexes. L, axial ligands and R, carbon chain of the carboxylate groups. R = $-CH_3$, tetra-μ-acetatodirhodium(II); R = $-CH_2CH_3$, tetra-μ-propionatodirhodium(II); R = $-CH_2-OCH_3$, tetrakis-μ-methoxyacetatodirhodium(II).

Recently, we reported thermodynamic and kinetic parameters for adduct formation reactions involving several tetra-μ-carboxylatodirhodium(II) complexes with a variety of nitrogen donor ligands [1–3]. These studies indicated that the π-acceptor ability of the nitrogen donor ligand was an important factor in determining the stability of the adducts. Also by changing the carboxylate ion bridging the two rhodium ions and measuring the stability of the adducts formed with a given ligand such as histidine, it was found that the stability increased with decreasing basicity of the carboxylate ion. However, with imidazole this apparent inductive effect was not the stability controlling factor. For example, tetra-μ-propionatodirhodium(II) forms a more stable adduct with imidazole than does tetra-μ-methoxyacetatodirhodium(II). Apparently the lipophilic nature of the bridging carboxylate ion is also a significant factor in determining the stability of these adducts.

The kinetic studies [3] showed that changing the bridging carboxylate ion did not have a significant

effect on the rate of axial ligand exchange. However, with the ligands 5′-AMP, histidine and imidazole, the rate of monoadduct formation of tetra-μ-propionatodirhodium(II) was consistently faster than the corresponding reactions involving the tetrakis-μ-methoxyacetato and tetra-μ-acetatodirhodium(II) species. Apparently the more lipophilic side chain of the propionate ion weakens the metal water interaction at the axial positions. The variation of the rate constants for a particular carboxylate complex reacting with 5′-AMP, histidine, imidazole and pyridine was found to be greater than an order of magnitude in some cases. This variation seemed to be related to the number of donor atoms on the entering ligand; those with more than one donor atom reacting faster.

Very little is known about the thermodynamic and kinetic stability of the tetra-μ-carboxylatodirhodium(II) adducts in aqueous solutions. For this reason we have determined the formation constants and measured the forward and reverse rate constants for the adducts formed between tetrakis-μ-methoxyacetato, tetra-μ-acetato and tetra-μ-propionatodirhodium(II) with pyridine, picoline, and niacin and isonicotine acid. These ligands were chosen because of their varying π-bonding ability as well as to determine how steric factors effect the thermodynamic and kinetic stability of the complexes.

Experimental

Chemicals

Tetra-μ-acetatodirhodium(II) was purchased from Matthey Bishop, Inc., Malvern, Pa. 19335. Tetra-μ-propionatodirhodium(II) and tetrakis-μ-methoxyacetatodirhodium(II) were synthesized by a method previously described [4]. All rhodium(II) complexes were recrystallized before use and dried for 1 hr at 80 °C in a vacuum oven to remove acetone and water.

All the solutions were made in phosphate buffer. The buffer was prepared by dissolving K_2HPO_4 and KH_2PO_4 in a ratio suitable for the desired pH (7.4) and ionic strength (0.1) in deionized water.

Formation Constants from Spectral Data

Because of the blue to pink color change produced by the complexation reaction, the extent to which the reaction has proceeded can be monitored by scanning the visible region. A Cary Model 14 spectrophotometer and 10-cm path length cells were used in this study. The solutions were mixed in the spectrophotometric cell by titrating 24 ml of 3.17×10^{-4} *M* rhodium(II) carboxylate with varying volumes of the ligand, followed by diluting the mixture with phosphate buffer to a total volume of 28.4 ml. The visible region was then scanned from 600 nm to 500 nm and the absorbances recorded at 585, 550, and 515 nm. This procedure was repeated for twenty-two different ligand concentrations.

