

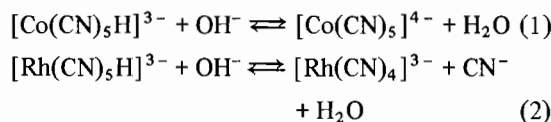
## The Synthesis, Characterization and Reactivity of Tetracyanorhodate(I)

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Whereas the acid-base reaction of  $[\text{Co}(\text{CN})_5\text{H}]^{3-}$  according to equation (1) has been described,<sup>1-3</sup> the corresponding reactions of  $[\text{Rh}(\text{CN})_5\text{H}]^{3-}$  and  $[\text{Ir}(\text{CN})_5\text{H}]^{3-}$  have not hitherto been identified. We have now found that  $[\text{Rh}(\text{CN})_5\text{H}]^{3-}$  does react reversibly with  $\text{OH}^-$  in aqueous solution to form tetracyanorhodate(I),  $[\text{Rh}(\text{CN})_4]^{3-}$ , 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  $[\text{Rh}(\text{CN})_4]^{3-}$  and the examination of some aspects of its chemistry.



The equilibrium of reaction (2) was monitored spectrophotometrically by determining the equilibrium concentrations of  $[\text{Rh}(\text{CN})_4]^{3-}$  in aqueous solutions prepared either (a) by adding  $\text{OH}^-$  to a solution initially containing  $[\text{Rh}(\text{CN})_5\text{H}]^{3-}$  or (b) adding  $\text{CN}^-$  to a preformed solution of  $[\text{Rh}(\text{CN})_4]^{3-}$  (prepared as described below), equilibrium thus being approached from both directions. The range of concentrations encompassed by these measurements was  $3.0 \times 10^{-4}$  to  $3.6 \times 10^{-3} M \text{CN}^-$  and  $0.5$  to  $3.0 M \text{OH}^-$ . The total Rh concentration was typically *ca.*  $5 \times 10^{-4} M$ . These measurements yielded a constant value of  $(3.5 \pm 0.5) \times 10^{-5}$  at  $25^\circ\text{C}$  and  $3.0 M$  ionic strength (maintained with NaCl) for the equilibrium quotient  $K_2$  defined by

$$K_2 = \frac{[\text{Rh}(\text{CN})_4]^{3-} [\text{CN}^-]}{[\text{Rh}(\text{CN})_5\text{H}]^{3-} [\text{OH}^-]} \quad (3)$$

$[\text{Rh}(\text{CN})_4]^{3-}$  was also prepared by reduction of a suspension of  $\text{RhCl}_3$  ( $2.5 mM$ ) in  $3M \text{NaOH}$  ( $15 \text{ml}$ ) containing a stoichiometric amount of  $\text{KCN}$  ( $10 mM$ ), by gentle refluxing with zinc powder. Dropwise

addition of an aqueous solution of  $[\text{M}(\text{en})_3]^{3+}$  ( $M = \text{Cr}$  or  $\text{Co}$ ) yielded a yellow precipitate of the corresponding pure salt,  $[\text{M}(\text{en})_3][\text{Rh}(\text{CN})_4]$  (yield 75 - 85%), which was characterized analytically and spectrally:  $\nu_{\text{CN}}$ ,  $2065 \text{ cm}^{-1}$  (ir),  $2086, 2108 \text{ cm}^{-1}$  (raman), consistent with a square planar configuration.

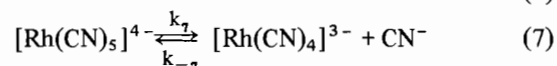
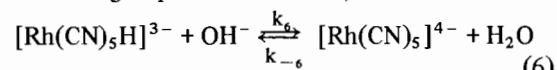
The solution spectrum of  $[\text{Rh}(\text{CN})_4]^{3-}$  prepared by either of the above procedures ( $\lambda_{\text{max}}$   $322 \text{ nm}$ ,  $\epsilon = 1.8 \times 10^4 M^{-1} \text{ cm}^{-1}$ ;  $\lambda_{\text{max}}$   $365$ ,  $\epsilon = 8.4 \times 10^3$ ;  $\lambda_{\text{min}}$   $350$ ,  $\epsilon = 5.8 \times 10^3$ ) is in *qualitative* agreement with that of the transient species previously observed by Jewsbury and Maher<sup>4</sup> to form by the reaction of  $\text{CN}^-$  with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  and also identified by them as  $[\text{Rh}(\text{CN})_4]^{3-}$  (reported<sup>4</sup>  $\lambda_{\text{max}}$   $320$ ,  $\epsilon = 1.2 \times 10^4$ ;  $\lambda_{\text{max}}$   $366$ ,  $\epsilon = 6.7 \times 10^3$ ). Formation of  $[\text{Rh}(\text{CN})_4]^{3-}$  by the latter procedure requires addition of *an excess* of  $\text{CN}^-$  (to displace CO). Under these conditions  $[\text{Rh}(\text{CN})_4]^{3-}$  has only a transient existence such that, while detectable in stopped-flow experiments, it undergoes further reaction to form  $[\text{Rh}(\text{CN})_5\text{H}]^{3-}$  [reverse of reaction (2)]. In contrast to this the two procedures described above yield stable aqueous solutions of  $[\text{Rh}(\text{CN})_4]^{3-}$ .

