The Formation of Pentacyanohydridorhodate(III): Kinetic and Spectral Evidence for the Oxidative Addition of Hydrogen Cyanide to the Intermediate Tetracyanorhodate(I)

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In the reaction of NaCN with $[Rh(CO)_2Cl]_2$ evidence has been found for the formation of a transient intermediate which is probably $Rh(CN)_4^{3-}$; the u.v.–visible spectrum of the intermediate is reported. The decay of the intermediate, studied by the stopped-flow method, has been identified as the oxidative addition of HCN to $Rh(CN)_4^{3-}$ to form $Rh(CN)_5H^{3-}$; the pH dependence and isotope effect of D_2O on the rate constant have been examined. The oxidative addition of alkyl halides to $Rh(CN)_4^{3-}$, $Rh(CN)_3CO^{2-}$, and $Rh(CN)_2(CO)_2^-$ is reported and the mechanism of formation of acyl rhodium(III) compounds $Rh(CN)_5(COCH_3)^{3-}$ is discussed.

In a previous paper[1] we reported that the reaction between $[Rh(CO)_2Cl]_2$ and NaCN in methanol gave the anion $Rh(CN)_5H^{3-}$. Although, using spectroscopic techniques, we were able to identify intermediates containing one, two, and three cyanide groups per rhodium atom, we did not succeed in detecting one containing four. Using the stopped-flow technique, we have now examined the latter part of the reaction in which $Rh(CN)_3CO^{2-}$ reacts with CN^- ion to form $Rh(CN)_4^{3-}$, and then this anion reacts further to form $Rh(CN)_5H^{3-}$.

RESULTS AND DISCUSSION

The final product of the reaction of $[Rh(CO)_2Cl]_2$ with NaCN, the anion $Rh(CN)_5H^{3-}$, has no absorption in its u.v. spectrum below 40 kK, and only a slight absorption at higher frequency. $Rh(CN)_3CO^{2-}$, however, has three peaks in this region: 34·7(5·0 × 10^3), 29·3(4·0 × 10^3), and 25·8(3·8 × 10^3) [frequencies in kK (molar extinction coefficient)]. On mixing water–methanol (19 : 1) solutions of $Rh(CN)_3CO^{2-}$ with an excess of NaCN solution a reaction was observed which had a rate suitable for study by a stopped-flow apparatus. Initially it was thought that this reaction was the displacement of CO in $Rh(CN)_3CO^{2-}$ by CN^- to form $Rh(CN)_4^{3-}$. However, when the kinetics were studied at differing frequencies, it was clear that the initial absorption values did not agree with those expected for $Rh(CN)_3CO^{2-}$, and that what was being observed was the decay of a rapidly formed intermediate; this we expected to be $Rh(CN)_4^{3-}$. Since no evidence was observed on the kinetic traces for the build-up of this intermediate, this must take place in less than *ca.* 10^{-3} s. It was, in fact, shown that all the displacement reactions were very rapid by allowing $[Rh(CO)_2Cl]_2$ to react directly with an excess of NaCN. In this case the initial absorbances and kinetic patterns were the same as those observed in the decay of the intermediate, indicating that the same reaction was being followed, and that the displacement reactions were all

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[1] R. A. Jewsbury and J. P. Maher, *J. Chem. Soc.* (*A*), 1971, 2847.

very rapid. Very rapid displacement reactions for d^8 square-planar complexes are observed in other systems.[2]

A spectrum of the intermediate was obtained by using the stopped-flow machine under continuous-flow conditions, together with a frequency drive on the monochromator and an approximately constant energy slit-width cam. The result, after applying a baseline correction and conversion of transmission values into absorbance, is shown in Figure 1. The conditions chosen for the reaction ([NaCN] = 4×10^{-3}M, pH 10·8, ionic strength 0·11M, and 23·5 °C) were such that the disappearance of the intermediate was fairly slow; the intermediate was observed *ca.* 0·3 s after it was formed and the half-life for its decay was *ca.* 3 min. Any reaction of the intermediate before measurement of the spectrum was negligible. The spectrum of the intermediate has two peaks: 31·2 ± 0·2 [(1·24 ± 0·3) × 10^4] and 27·3 ± 0·3 [(6·7 ± 0·2) × 10^3] (frequencies in kK [molar extinction coefficient]). The absorptions can be assigned as charge-transfer bands of the metal-to-ligand type and are analogous to the spectra of other d^8 square-planar tetracyano-complexes.[3] The spectrum is consistent with an Rh^I rather than an Rh^{III} complex.