Formation Constant Calculations

The formation of the 1:1 metal complex, ML, and the 1:2 metal complex, ML_2, may be expressed as

$$M + L \underset{}{\overset{K_1}{\rightleftharpoons}} ML \qquad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \underset{}{\overset{K_2}{\rightleftharpoons}} ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

where [M] represents the unbound tetra-μ-carboxylatodirhodium(II) species and [L] represents the free ligand. The total concentration of the metal, C_M, and the total concentration of the ligand, C_L, are equal to

$$C_M = [M] + [ML] + [ML_2]$$

$$C_L = [L] + [ML] + 2[ML_2]$$

By the manipulation of the above equations, the following cubic equation is obtained.

$$\frac{C_L - [L]}{C_M} \qquad \frac{K_1[L] + 2K_1K_2[L]^2}{1 + K_1[L] + 2[L]^2K_1K_2}$$

By knowing the total concentration of rhodium(II) species, C_M, and the total concentration of ligand, C_L, and given any K_1 and K_2, this equation becomes susceptible to numerical evaluation yielding the equilibrium concentration of free ligand. Therefore, the concentrations of all species at equilibrium can be calculated from the equations

$$[M] = \frac{C_L - [L]}{K_1[L] + 2[L]^2K_1K_2}$$

$$[ML] = K_1[M][L]$$

$$[ML_2] = K_2[ML][L]$$

From the use of the Beer–Lambert relationship the equilibrium concentration of all species at different M:L ratios were calculated.

The absorbances were measured at the three different wavelengths, 585, 550, and 515 nm. The molar absorptivities at these wavelengths were experimentally determined for the tetra-μ-carboxylatodirhodium(II) complexes. The formation constants and the absorptivities of ML and ML_2 were given as first approximations which were subsequently refined using the rigorous least-squares method previously described [1].

Determination of Rate Constants

The apparatus used in this study was a joule-heating temperature-jump apparatus that employs a

spectrophotometric method of detection [5]. All determinations were carried out at a room temperature of 23 °C. The temperature rise for solution between the two electrodes was calculated to be 2 °C. Relaxation times were determined for at least nine different solutions with varying concentrations.

The second-order forward rate constants for the reactions of the type

$$Rh_2X_4 \cdot 2H_2O + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Rh_2X_4 \cdot L(H_2O) + H_2O$$

where X is a carboxylate ion, were obtained as the slope of the plot of $1/\tau$ against $[(\bar{M} + \bar{L}) + 1/K_{eq}]$ according to the equation:

$$\frac{1}{\tau} = k_f[(\bar{M} + \bar{L}) + \frac{1}{K_{eq}}]$$

where τ = relaxation time, $\bar{M}$ and $\bar{L}$ are the equilibrium concentration of reactants and K_{eq} is the formation constant.

Results and Discussion

The stability constants for the adduct formation reactions of some selected tetra-μ-carboxylatodirhodium(II) complexes with isonicotinic acid, niacin, and pyridine are shown in Table I. Picolinic acid was also tested as a potential ligand, however, the *ortho* substituted carboxylate group apparently sterically inhibits complex formation since sufficient adduct formation to induce a spectral shift did not occur. In addition, the investigation of the pyridine adducts of tetra-μ-acetatodirhodium(II) and tetra-μ-propionatodirhodium(II) was not possible due to the formation of water insoluble complexes.

The pK_a of the nitrogen donor atom of pyridine, isonicotinic acid and niacin are 5.21, 4.96, and 4.85 respectively. Since the experimentally observed stability trend is isonicotinic acid > pyridine ≃ niacin the basicity of the ligand, which predicts the order of stability to be pyridine > isonicotinic acid ≃ niacin, is precluded from being the controlling factor in the complex formation reaction. Apparently the π-bonding ability of the ligands determines the order of stability of these adducts. By making use of the molecular orbital scheme proposed by Cotton [6] and Rubecki and Martin [7] it is easy to see how metal–ligand π-bonding could result from the overlap of the π^*(eg) orbitals of the rhodium(II) dimer with the ligands' π^* orbitals. Both isonicotinic acid and niacin may be predicted to possess somewhat better π-acceptor capability than pyridine since the electron withdrawing carboxylate group depletes electron density from the π system of the ligand [8] making $d\pi^*$–$p\pi^*$ backdonation more favorable. Also, since the π coefficients at the *para* carbon in the pyridine π^* orbital is larger than that at the *meta* position [9] any electron withdrawing group substituted at the *para* position should be more effective at lowering the energy of the π^* orbital than would the same group *meta* substituted.