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  $k_F = 8.4 \times 10^{-4} M^{-1} \text{ sec}^{-1}$  and  $k_R = 22 M^{-1} \text{ sec}^{-1}$ , both at  $25^\circ\text{C}$ ,  $3M$  ionic strength:

$$\text{RATE} = \frac{d[\text{Rh}(\text{CN})_4]^{3-}}{dt} = k_F \frac{[\text{Rh}(\text{CN})_5\text{H}]^{3-}}{[\text{OH}^-]} \quad (4)$$

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

It seems likely, both on *a priori* considerations and by analogy with the corresponding behavior of  $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ <sup>1-2</sup> that reaction (2) proceeds through the following stepwise mechanism,

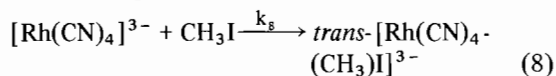


Assuming the steady state approximation for  $[\text{Rh}(\text{CN})_5]^{4-}$ , this yields  $k_F = k_6 k_7 / (k_{-6} + k_7)$  and  $k_R = k_{-6} k_{-7} / (k_{-6} + k_7)$ .

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  $[\text{Co}(\text{CN})_5\text{H}]^{3-}$  it has been determined that  $k_{-6}/k_7 = 25$ .<sup>2</sup> 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  $[\text{Rh}(\text{CN})_5]^{4-}$  to dissociate to form  $[\text{Rh}(\text{CN})_4]^{3-}$  is considerably greater than the corresponding tendency for  $[\text{Co}(\text{CN})_5]^{4-}$ , *i.e.*,  $k_7(\text{Rh}) \gg k_7(\text{Co})$ . 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  $k_6 = 8.5 \times 10^{-4} M^{-1} \text{ sec}^{-1}$ , compared with the previously determined value of  $1.0 \times 10^{-1} M^{-1} \text{ sec}^{-1}$  for  $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ .<sup>1,2</sup> This difference is in the anticipated direction, *i.e.*, in accord with the expectation that  $[\text{Co}(\text{CN})_5\text{H}]^{3-}$  is a stronger acid than  $[\text{Rh}(\text{CN})_5\text{H}]^{3-}$ . Experiments (similar to those which had accomplished the same objective in the case of  $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ )<sup>1,2</sup> 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  $[\text{Rh}(\text{CN})_5]^{4-}$  ion, for example with  $[\text{Fe}(\text{CN})_6]^{3-}$  or  $\text{CH}_3\text{I}$ .

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

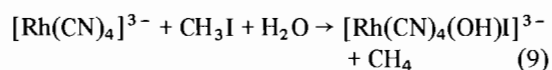
We have confirmed the earlier report<sup>4</sup> of the oxidative addition of methyl iodide to  $[\text{Rh}(\text{CN})_4]^{3-}$  according to equation (8).