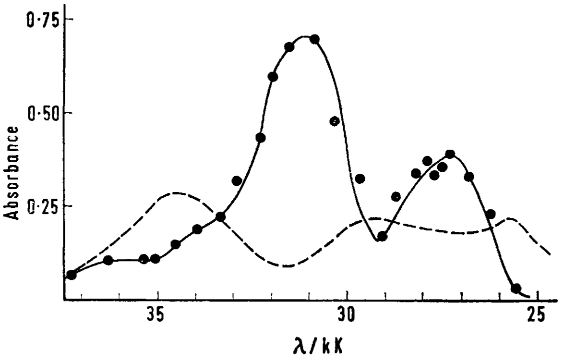

FIGURE 1 U.v.-visible spectrum of the intermediate $Rh(CN)_4^{3-}$ (——) and of $Rh(CN)_3CO^{2-}$ (— — —)

Experimental evidence was also obtained that the intermediate is an Rh^I and not an Rh^{III} species. [It will be shown that Rh^I carbonyl cyanide species react with methyl iodide to form acetyl or methyl complexes; on the other hand, $Rh(CN)_5H^{3-}$ does not react with methyl iodide.] Solutions of $Rh(CN)_3CO^{2-}$ and NaCN were mixed in the stopped-flow apparatus under conditions such that the half-life of the reaction to form the hydride was *ca.* 1 min. Using a continuous-flow arrangement, the mixed solution was quenched in an excess of MeI in methanol within 1 s of mixing. A ^{1}H n.m.r. spectrum of the product showed that it consisted of $Rh(CN)_5CH_3^{3-}$ with *ca.* 15% of acetate. The latter is thought to have arisen from the decomposition of acetyl products by the alkaline residue in the solution. No hydride was observed. This result suggests that the intermediate species is Rh^I rather than Rh^{III}, and furthermore, since the majority of the product was the methyl rather than the acetyl compound, a species which does not contain CO is implied. Figure 1 shows that it would not be possible to detect a small quantity of $Rh(CN)_3CO^{2-}$ in the presence of the intermediate due to the more intense absorption of the latter, thus it is possible that the small quantity of acetate which is formed may result from unchanged $Rh(CN)_3CO^{2-}$ reacting with MeI or from $Rh(CN)_4CO^{3-}$ (*vide infra*).

It was not possible to react 1 mol of NaCN with 1 mol of $Rh(CN)_3CO^{2-}$ to give $Rh(CN)_4^{3-}$. When this was tried the product consisted half of $Rh(CN)_5H^{3-}$ and half of $Rh(CN)_3CO^{2-}$ as was reported previously.[1] This is due to the displacement of the equilibrium (1) as CN^-

$$Rh(CN)_3CO^{2-} + CN^- \rightleftharpoons Rh(CN)_4^{3-} + CO \qquad (1)$$

is removed by the irreversible formation of the hydride product. Although it would be possible to test this hypothesis by following both the decay of $Rh(CN)_4^{3-}$ and the reformation of $Rh(CN)_3CO^{2-}$, this was not practical due to the absorption intensity differences in the spectra of these anions (Figure 1).

Kinetics.—The kinetics of the decay of the $Rh(CN)_4^{3-}$ anion were studied as a function of pH. The first-order rate constant, at a constant NaCN concentration of 4×10^{-2}M and a Rh^I concentration of 4×10^{-4}M, varies in the manner shown in Figure 2. This suggests a rate law of the type (2).

$$\text{rate} = k[\text{HCN}] + k'[\text{CN}] \qquad (2)$$

This can be used to explain the major part of the curve, with values of k and k' such that in the region of pH 9—10·5 the first term of the rate law is predominant and in solutions more alkaline than pH 11 the second term predominates.