Hence, the order of π-acceptor ability among these ligands should be isonicotinic acid > nicotinic acid > pyridine. The experimentally observed trend shows that isonicotinic acid does form significantly more stable complexes than either nicotinic acid or pyridine. The fact that the stabilities of pyridine and niacin adducts are approximately the same indicates that σ-bonding to the more basic pyridine nitrogen must counter the decreased π-acceptor ability of this ligand.

Additional evidence in support of metal–ligand π-bonding is that, in all cases, K_1 is considerably larger than K_2. The relatively large ratio of K_1/K_2 (≃30) cannot be explained solely by statistical factors. Ahrland and co-workers [10] also found large K_1/K_2 ratios with their studies of silver(I) and platinum(II) complexes with S-, Se-, P-, N- and oxygen containing ligands and concluded that the greater the tendency of the coordinating atoms to form dative $d\pi$ bonds the larger the K_1/K_2 ratio. Apparently, the formation of a π-bond with the first ligand makes the orbital of suitable symmetry of the metal ion less available for the formation of the second bond. This same analogy

TABLE I. Formation Constants for the Adduct Formation Reactions.

Rh(II) Carboxylate	Ligand	K_1	K_2
Methoxyacetate	Niacin	10700 ± 400	340 ± 10
Methoxyacetate	Pyridine	11300 ± 400	490 ± 10
Methoxyacetate	Isonicotinic Acid	14800 ± 400	420 ± 10
Acetate	Niacin	8300 ± 300	310 ± 10
Acetate	Isonicotinic Acid	12300 ± 600	480 ± 10
Propionate	Niacin	10600 ± 500	360 ± 10
Propionate	Isonicotinic Acid	14600 ± 700	550 ± 10

may be drawn to explain the ratios of the stability constants found for tetra-μ-carboxylatodirhodium(II) adducts. In addition, inspection of the experimentally determined K_2 values reveals a stability trend among the ligands that is identical to the basicity trend, pyridine > isonicotinic acid > niacin. This supports the hypothesis that once π-bonding has occurred between the metal and the first complexing ligand sufficient electron density does not remain in the π^*-(eg) orbitals of the metal to allow formation of a second metal–ligand π-bond. Therefore, the thermodynamic stability of the ML_2 species is determined primarily by the basicity of the complexing donor atom.

The variation of the stabilities of the adducts formed from different tetra-μ-carboxylatodirhodium-(II) complexes and a given ligand is methoxyacetato $\simeq$ propionato > acetato. If the only influence of the equatorial acids on adduct formation at the axial positions is a result of inductive effects then, since the removal of electron density from the dimeric rhodium(II) system will be related to the pK_a of the equatorial acid, the order of stability should be methoxyacetato > acetato $\simeq$ propionato (pK_a's are 3.57, 4.76 and 4.87 respectively). The increase in the stability of adducts formed with the propionato relative to the acetato complex suggests that perhaps the more hydrophobic character of the propionate species tends to exert a desolvating effect at the two axial positions which weakens the metal–water bond. Desolvation would not only make the formation of axial adducts thermodynamically more favorable but should also increase the rate, k_f, of adduct formation since the rate determining step appears to be the loss of axially ligated water [3]. The forward rate constants for the propionate complex with isonicotinic acid and niacin as ligands are $(1.7 \pm 0.4) \times 10^6\ M^{-1}\ sec^{-1}$ and $(1.3 \pm 0.2) \times 10^6\ M^{-1}\ sec^{-1}$ respectively while for the acetato complex with the same ligands are $(1.0 \pm 0.2) \times 10^6\ M^{-1}\ sec^{-1}$ and $(0.8 \pm 0.2) \times 10^6\ M^{-1}\ sec^{-1}$ respectively. This data shows the same trend as previously published work using as ligands imidazole, L-histidine and 5'-AMP [3] and, in all cases, supports the hypothesis that the more lipophylic propionate side chain tends to "push out" the axially bound water molecules of the solvated tetra-μ-propionatodirhodium(II) complex.

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