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The Synthesis, Characterization and Reactivity of Tetracyanorhodate(I)

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Whereas the acid–base reaction of $[Co(CN)_5H]^{3-}$ according to equation (1) has been described,[1 - 3] the corresponding reactions of $[Rh(CN)_5H]^{3-}$ and $[Ir(CN)_5H]^{3-}$ have not hitherto been identified. We have now found that $[Rh(CN)_5H]^{3-}$ does react reversibly with OH^- in aqueous solution to form tetracyanorhodate(I), $[Rh(CN)_4]^{3-}$, according to equation (2). We report here some measurements on the equilibrium and kinetics of reaction (2), as well as the preparation and characterization of $[Rh(CN)_4]^{3-}$ and the examination of some aspects of its chemistry.

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

$$[Rh(CN)_5H]^{3-} + OH^- \rightleftharpoons [Rh(CN)_4]^{3-} + CN^- + H_2O \quad (2)$$

The equilibrium of reaction (2) was monitored spectrophotometrically by determining the equilibrium concentrations of $[Rh(CN)_4]^{3-}$ in aqueous solutions prepared either (a) by adding OH^- to a solution initially containing $[Rh(CN)_5H]^{3-}$ or (b) adding CN^- to a preformed solution of $[Rh(CN)_4]^{3-}$ (prepared as described below), equilibrium thus being approached from both directions. The range of concentrations encompassed by these measurements was 3.0×10^{-4} 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*. These measurements yielded a constant value of $(3.5 \pm 0.5) \times 10^{-5}$ at 25 °C and 3.0 *M* ionic strength (maintained with NaCl) for the equilibrium quotient K_2 defined by

$$K_2 = \frac{[Rh(CN)_4{}^{3-}]\,[CN^-]}{[Rh(CN)_5H^{3-}]\,[OH^-]} \quad (3)$$

$[Rh(CN)_4{}^{3-}]$ was also prepared by 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. 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: ν_{CN}, 2065 cm^{-1} (ir), 2086, 2108 cm^{-1} (raman), consistent with a square planar configuration.

The solution spectrum of $[Rh(CN)_4]^{3-}$ prepared by either of the above procedures (λ_{max} 322 nm, $\epsilon = 1.8 \times 10^4$ M^{-1} cm^{-1}; λ_{max} 365, $\epsilon = 8.4 \times 10^3$; λ_{min} 350, $\epsilon = 5.8 \times 10^3$) is in *qualitative* agreement with that of the transient species previously observed by Jewsbury and Maher[4] to form by the reaction of CN^- with $[Rh(CO)_2Cl]_2$ and also identified by them as $[Rh(CN)_4]^{3-}$ (reported[4] 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 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 (2)]. In contrast to this the two procedures described above yield stable aqueous solutions of $[Rh(CN)_4]^{3-}$.

Measurements of the rate of approach to equilibrium, in experiments similar to those described above, yielded determinations of the rate-laws of reaction (2) in both the forward and reverse directions. These rate-laws are as follows where $k_F = 8.4 \times 10^{-4}$ M^{-1} sec^{-1} and $k_R = 22$ M^{-1} sec^{-1}, both at 25 °C, 3*M* ionic strength:

$$\overrightarrow{\text{RATE}} = d[Rh(CN)_4{}^{3-}]/dt = k_F[Rh(CN)_5H^{3-}]\,[OH^-] \quad (4)$$

$$\overleftarrow{\text{RATE}} = -d[Rh(CN)_4{}^{3-}]/dt = k_R[Rh(CN)_4{}^{3-}]\,[CN^-] \quad (5)$$

It seems likely, both on *a priori* considerations and by analogy with the corresponding behavior of $[Co(CN)_5H]^{3-}$ [1-2] that reaction (2) proceeds through the following stepwise mechanism,

$$[Rh(CN)_5H]^{3-} + OH^- \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} [Rh(CN)_5]^{4-} + H_2O \quad (6)$$

$$[Rh(CN)_5]^{4-} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} [Rh(CN)_4]^{3-} + CN^- \quad (7)$$

Assuming the steady state approximation for $[Rh(CN)_5]^{4-}$, this yields $k_F = k_6k_7/(k_{-6} + k_7)$ and $k_R = k_{-6}k_{-7}/(k_{-6} + k_7)$.

These measurements do not permit the separate evaluation of the component rate-constants, k_6, k_7, k_{-6} and k_{-7}. In the case of the corresponding reactions of $[Co(CN)_5H]^{3-}$ it has been determined that $k_{-6}/k_7 = 25$.[2] In accord with the usual vertical trend of relative stabilities of 4- and 5-coordinate d^8 complexes it is likely that the tendency of $[Rh(CN)_5]^{4-}$ to dissociate to form $[Rh(CN)_4]^{3-}$ is considerably greater than the corresponding tendency for $[Co(CN)_5]^{4-}$, *i.e.*, $k_7(Rh) \gg k_7(Co)$. Under the conditions of the limiting assumption that $k_{-6}/k_7 \ll 1$, the kinetic equations reduce to $k_F = k_6$ and $k_R = k_{-6}k_{-7}/k_7$. This yields $k_6 = 8.5 \times 10^{-4}$ M^{-1} sec^{-1}, compared with the previously determined value of 1.0×10^{-1} M^{-1} sec^{-1} for $[Co(CN)_5H]^{3-}$.[1,2] This difference is in the anticipated direction, *i.e.*, in accord with the expectation that $[Co(CN)_5H]^{3-}$ is a stronger acid than $[Rh(CN)_5H]^{3-}$. Experiments (similar to those which had accomplished the same objective in the case of $[Co(CN)_5H]^{3-}$)[1,2] are in progress to test the above assumption (*i.e.*, that $k_{-6}/k_7 \ll 1$, hence $k_F \sim k_6$) by trapping the intermediate $[Rh(CN)_5]^{4-}$ ion, for example with $[Fe(CN)_6]^{3-}$ or CH_3I.

