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SOME ASPECTS OF THE CHEMISTRY OF RHODIUM CYANIDE COMPLEXES

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INTRODUCTION

Extensive investigations of the chemistry of cobalt cyanide complexes have encompassed the +3, +2 and +1 oxidation states of cobalt, exemplified by $[Co^{III}(CN)_6]^{3-}$, $[Co^{II}(CN)_5]^{3-}$ and $[Co^{I}(CN)_5]^{4-}$, respectively, as well as various mixed ligand derivatives, e.g., $[Co^{III}(CN)_5X]^{3-}$, where X = CN, Cl, OH, H, etc. [1—6]. Interconversion among these oxidation states can be effected through a variety of reactions, including the following distinctive reactions of $[Co^{III}(CN)_5H]^{3-}$ [4, 5, 7].

$$[Co^{III}(CN)_5H]^{3-} + OH^- \rightleftharpoons [Co^{I}(CN)_5]^{4-} + H_2O \qquad (1)$$

$$2[Co^{III}(CN)_5H]^{3+} \rightleftharpoons 2[Co^{II}(CN)_5]^{3-} + H_2 \qquad (2)$$

The corresponding chemistry of rhodium and iridium cyanide complexes has been far less extensively investigated, the known chemistry being restricted, for the most part, to complexes of rhodium(III) and iridium(III). In the present paper we describe attempts to extend the study of reaction (1) to the corresponding rhodium system. The results of this study encompass the identification of reaction (3), the elucidation of the equilibrium and kinetics of this reaction, the preparation and characterization of the rhodium(I) cyanide complex, $[Rh^{I}(CN)_4]^{3-}$, and the examination of some aspects of the chemistry of this complex.

$$[Rh^{III}(CN)_5H]^{3-} + OH^- \rightleftharpoons [Rh^{I}(CN)_4]^{3-} + CN^- + H_2O \qquad (3)$$

PREPARATION AND CHARACTERIZATION OF TETRACYANORHODATE(I)

Reduction of a suspension of $RhCl_3$ (2.5 m*M*) in 3 *M* NaOH (15 ml) containing a stoichiometric amount of KCN (10 m*M*), by gentle refluxing with zinc powder under nitrogen yielded a solution of $[Rh(CN)_4]^{3-}$. Dropwise addition of an aqueous solution of $[M(en)_3]^{3+}$ (M = Cr or Co) yielded a yellow precipitate of the corresponding pure salt, $[M(en)_3][Rh(CN)_4]$, (yield, 75—85%) which was characterized analytically and spectrally. Infrared and

Raman spectra of $[Co(en)_3][Rh(CN)_4]^{3-}$: ν_{CN}, 2065 cm^{-1} (IR), 2086, 2108 cm^{-1} (Raman), are consistent with a square planar configuration. UV spectrum of $[Rh(CN)_4]^{3-}$ in aqueous solution: λ_{max} 322 nm ($\epsilon = 1.8 \times 10^4\ M^{-1}\ cm^{-1}$); λ_{max} 365 nm ($\epsilon = 8.4 \times 10^3$); λ_{min} 350 nm ($\varepsilon = 5.8 \times 10^3$).

The solution spectrum of $[Rh(CN)_4]^{3-}$, generated as described above, agreed quantitatively with that of a solution of $[Rh(CN)_5H]^{3-}$ in 12.5 *M* NaOH. Under these conditions the conversion of $[Rh(CN)_5H]^{3-}$ to $[Rh(CN)_4]^{3-}$ according to eqn. (3), is virtually complete (confirmed by monitoring the ^1H NMR signal of $[Rh(CN)_5H]^{3-}$ at $\delta = 10.1$ p.p.m.).

This solution spectrum is also in *qualitative* agreement with that of the transient species that has previously been observed by Jewsbury and Maher [8], to form by the reaction of CN^- with $[Rh(CO)_2Cl]_2$ and identified by them as $[Rh(CN)_4]^{3-}$, (λ_{max} 320 [$\epsilon = 1.2 \times 10^4$]; λ_{max} 366 [$\epsilon = 6.7 \times 10^3$]. Formation of $[Rh(CN)_4]^{3-}$ by the latter procedure requires the addition of *an excess* of CN^- (to displace CO). Under these conditions $[Rh(CN)_4]^{3-}$ has only a transient existence such that, while detectable in stopped-flow experiments, it undergoes further reaction to form $[Rh(CN)_5H]^{3-}$ (reverse of reaction (3)). In contrast the two procedures described above yield stable aqueous solutions of $[Rh(CN)_4]^{3-}$.