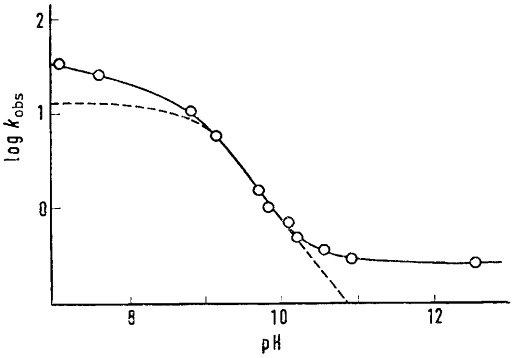

FIGURE 2 pH Dependence for the observed rate of decomposition, k_{obs}, of the intermediate $Rh(CN)_4^{3-}$. Dashed line indicates theoretical curve for a reaction between the intermediate and HCN (see text)

A reaction between $Rh(CN)_4^{3-}$ and HCN in equilibrium with an excess of NaCN would have a pseudo-first-order rate constant k_{obs} which was linearly dependent upon pH in solutions more alkaline than the pK of HCN, but which levelled off to a constant value in more acid solutions where, at constant NaCN con-

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[2] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn, Wiley, New York, 1967.

[3] H. B. Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.*, 1963, **85**, 260.

centration, a limiting concentration of HCN would be reached. The pK of HCN in water is 9·1, and assuming this value holds for the 5% methanol solution used, then the graph, which is a log–log plot, would have a slope of unity in solutions of pH more alkaline than 9·1, and level off in more acid solutions. This is shown by the dashed line in Figure 2.

Thus it appears that in the region of pH 9—10·5 the major reaction is with HCN. The mechanism, which can also be expected to apply in solutions which are not buffered, can be expressed as in equations (3)—(6).

$$\mathrm{Rh(CN)_3CO^{2-} + CN^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Rh(CN)_4{}^{3-} + CO} \qquad (3)$$

$$\mathrm{CN^- + H_2O} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{HCN + OH^-} \qquad (4)$$

$$\mathrm{CN^- + H_3O^+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{HCN + H_2O} \qquad (5)$$

$$\mathrm{Rh(CN)_4{}^{3-} + HCN} \xrightarrow{k_4} \mathrm{Rh(CN)_5H^{3-}} \qquad (6)$$

The rate constants k_2 and k_{-2} have been determined by an ultrasonic technique[4] and found to be $5{\cdot}2 \times 10^4$ s^{-1} and $3{\cdot}7 \times 10^9$ l mol^{-1} s^{-1} respectively for aqueous KCN at 25 °C. The rates of reactions of anions of simple inorganic acids with H_3O^+ are all found in the range 10^{10}—10^{11} l mol^{-1} s^{-1} [5] and although k_3 has not been measured it is presumably within this range. k_{-3} Can be estimated from the pK of HCN as 10—100 l mol^{-1} s^{-1}. It is thus clear that the formation of HCN is very much faster than the rate of the reaction being measured, and thus cannot be rate determining. The rate of formation of $Rh(CN)_4{}^{3-}$ is too fast to observe and thus $k_1[CN^-] \geqslant 10^3$ s^{-1}, so that $k_1 \geqslant 4 \times 10^5$ l mol^{-1} s^{-1}. It is also likely that the equilibrium constant for this reaction is such that most of the Rh^I is present as $Rh(CN)_4{}^{3-}$ and is formed immediately. The observed first-order rate constant according to the above scheme is k_4[HCN]. The HCN concentration has been calculated at each pH assuming a pK of 9·1 and k_{obs} divided by [HCN] to give values of k_4 (Table 1). These are constant for pH values between 9·72 and 10·20, and their weighted mean gives $k_4 = (1{\cdot}98 \pm 0{\cdot}1) \times 10^2$ l mol^{-1} s^{-1}.

At a pH of 10·1 the observed pseudo-first-order rate constant was found to be linearly dependent upon NaCN concentration, consistent with a rate law involving either CN$^-$ or HCN (Figure 3). The scatter on these points is hard to explain, being outside the expected experimental random errors. It was possibly caused by uncertainty in the pH, this being one of the hardest variables to control (see Experimental section). The reaction is only slightly faster in a medium of higher ionic strength, which is consistent with a reaction between HCN and $Rh(CN)_4{}^{3-}$. From the temperature dependence of the observed rate constants (Table 2) the activation parameters for the reaction are $\Delta H^{\ddagger} = 1{\cdot}8 \pm 1{\cdot}0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -42 \pm 4$ cal K^{-1} mol^{-1}. The very negative entropy of activation is a characteristic of other oxidative–addition reactions[6] and indicates a considerable loss of freedom in the transition state, as might be expected for the addition of one molecule to another.