It is noteworthy that, despite the expectation that $[Co(CN)_5H]^{3-}$, is a stronger acid than $[Rh(CN)_5H]^{3-}$ the equilibria corresponding to reactions (1) and (2) lie far to the left for $[Co(CN)_5H]^{3-}$ so that dissociation of the latter is negligible even in strongly basic solutions.[1-3] The much higher degree of dissociation of $[Rh(CN)_5H]^{3-}$ according to reaction (2) apparently reflects the more favorable contribution of equilibrium (7), *i.e.*, the relatively greater tendency of $[Rh(CN)_5]^{4-}$ (as compared with $[Co(CN)_5]^{4-}$) to dissociate to the four-coordinate complex $[Rh(CN)_4]^{3-}$.

We have confirmed the earlier report[4] of the oxidative addition of methyl iodide to $[Rh(CN)_4]^{3-}$ according to equation (8).

$$[Rh(CN)_4]^{3-} + CH_3I \xrightarrow{k_8} trans\text{-}[Rh(CN)_4(CH_3)I]^{3-} \qquad (8)$$

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 (8) (followed spectrophotometrically) yielded the second order rate-law, $-d[Rh(CN)_4{}^{3-}]/dt = k_8[Rh(CN)_4{}^{3-}][CH_3I]$, where $k_8 = 4.0 \times 10^2$ M^{-1} sec^{-1} at 25 °C, 1.5 M ionic strength, independent of $[OH^-]$ between 0.3 and 1.5 M (compared with the value of 5.9×10^2 M^{-1} sec^{-1} reported by Jewsbury and Maher).[4]

In *aqueous methanol* (1:1) solutions containing NaOH the reaction of CH_3I with $[Rh(CN)_4]^{3-}$ exhibited similar kinetics ($k_8 = 4.4 \times 10^3$ M^{-1} sec^{-1}) but yielded different products in accord with the stoichiometry described by equation (9) (CH_4 determined mass-spectrometrically; $[Rh(CN)_4(OH)I]^{3-}$ isolated and characterized as the $[Co(en)_3]^{3+}$ salt).

$$[Rh(CN)_4]^{3-} + CH_3I + H_2O \rightarrow [Rh(CN)_4(OH)I]^{3-} + CH_4 \qquad (9)$$

It seems likely that under these conditions the primary reaction is still oxidative addition [*i.e.*, eq. (8)] and that the observed products arise through a secondary reaction of $[Rh(CN)_4(CH_3)I]^{3-}$. 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.*,

$$\begin{aligned}&[Rh^{III}(CN)_4(CH_3)I]^{3-} + [Rh^I(CN)_4]^{3-} + OH^- \\ &\rightarrow [(OH)(CN)_4\underset{2e^-}{\underset{\curvearrowright}{Rh^I{-}I{-}Rh^{III}}}(CN)_4(CH_3)]^{7-} \\ &\rightarrow [Rh^{III}(CN)_4(OH)I]^{3-} + [Rh^I(CN)_4(CH_3)]^{4-} \qquad (10)\end{aligned}$$

$$[Rh^I(CN)_4(CH_3)]^{4-} + H_2O \rightarrow [Rh^I(CN)_4]^{3-} + CH_4 + OH^- \qquad (11)$$

Whereas analogous examples of Rh^I-catalyzed substitution reactions of Rh^{III}-complexes have indeed been identified,[5] such a mechanism remains to be demonstrated in the present system. Experiments to test this suggestion are in progress.

Similar kinetic and stoichiometric behavior [*i.e.*, corresponding to eqn. (9)] 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 eq. (8) yielding the organorhodium product, $[Rh(CN)_4(CH_2C_6H_5)Cl]^{3-}$.

The reactivities of different organic halides toward $[Rh(CN)_4]^{3-}$ exhibited the following characteristic trends for oxidative addition reactions (values in parentheses are k_8, M^{-1} sec^{-1}, in 1:1 H_2O:CH_3OH containing 3*M* NaOH at 25 °C): CH_3I (4.4×10^3) $\gg$ C_2H_5I (22) > n-C_3H_7I (7), reflecting the influence of increasing steric hindrance, and $C_6H_5CH_2I$ (1.7×10^3) > $C_6H_5CH_2Br$ (3.2×10^2) > $C_6H_5CH_2Cl$ (6), 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 $k_8 = 4.4 \times 10^3$ M^{-1} sec^{-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} sec^{-1}) for the corresponding oxidative addition of CH_3I to *trans*-$[Ir(PPh_3)_2(CO)Cl]$.[6]

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