EQUILIBRIUM MEASUREMENTS

The equilibrium of reaction (3) was monitored spectrophotometrically by determining the equilibrium concentration of $[Rh(CN)_4]^{3-}$ in aqueous solutions prepared by either (a) adding OH^- to a solution initially containing $[Rh(CN)_5H]^{3-}$ or (b) adding CN^- to a preformed solution of $[Rh(CN)_4]^{3-}$, equilibrium thus being approached from both directions. The range of concentrations encompassed by these measurements was 0.3×10^{-3} to 3.6×10^{-3} *M* CN^- and 0.5 to 3.0 *M* OH^-. The total Rh concentration was typically ca. 5×10^{-4} *M* and the ionic strength was maintained constant at 3.0 *M* with NaCl. These measurements yielded a constant value of $(3.5 \pm 0.5) \times 10^{-5}$ at 25°C for the equilibrium quotient K_3 defined by,

$$K_3 = \frac{[Rh(CN)_4^{3-}][CN^-]}{[HRh(CN)_5^{3-}][OH^-]} \tag{4}$$

KINETICS OF REACTION (3)

Measurements of the rate of approach to equilibrium in experiments similar to those described above yielded determinations of the rate laws of reaction (3) in both the forward and reverse directions. These rate laws are as follows, where $\overrightarrow{k} = 8.4 \times 10^{-4}\ M^{-1}\ s^{-1}$ and $\overleftarrow{k} = 22\ M^{-1}\ s^{-1}$ (both at 25°, 3 *M* ionic strength).

$$\overrightarrow{RATE} = d[Rh(CN)_4^{3-}]/dt = \overrightarrow{k}[Rh(CN)_5H^{3-}][OH^-] \tag{5}$$

$$\overleftarrow{RATE} = -d[Rh(CN)_4^{3-}]/dt = \overleftarrow{k}[Rh(CN)_4^{3-}][CN^-] \tag{6}$$

It seems likely, both on a priori considerations and by analogy with the corresponding behavior of $[Co(CN)_5H]^{3-}$ [4, 5], that reaction (3) proceeds through the following stepwise mechanism,

$$[Rh(CN)_5H]^{3-} + OH^- \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} [Rh(CN)_5]^{4-} + H_2O \qquad (7)$$

$$[Rh(CN)_5]^{4-} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} [Rh(CN)_4]^{3-} + CN^- \qquad (8)$$

Assuming the steady state approximation for $[Rh(CN)_5]^{4-}$, this yields

$$\overrightarrow{k} = k_7k_8/(k_{-7} + k_8) \qquad (9)$$

$$\overleftarrow{k} = k_{-7}k_{-8}/(k_{-7} + k_8) \qquad (10)$$

The value of K_3 ($= k_7k_8/k_{-7}k_{-8} = \overrightarrow{k}/\overleftarrow{k}$), deduced from the kinetic measurements is, accordingly, 3.8×10^{-5}, in satisfactory agreement with the spectrophotometrically determined value of 3.5×10^{-5}.

These measurements do not permit the separate evaluation of the component rate constants, k_7, k_8, k_{-7} and k_{-8}. In the case of the corresponding reactions of $[Co(CN)_5H]^{3-}$ it has been determined that $k_{-7}/k_8 = 25$ [5]. In accord with the usual vertical trend of relative stabilities of 4- and 5-coordinate d^8 complexes it is likely that the tendency for $[Rh(CN)_5]^{4-}$ to dissociate to form $[Rh(CN)_4]^{3-}$ is considerably greater than the corresponding tendency for $[Co(CN)_5]^{4-}$, i.e., $k_8^{Rh} \gg k_8^{Co}$. Under the conditions of the limiting assumption that $k_{-7}/k_8 \ll 1$, eqns. (9) and (10) reduce to $\overrightarrow{k} = k_7$ and $\overleftarrow{k} = k_{-7}k_{-8}/k_8$. This yields $k_7 = 8.5 \times 10^{-4}\ M^{-1}\ s^{-1}$, compared with the previously determined corresponding value of $1.0 \times 10^{-1}\ M^{-1}\ s^{-1}$ for $[Co(CN)_5H]^{3-}$ [4, 5]. This difference is in the anticipated direction, i.e., in accord with the expectation that $[Co(CN)_5H]^{3-}$ is a stronger acid than $[Rh(CN)_5H]^{3-}$.