TABLE 1

pH Dependence of rate of reaction of $Rh(CN)_4{}^{3-}$ with HCN $I = 0{\cdot}14$M (5% MeOH, 95% H_2O); [NaCN] $= 4 \times 10^{-2}$M; [Rh^I] $= 4 \times 10^{-4}$; $t = 23{\cdot}5$ °C

pH	[HCN]/mol l^{-1}	k_{obs}/s^{-1}	$10^{-2}k_4$/ l mol^{-1} s^{-1}
7·08	$3{\cdot}97 \times 10^{-2}$	35·7	
7·52	$3{\cdot}90 \times 10^{-2}$	28·9	
8·85	$2{\cdot}56 \times 10^{-2}$	11·50	
9·17	$1{\cdot}83 \times 10^{-2}$	6·0	3·30
9·72	$7{\cdot}73 \times 10^{-3}$	1·64	2·12
9·87	$5{\cdot}81 \times 10^{-3}$	1·08	1·86
10·20	$2{\cdot}95 \times 10^{-3}$	0·53	1·80
10·54	$1{\cdot}40 \times 10^{-3}$	0·37	2·64
10·90	$6{\cdot}24 \times 10^{-4}$	0·31	4·97
12·56	$1{\cdot}39 \times 10^{-5}$	0·27	19·4

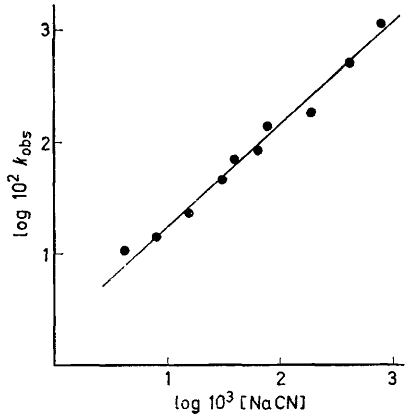

FIGURE 3 Dependence of the rate of decomposition, k_{obs}, of the intermediate $Rh(CN)_4{}^{3-}$ on [NaCN]

The stereochemistry of oxidative-addition reactions is of interest; this may be either stepwise or concerted and *cis* or *trans*. Both *cis*- and *trans*-additions of hydrogen halides have been reported for reactions with IrCl(CO)-$(PPh_3)_2$ and similar complexes. The stereochemistry of the product appears to be dependent upon the solvent.[7] Bond breaking is likely to be much more important in *trans*- rather than *cis*-addition. It was thought that an examination of the isotope effect for the addition of DCN might provide evidence on this matter. It is possible to estimate theoretically[8] a value of *ca.* 11 for

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[4] J. Stuehr, E. Yeager, T. Sachs, and F. Hovorka, *J. Chem. Phys.*, 1963, **38**, 587.

[5] E. F. Caldin, 'Fast Reactions in Solution,' Blackwell, Oxford, 1964.

[6] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 1966, **88**, 3511; I. C. Dovek and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 2604; P. Uguagliati, A. Palazzi, G. Degonello, and U. Belluco, *Inorg. Chem.*, 1970, **9**, 724.

[7] M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, 1967, **6**, 1647; J. P. Collman and C. T. Sears, *ibid.*, 1968, **7**, 27; A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1128, 1562; D. M. Blake and M. Kubota, *Inorg. Chem.*, 1970, **9**, 989.

[8] R. P. Bell, 'The Proton in Chemistry,' Methuen, London, 1959.

the isotope effect based on the energy difference for breaking the H–C and the D–C bonds, assuming that this will be important in determining the energy of the rate-determining step.

TABLE 2

Kinetic data and temperature dependence of the rate of reaction between $Rh(CN)_4^{3-}$ and HCN