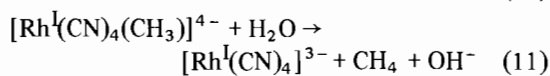
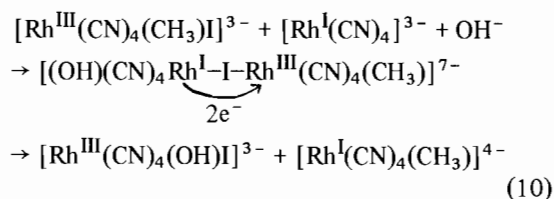
The stoichiometry of the above reaction was quantitatively established in aqueous solution, and the product ion characterized;  $\lambda_{\text{max}}$  308 nm ( $\epsilon = 4.8 \times 10^2 M^{-1} \text{ cm}^{-1}$ ),  $\lambda_{\text{min}}$  260 nm ( $\epsilon = 3.2 \times 10^2$ ); <sup>1</sup>H nmr,  $\delta_{\text{CH}_3}$  (d)  $-0.8$ ,  $J_{\text{Rh-H}}$  2.1 Hz.  $[\text{Rh}(\text{CN})_4(\text{CH}_3)\text{I}]^{3-}$  was also isolated by precipitation as the pure  $[\text{Co}(\text{en})_3]^{3+}$  salt:  $\nu_{\text{CN}}$ , 2128, 2156  $\text{cm}^{-1}$  (ir); 2153, 2136, 2128  $\text{cm}^{-1}$  (raman). Kinetic measurements on reaction (8) (followed spectro-

photometrically) yielded the second order rate-law,  $-d[\text{Rh}(\text{CN})_4]^{3-}/dt = k_8[\text{Rh}(\text{CN})_4]^{3-}[\text{CH}_3\text{I}]$ , where  $k_8 = 4.0 \times 10^2 M^{-1} \text{ sec}^{-1}$  at 25 °C, 1.5 *M* ionic strength, independent of  $[\text{OH}^-]$  between 0.3 and 1.5 *M* (compared with the value of  $5.9 \times 10^2 M^{-1} \text{ sec}^{-1}$  reported by Jewsbury and Maher).<sup>4</sup>

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



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  $[\text{Rh}(\text{CN})_4(\text{CH}_3)\text{I}]^{3-}$ . 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  $[\text{Rh}(\text{CN})_4(\text{CH}_3)\text{I}]^{3-}$  did *not* result in decomposition of the latter. A possible explanation of this behavior is a  $[\text{Rh}^{\text{I}}(\text{CN})_4]^{3-}$ -induced decomposition of  $[\text{Rh}^{\text{III}}(\text{CN})_4(\text{CH}_3)\text{I}]^{3-}$  through an I-bridged electron transfer reaction, *i.e.*,



Whereas analogous examples of Rh<sup>I</sup>-catalyzed substitution reactions of Rh<sup>III</sup>-complexes have indeed been identified,<sup>5</sup> 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  $[\text{Rh}(\text{CN})_4]^{3-}$  were examined in aqueous methanol. Thus, the reaction with  $\text{C}_2\text{H}_5\text{I}$  yielded  $[\text{Rh}(\text{CN})_4(\text{OH})\text{I}]^{3-}$  and  $\text{C}_2\text{H}_6$ , *etc.* Only in one other instance, namely with  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ , did the reaction follow the course of eq. (8) yielding the organorhodium product,  $[\text{Rh}(\text{CN})_4(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}]^{3-}$ .

The reactivities of different organic halides toward  $[\text{Rh}(\text{CN})_4]^{3-}$  exhibited the following characteristic trends for oxidative addition reactions (values in parentheses are  $k_8, M^{-1} \text{ sec}^{-1}$ , in 1:1  $\text{H}_2\text{O}:\text{CH}_3\text{OH}$  containing 3M NaOH at 25 °C):  $\text{CH}_3\text{I}$  ( $4.4 \times 10^3$ )  $\gg$   $\text{C}_2\text{H}_5\text{I}$  (22)  $>$   $n\text{-C}_3\text{H}_7\text{I}$  (7), reflecting the influence of increasing steric hindrance, and  $\text{C}_6\text{H}_5\text{CH}_2\text{I}$  ( $1.7 \times 10^3$ )  $>$   $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$  ( $3.2 \times 10^2$ )  $>$   $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  (6), reflecting the influence of decreasing carbon-halogen bond strength. It should be noted that the reactivity of  $[\text{Rh}(\text{CN})_4]^{3-}$  for oxidative addition is very high. Thus, the value of  $k_8 = 4.4 \times 10^3 M^{-1} \text{ sec}^{-1}$  for the reaction of  $\text{CH}_3\text{I}$  with  $[\text{Rh}(\text{CN})_4]^{3-}$  is some  $10^6$ -fold higher than the rate constant (*ca.*  $3.5 \times 10^{-3} M^{-1} \text{ sec}^{-1}$ ) for the corresponding oxidative addition of  $\text{CH}_3\text{I}$  to *trans*- $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ .<sup>6</sup>

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