Some support for the above assumptions (i.e., that $k_{-7}/k_8 \ll 1$, hence $\overrightarrow{k} \sim k_7$) is provided by the results of preliminary experiments (similar to those which had accomplished the same objective in the case of $[Co(CN)_5H]^{3-}$), in which direct measurement of k_7 (i.e., of the rate of reaction (7)) was attempted by trapping the intermediate $[Rh(CN)_5]^{4-}$ ion, for example with $[Fe(CN)_6]^{3-}$ or CH_3I, thereby suppressing reaction (−7). The range of apparent values of "k_7" yielded by these preliminary experiments, namely 3×10^{-4} to $3 \times 10^{-3}\ M^{-1}\ s^{-1}$, is compatible with the value of $8.5 \times 10^{-4}\ M^{-1}\ s^{-1}$ for k_7 derived above.

It is of interest that, despite the expectation that $[Co(CN)_5H]^{3-}$ is a stronger acid than $[Rh(CN)_5H]^{3-}$, the equilibria of reactions (2) and (3) lie far to the left for $[Co(CN)_5H]^{3-}$ so that dissociation of the latter is negligible even in strongly basic solutions [5, 6]. The much higher degree of dissociation of $[Rh(CN)_5H]^{3-}$ thus reflects the more favorable contribution of equilibrium (8), i.e., the relatively greater tendency of $[Rh(CN)_5]^{4-}$ to dissociate to the four-coordinate complex $[Rh(CN)_4]^{3-}$.

The earlier report [8] of the oxidative addition of methyl iodide to $[Rh(CN)_4]^{3-}$ according to eqn. (11) has been confirmed.

$$[Rh(CN)_4]^{3-} + CH_3I \xrightarrow{k_{11}} trans\text{-}[Rh(CN)_4(CH_3)I]^{3-} \qquad (11)$$

The stoichiometry of the above reaction was quantitatively established in aqueous solution, and the product ion characterized; λ_{max} 308 nm ($\epsilon = 4.8 \times 10^2\ M^{-1}\ cm^{-1}$), λ_{min} 260 nm ($\epsilon = 3.2 \times 10^2$); ^1H NMR, δ_{CH_3}(d) −0.8, J_{Rh-H} 2.1 Hz. $[Rh(CN)_4(CH_3)I]^{3-}$ was also isolated by precipitation as the pure $[Co(en)_3]^{3+}$ salt: ν_{CN}, 2128, 2156 cm^{-1} (IR); 2153, 2136, 2128 cm^{-1} (Raman). Kinetic measurements on reaction (11) (followed spectrophotometrically) yielded the following rate law, where $k_{11} = 4.0 \times 10^2\ M^{-1}\ s^{-1}$ at 25°, 1.5 M ionic strength, independent of $[OH^-]$ between 0.3 and 1.5 M (compared with the value of $5.9 \times 10^2\ M^{-1}\ s^{-1}$ reported by Jewsbury and Maher) [8].

$$-d[Rh(CN)_4^{3-}]/dt = k_{11}[Rh(CN)_4^{3-}][CH_3I] \qquad (12)$$

In aqueous metahnol (1:1) solutions containing NaOH the reaction of CH_3I with $[Rh(CN)_4]^{3-}$ exhibited similar kinetics ($k_{11} = 4.4 \times 10^3\ M^{-1}\ s^{-1}$) but yielded different products in accord with the stoichiometry described by eqn. (13) (CH_4 determined mass-spectrometrically; $[Rh(CN)_4(OH)I]^{3-}$ isolated and characterized as the $[Co(en)_3]^{3+}$ salt).