$10^4[Rh(CN)_4^{3-}]$/mol l⁻¹	[NaCN]/mol l⁻¹	% Methanol	Ionic strength/mol l⁻¹	t/°C	pH	k_{obs}/s⁻¹
4	4×10^{-2}	5	0·18	23·5	10·1	0·728
4	8×10^{-2}	5	0·18	23·5	10·1	1·403
4	2×10^{-1}	5	0·30	23·5	10·1	1·907
4	4×10^{-1}	5	0·50	23·5	10·1	5·305
4	8×10^{-1}	5	0·90	23·5	10·1	11·49
2	4×10^{-3}	10	0·10	23·5	10·1	$8{\cdot}81 \times 10^{-2}$
2	8×10^{-4}	10	0·10	23·5	10·1	$1{\cdot}90 \times 10^{-2}$
4	4×10^{-3}	10	0·10	23·5	10·1	0·106
4	8×10^{-3}	10	0·11	23·5	10·1	0·143
4	$1{\cdot}6 \times 10^{-2}$	10	0·12	23·5	10·1	0·244
4	$3{\cdot}2 \times 10^{-2}$	10	0·13	23·5	10·1	0·482
4	$6{\cdot}4 \times 10^{-2}$	10	0·16	23·5	10·1	0·843
4	4×10^{-3}	5	0·10	5·1	10·25	$4{\cdot}54 \times 10^{-2}$
4	4×10^{-3}	5	0·10	9·9	10·21	$4{\cdot}91 \times 10^{-2}$
4	4×10^{-3}	5	0·10	14·8	10·19	$6{\cdot}2 \times 10^{-2}$
4	4×10^{-3}	5	0·10	23·5	10·18	$7{\cdot}5 \times 10^{-2}$
4	4×10^{-3}	5	0·10	30·4	10·17	$8{\cdot}3 \times 10^{-2}$
4	4×10^{-3}	5	0·10	40·4	10·09	0·121
4	4×10^{-3}	5	0·10	49·5	9·91	0·149
4	8×10^{-3}	5	0·11	23·5	10·8	4·72
1	2×10^{-3}	5	0·11	23·5	10·8	$1{\cdot}63 \times 10^{-2}$
1	4×10^{-3}	5	0·10	23·5	10·8	$2{\cdot}30 \times 10^{-3}$
8	8×10^{-2}	5	0·08	23·5	10·09	0·600
8	$3{\cdot}2 \times 10^{-1}$	5	0·32	23·5	10·9	3·00
2	4×10^{-2}	2·5	0·04	23·5	10·9	0·276
4	4×10^{-2}	5	0·24	1·5	11·1	0·282
4	4×10^{-2}	2·5	0·24	10·9	11·1	0·307
4	4×10^{-2}	2·5	0·24	23·5	11·1	0·391
4	4×10^{-2}	2·5	0·24	40·2	11·1	0·514
4	4×10^{-2}	2·5	0·24	48·6	11·1	6·641

TABLE 3

Variation of observed rate constant, k_{obs}, with percentage D_2O

$[NaCN] = 4 \times 10^{-2}$M; $[Rh^I] = 4 \times 10^{-4}$M; $t = 23{\cdot}5$ °C; $I = 0{\cdot}14$M (5% MeOH; 95% H_2O)

% D_2O	k_{obs}/s⁻¹	pH-Meter reading
90	0·177	10·5
45	0·328	10·3
0	0·529	10·1

In order to determine the isotope effect on the rate constant the rate was measured in D_2O–H_2O mixtures. The variation in magnitude of k_{obs} together with the pH-meter readings are shown in Table 3. Extrapolation to 100% D_2O gives $k_{obs} = 0{\cdot}138$ s⁻¹ at an actual pH of 10·9 using the formula: pD = pH-meter reading + 0·40.[9] This can be related to k_4 by calculating the HCN concentration for the HCN and the DCN reactions. Although the pK for DCN has not been measured, values for other deuterio-acids have and it has been shown that $\log K_H/K_D$ is an approximately linear function of $\log K_H$. Thus the pK of DCN can be estimated as $9{\cdot}7 \pm 0{\cdot}2$ which gives k_4 in H_2O/k_4 in $D_2O = 2{\cdot}4 \pm 0{\cdot}6$. This is a smaller ratio than would be expected if the rate-determining step were bond breakage in HCN but it is clearly a primary isotope effect. It is also necessary to distinguish between changes in $\Delta H^\ddagger$ and $\Delta S^\ddagger$. We attempted to obtain these for the DCN system but the differences were within the error limits for the determinations.

In solutions with pH > 11 the concentration of HCN becomes so low that the rate term involving $[CN^-]$ becomes predominant. Thus we have equation (7) at pH > 9. It is not known for certain that the hydride

$$\text{rate} = 198[HCN] + 9{\cdot}8[CN^-] \qquad (7)$$

$Rh(CN)_5H^{3-}$ is formed when this rate law predominates since it is unstable in alkaline solutions. However, a ^1H n.m.r. spectrum on the reaction product, under these conditions, showed that some of the hydride was still formed. The rate of reaction showed a first-order dependence upon [NaCN] indicating that the rate-determining step still involves CN^-. It is possible that $Rh(CN)_5^{4-}$ is formed in these media and that this subsequently reacts with water to form the hydride as in (8) and (9). Although there is no evidence for $Rh(CN)_5^{4-}$,

$$Rh(CN)_4^{3-} + CN^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Rh(CN)_5^{4-} \qquad (8)$$

$$Rh(CN)_5^{4-} + H_2O \xrightarrow{k_6} Rh(CN)_5H^{3-} + OH^- \qquad (9)$$

the analogous species $Co(CN)_5^{4-}$ has been postulated by several authors and its rate of formation from the pulse radiolysis of $Co(CN)_5^{3-}$ has been measured.[10] In the

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[9] P. K. Glascoe and F. A. Long, *J. Phys. Chem.*, 1960, **64**, 188.

[10] G. D. Venerable II and J. Halpern, *J. Amer. Chem. Soc.*, 1971, **93**, 2176.

$Co(CN)_5^{4-}$ system the reaction with water to form $Co(CN)_5H^{3-}$ is very rapid and it is therefore likely that the rate-determining step in the above scheme is k_5.

The most difficult region of pH to interpret is that with pH < 9. The plot does not level off as expected, so that it is apparent that in this region yet another mechanism is operative. The order with respect to NaCN is still approximately unity but, at lower concentrations of NaCN, non-first-order rate plots are observed. Moreover the product only contains about 25% hydride. Acid hydrolysis of the hydride has been reported at pH 4; this might effect detection, though the solutions are still relatively alkaline.[11] We can offer no ready explanation for this portion of the graph apart from the possibility that protonated $Rh(CN)_4^{3-}$ species are being formed and the rate consequently increased; the excess order in $[H^+]$ is 0·4. This might be a reasonable p*K* range for acid species such as $H[Rh(CN)_4]^{2-}$, $H_2[Rh(CN)_4]^-$, or $H_3[Rh(CN)_4]$.

Formation of Alkyl-rhodium Compounds.—If the reaction of $[Rh(CO)_2Cl]_2$ with NaCN is carried out in the presence of MeI then the intermediate $Rh(CN)_4^{3-}$ undergoes oxidative addition to an alkyl-rhodium compound. Similar reactions are observed for the intermediates $Rh(CN)_3CO^{2-}$ and $Rh(CN)_2(CO)_2^-$. The final products in the reactions have not yet been adequately characterised but some preliminary kinetic data can be presented here.

By choosing conditions such that the formation of the hydride $Rh(CN)_5H^{3-}$ is slow, it is possible to follow the reaction of $Rh(CN)_4^{3-}$ with alkyl halides. A mixture of an excess of MeI together with the stoicheiometric quantity of NaCN was reacted with $Rh(CN)_3CO^{2-}$ in an aqueous solution at pH 10·1 and ionic strength 0·1M, containing 5% methanol. The reaction is first order in MeI and Rh^I with a rate constant of $(5{\cdot}9 \pm 1{\cdot}0) \times 10^2$ l mol^{-1} s^{-1} at 23·5 °C. Most of the uncertainty in the rate constant arises from the uncertainty in the concentration of MeI. The reaction was repeated at pH 11 and the rate was the same, indicating a lack of a pH dependence. A study of the rate in more acid solutions was precluded by the more rapid reaction with cyanide in that region. The temperature dependence of the observed rate constant at pH 11 gives $\Delta H^\ddagger = 8{\cdot}4 \pm 2{\cdot}0$ kcal mol^{-1} and $\Delta S^\ddagger = -18 \pm 7$ cal K^{-1} mol^{-1}. Whilst $\Delta H^\ddagger$ is similar to values obtained for the reactions of various other d^8 complexes with MeI, the value for $\Delta S^\ddagger$ is the lowest yet observed, though still negative.[6] One reason, often suggested in the past, for the large negative $\Delta S^\ddagger$ in oxidative–addition reactions has been that the transition state involves a charge separation which causes a decrease in the entropy of the solution. However, where one reactant already has a charge of −3, this effect may appear relatively smaller. The highly negative $\Delta S^\ddagger$ may therefore have its origin in steric factors. The latter will be greater in groups with bulky phosphine groups than in $Rh(CN)_4^{3-}$ and also explains why Ir^I complexes show more negative $\Delta S^\ddagger$ values than their Rh^I analogues.