$$[Rh(CN)_4]^{3-} + CH_3I + H_2O \rightarrow [Rh(CN)_4(OH)I]^{3-} + CH_4 \qquad (13)$$

It seems likely that under these conditions the primary reaction is still oxidative addition [i.e., eqn. (11)] and that the observed products arise through a secondary reaction of $[Rh(CN)_5(CH_3)I]^{3-}$. It was established that this secondary reaction is not a simple solvent-induced decomposition since the addition of methanol to an aqueous solution of preformed $[Rh(CN)_4(CH_3)I]^{3-}$ did not result in decomposition of the latter. A possible explanation of this behavior is a $[Rh^I(CN)_4]^{3-}$-induced decomposition of $[Rh^{III}(CN)_4(CH_3)I]^{3-}$ through an I^--bridged electron transfer reaction, i.e.,

$$\begin{aligned}&[Rh^{III}(CN)_4(CH_3)I]^{3-} + [Rh^I(CN)_4]^{3+} + OH^- \rightarrow\\ &\quad [(OH^-)\underbrace{Rh^I(CN)_4-I-Rh^{III}}_{2e^-}(CN)_4(CH_3)]^{7-} \rightarrow\\ &\quad [Rh^{III}(CN)_4(OH)I]^{3-} + [Rh^I(CN)_4(CH_3)]^{4-} \qquad (14)\end{aligned}$$

$$[Rh^I(CN)_4(CH_3)]^{4-} + H_2O \rightarrow [Rh^I(CN)_4]^{3-} + CH_4 + OH^- \qquad (15)$$

Whereas analogous examples of Rh^I-catalyzed substitution reactions of Rh^{III}-complexes have indeed been identified [9], such a mechanism remains to be demonstrated in the present system. Experiments to test this suggestion are in progress.

TABLE 1

Kinetic data for the oxidative addition of organic halides to $[Rh(CN)_4]^{3-}$ [a]

Organic halide	k_{11} (M^{-1} s^{-1})
CH_3I	4.4×10^3
CH_3CH_2I	22
$CH_3CH_2CH_2I$	7
$C_6H_5CH_2I$	1.7×10^3
$C_6H_5CH_2Br$	3.2×10^2
$C_6H_5CH_2Cl$	6

[a] In aqueous methanol (1:1 v:v) containing 1.5 *M* NaOH at 25°.

Similar kinetic and stoichiometric behavior (i.e., corresponding to eqns. (12) and (13)) were observed for several other organic halides whose reactions with $[Rh(CN)_4]^{3-}$ were examined in aqueous methanol. Thus, the reaction with C_2H_5I yielded $[Rh(CN)_4(OH)I]^{3-}$ and C_2H_6, etc. Only in one other instance, namely with $C_6H_5CH_2Cl$, did the reaction follow the course of eqn. (11) yielding the organorhodium product, $[Rh(CN)_4(CH_2C_6H_5)Cl]^{3-}$.

The results of the kinetic measurements are summarized in Table 1. The trends follow those expected for oxidative addition reactions, i.e., $CH_3I \gg C_2H_5I > C_3H_7I$ (reflecting the influence of increasing steric hindrance) and $C_6H_5CH_2I > C_6H_5CH_2Br > C_6H_5CH_2Cl$ (reflecting the influence of decreasing carbon—halogen bond strength). It should be noted that the reactivity of $[Rh(CN)_4]^{3-}$ for oxidative addition is very high. Thus, the value of $k_{11} = 4.4 \times 10^3$ M^{-1} s^{-1} for the reaction of CH_3I with $[Rh(CN)_4]^{3-}$ is some 10^6-fold higher than the rate constant (ca. 3.5×10^3 M^{-1} s^{-1}) for the corresponding oxidative addition of CH_3I to *trans*-$[Ir(PPh_3)_2(CO)Cl]$ [10].

Under the conditions of the above experiments no corresponding reactions with OH^- (or with organic halides in the presence of OH^-) could be detected for $[Ir(CN)_5H]^{3-}$.

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