An attempt was also made to look at the rate of reaction of $Rh(CN)_4^{3-}$ with other simple alkyl halides. EtI Gives a rate constant of $(3{\cdot}6 \pm 0{\cdot}7) \times 10$ l mol^{-1} s^{-1} at 23·5 °C. It was not possible to obtain a rate constant for the reaction with Pr^nI since the reaction to form the hydride was faster at the maximum solubility of Pr^nI. The low solubility of both MeI and EtI precluded studies over a wide concentration range; unfortunately the reaction is not first order in pure methanol solutions. The 17-fold greater rate of reaction of MeI over EtI with $Rh(CN)_4^{3-}$ is typical of S_N2 type reactions, with which oxidative-addition reactions have been compared; the rate difference is similar to that observed in other oxidative-addition reactions.[6] Kinetic data for these reactions are collected in Table 4.

TABLE 4

Data for reactions of $Rh(CN)_{4-n}(CO)_n$ compounds with alkyl halides

$[Rh] = 2 \times 10^{-4}$M, $I = 0{\cdot}1$M (95% H_2O, 5% MeOH)

Compound	[MeI] mol l^{-1}	t/°C	pH	k_{obs}/s^{-1}
$Rh(CN)_4^{3-}$	$1{\cdot}94 \times 10^{-3}$	23·5	10·0	1·29
$Rh(CN)_4^{3-}$	$1{\cdot}94 \times 10^{-2}$	23·5	10·0	11·6
$Rh(CN)_4^{3-}$	$5{\cdot}15 \times 10^{-3}$ [a]	23·5	10·0	0·187
$Rh(CN)_3CO^{2-}$	$1{\cdot}74 \times 10^{-2}$	23·5	10·0	0·2060
$Rh(CN)_2(CO)_2$ [b]	$2{\cdot}3 \times 10^{-3}$	21·0		$3{\cdot}4 \times 10^{-3}$
$Rh(CN)_4^{3-}$	$1{\cdot}98 \times 10^{-2}$	0·6	11·0	2·3
$Rh(CN)_4^{3-}$	$1{\cdot}98 \times 10^{-2}$	23·5	11·0	9·7
$Rh(CN)_4^{3-}$	$1{\cdot}98 \times 10^{-2}$	37·6	11·0	16·0
$Rh(CN)_4^{3-}$	$1{\cdot}98 \times 10^{-2}$	48·6	11·0	30·1

[a] EtI. [b] In 90% H_2O, 10% MeOH.

The rates of reaction of both $Rh(CN)_3CO^{2-}$ and $Rh(CN)_2(CO)_2^-$ with MeI were measured in the methanol–water solvent under the same conditions as before. Both reactions showed good pseudo-first-order plots and give k_2 values of respectively $(1{\cdot}14 \pm 0{\cdot}2)$ and $(0{\cdot}15 \pm 0{\cdot}03)$ l mol^{-1} s^{-1}. It is interesting that the difference in the rates for $Rh(CN)_4^{3-}$ and $Rh(CN)_3CO^{2-}$ is a factor of 500, whereas for $Rh(CN)_3CO^{2-}$ and $Rh(CN)_2(CO)_2^-$ it is only 7.

It is clear from the large difference in the rates of reaction of $Rh(CN)_4^{3-}$ and $Rh(CN)_3CO^{2-}$ with MeI that the formation of some acetyl product [12] cannot be due to reaction of MeI with $Rh(CN)_3CO^{2-}$ followed by an insertion reaction for the product $Rh(CN)_3(CO)MeI^{2-}$. The intermediates in the reaction of $[Rh(CO)_2Cl]_2$ with NaCN in the presence of MeI have been investigated spectroscopically and, although we have not been able to interpret these spectra, due we believe to a very complex mixture of species being present, at each Rh : CN ratio the i.r. and ^1H n.m.r. are characteristic. In the presence of MeI the Rh^{III} alkyl and acyl species appear to be formed reversibly. Thus if the reaction conditions are such that Rh^{III} methyl compounds [*e.g.*, possibly $Rh(CN)_5CH_3^{3-}$] are predominantly formed, then on addition of more $[Rh(CO)_2Cl]_2$ to the mixture the reaction is reversed to give a solution whose i.r. spectrum is now characteristic of the new Rh : CN ratio. Further

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[11] H. L. Roberts and W. R. Symes, *J. Chem. Soc.* (*A*), 1968, 1450.

[12] J. P. Maher, *Chem. Comm.*, 1966, 785.

addition of CN^- pushes the reaction to the right-hand side again.

It is therefore probable that Rh^I species catalyse the interconversion of the different Rh^{III} species and if this type of reaction is sufficiently rapid it may provide an explanation for the formation of acyl compounds in the quantities previously noted. This catalysis would be analogous to that by Pt^{II} in Pt^{IV} substitutions; catalysis [2] by Rh^I in nucleophilic substitutions at Rh^{III} [13] and in alkyl transfer between Co^I and Co^{III} [14] has been noted recently.

An alternative explanation is that another species $Rh(CN)_4CO^{3-}$, analogous to the species $Rh(CN)_5{}^{4-}$ which we postulated, is present. Such a carbonyl species would certainly react rapidly with MeI or other alkyl halides [as would $Rh(CN)_5{}^{4-}$]. Unfortunately it was not possible to measure the rate dependence of either the hydride- or alkyl-forming reactions on CO concentration. In the hydride-forming system, we have assumed that $Rh(CN)_4{}^{3-}$ is the reactive species rather than $Rh(CN)_4CO^{3-}$; this seemed appropriate in view of our structural measurements on the other complexes in this system, all of which appear to be square planar.[1] The u.v. spectrum of the intermediate and the acid dependence of the reaction favour $Rh(CN)_4{}^{3-}$ over $Rh(CN)_5CO^{3-}$; however, this latter species may be present in sufficient concentrations, and have sufficiently rapid reactions with reactive species such as MeI, to influence the course of reaction. In the hydride system it might also be kinetically important for the $9{\cdot}0 > pH > 10{\cdot}5$ region previously discussed, and for which reaction of $Rh(CN)_4{}^{3-}$ with HCN is not applicable. We have not been able to obtain any evidence for other hydrides, *e.g.* $Rh(CN)_4(CO)H^{2-}$, in the system from the n.m.r. or i.r. spectra.

EXPERIMENTAL

In the previous study of the complexes in the carbonylcyanorhodate(I) system methanolic solutions were used. However, for the kinetics now presented, it was necessary to use a methanol–water solvent. A predominantly aqueous solution was used so that the solutions could be buffered at a constant ionic strength. Since $[Rh(CO)_2Cl]_2$ solutions cannot be made up in water, due to precipitation of colloidal metal, they were prepared in methanol. These concentrated solutions were prepared under N_2 and handled in a glove-bag and then transferred to the inlet flasks of the stopped-flow apparatus. The latter already contained N_2-purged solutions and were isolated from the atmosphere by a constant stream of N_2 passing over their surface. NaCN Solutions must be similarly made up since, on passage of N_2, HCN is displaced. The final diluted solutions had a solvent composition 95% H_2O, 5% MeOH; they were buffered and of known constant ionic strength throughout the kinetic measurements. Two buffer solutions were used: $NaHCO_3$–Na_2CO_3 (pH 9·2—10·9) and NaH_2PO_4–K_2HPO_4 (pH 6·0—9·5); the ionic strength of the buffers was either 0·1 or 0·2M. The pH of the solutions was measured with a pH meter; as might be expected the HCN–NaCN system itself behaves as a buffer and since this tends to interfere with the above carbonate and phosphate buffer systems the pH values taken from buffer tables cannot be used.

The stopped-flow apparatus used in this study has been described elsewhere.[15] Each kinetic result presented in this study is the average of a number of measured runs, all of which were first order over several (in some cases over 5 or 6) half-lives unless otherwise noted; rate constants are accurate to ±5% (estimated). U.v. and i.r. spectra were measured as described previously.[1]

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[2/514 *Received, 6th March*, 1972]

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[13] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc.* (*A*), 1971, 1840.

[14] D. Dodd and M. D. Johnson, *Chem. Comm.*, 1971, 1371.

[15] S. E. Brady, R. L. Cleaver, R. A. Jewsbury, J. S. Littler, and J. P. Maher, *Lab. Practice*, 1972, **21**, 15.