Mechanistic Studies on the Substitution Reactions between Aquatetracyanooxotungstate(IV) and HCN–CN^- and F^-

Jaap P. Smit, Walter Purcell, Andreas Roodt* and (the late) Johann G. Leipoldt
Department of Chemistry, University of the Orange Free State, Bloemfontein, 9300, South Africa

---

The kinetics of the substitution reaction between aquatetracyanooxotungstate(IV) ions and CN^- and HCN was studied, and compared with the corresponding molybdenum(IV) system. The aqua ligand in the $[WO(OH_2)(CN)_4]^{2-}$ complex is substituted by both CN^- ions and HCN *via* a dissociative mechanism according to the reaction: $[WO(OH_2)(CN)_4]^{2-} + CN^-\text{–HCN (L)} \rightleftharpoons [WO(L)(CN)_4]^{n-} + H_2O$. At 25 °C and $I = 1$ mol dm^{-3} (KNO_3), the equilibrium, forward and reverse rate constants of the reaction with CN^- ions were determined as $1.0(2) \times 10^3$ dm^3 mol^{-1}, 1.0(3) dm^3 mol^{-1} s^{-1}, $1.0(2) \times 10^{-3}$ s^{-1}, and for HCN as 1.0(2) dm^3 mol^{-1}, 9(1) dm^3 mol^{-1} s^{-1}, and 8.0(2) s^{-1}, respectively. Co-ordination of HCN to the metal centre results in a decrease in the pK_a value of hydrogen cyanide by approximately 3.2 pH units to 5.8(3), and the decrease is in direct correlation with the stability constants for monodentate substitution reactions for the molybdenum(IV) and tungsten(IV) systems. A free-energy correlation between the hydrolysis rate constant and the stability constant for all the known $[WO(L)(CN)_4]^{n-}$ complexes was constructed. A dissociative mechanism is postulated for the reaction where L = pyridine, N_3^-, NCS^- and CN^-. For the formation of $[WO(F)(CN)_4]^{3-}$, a volume of activation of $-28(2)$ cm^3 mol^{-1} was obtained, suggesting a more associative activation for the reaction with F^-, in agreement with the observed deviation from the linear relationship obtained for the aforementioned nucleophiles.

It has been shown over the past few years that protonation of the *trans*-dioxotetracyano-complexes of molybdenum(IV), tungsten(IV), technetium(V) and rhenium(V) results in the formation of the corresponding oxohydroxo- and oxoaqua-complexes.[1] These stepwise protonations for the tungsten(IV) complex may be represented by the reactions (1) and (2). The

$$[WO_2(CN)_4]^{4-} + H^+ \rightleftharpoons [WO(OH)(CN)_4]^{3-} (pK_{a2}) \quad (1)$$

$$[WO(OH)(CN)_4]^{3-} + H^+ \rightleftharpoons [WO(OH_2)(CN)_4]^{2-} (pK_{a1}) \quad (2)$$

protonated species undergo substitution reactions with mono-[1] (aqua substitution) and bi-dentate[2] (aqua and cyano substitution) nucleophiles. The protonation behaviour of these systems has recently been the subject of carbon-13 and oxygen-17 NMR[3,4] studies in order to investigate the water exchange of these complex ions.

Previous studies of substitution reactions included different monodentate nucleophiles such as F^-, N_3^-, NCS^- ions, pyridine and substituted thioureas for the complexes of W^{IV} and Re^{V}.[1] For the molybdenum(IV) system only the reaction with F^- and CN^-/HCN ions could be studied as a result of the high substitution lability of the co-ordinated aqua ligand in the $[MoO(OH_2)(CN)_4]^{2-}$ ion.[5] Therefore, extensive kinetic, and specifically high-pressure studies, could not be done for Mo^{IV}. Previous work in this laboratory showed that a linear free-energy relationship between ln k_{-L} and ln K_L {k_{-L} = hydrolysis rate constant and K_L = stability constant for $[WO(L)(CN)_4]^{n-}$ complexes} exists for the substitution reaction of $[WO(OH_2)(CN)_4]^{2-}$ by monodentate nucleophiles (L) such as N_3^-, NCS^- ions and pyridine, pointing to a dissociative mechanism for this metal centre. The reaction with F^- ions however does not fit the free-energy relation. We are interested in the substitution behaviour of $[WO(OH_2)(CN)_4]^{2-}$ in CN^-–HCN media in order to determine the type of mechanism for this reaction, which is also the first step in the formation of the higher co-ordinated cyano complexes, *i.e.* $[M(CN)_8]^{4-}$ for M = Mo^{IV} or W^{IV}. Since the mechanism of the latter process is also not known, a mechanistic study would provide additional knowledge on the formation of these octacyano complexes. Although it is known that the HCN entity can act as a monodentate ligand,[5–9] this fact was only recently observed in our laboratory for these dioxotetracyano systems.

This paper first describes a kinetic study of the reaction between $[WO(OH_2)(CN)_4]^{2-}$ and CN^-–HCN. A prime objective also included an attempt towards the better definition of the reaction profile as a function of pH for specifically the reaction with HCN (this was not well defined in the previous study with Mo^{IV}) and therefore the mechanism of activation. Secondly, in an attempt to broaden our knowledge on the mechanism of substitution reactions of these complexes in general, we again considered previously studied reactions, *i.e.* with F^-, N_3^-, NCS^- ions and pyridine, to evaluate the behaviour thereof with respect to high pressure. Owing to chemical restrictions, only the reaction with F^- ions could be studied and the results thereof are also reported herein.

Experimental

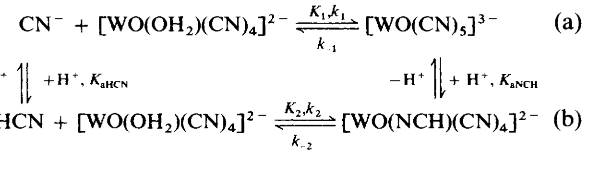
General.—All chemicals used were of analytical reagent grade and doubly distilled water was used in all the experiments. All pH measurements were done on an Orion 701 pH meter with a combined glass–calomel electrode, calibrated by standard buffer solutions, with pH = − log[H^+]. **CAUTION**: Cyanide is extremely toxic and HCN is generated throughout these experiments. Care was therefore taken to perform all manipulations in a fume hood as far as possible.

Preparation of Starting Complex.—The salt $K_3Na[WO_2(CN)_4]\cdot 6H_2O$ was prepared as previously described[10] and characterized by means of single-crystal and X-ray powder diffraction methods.

Data Collection and Other Measurements.—The kinetics was studied at 540 nm on a Durrum D-110 stopped-flow or a GBC UV/VIS 916 spectrophotometer coupled with a personal computer capable of performing least-squares analyses on the absorbance values *vs.* time. High-pressure studies were done on a GBC 916 spectrophotometer in a high-pressure vessel with pill-box cells of path length ≈15 mm. All the kinetic runs were performed under pseudo-first-order conditions in carbonate–hydrogen carbonate or mes (2-morpholinoethanesulfonic acid) buffer medium with $I = 1$ mol dm^{-3} (KNO_3). No interference from these substances was detected during this study, and was consequently used for buffer capacity and ionic strength adjustments ($NaClO_4$ could not be used due to the precipitation of $KClO_4$, interfering with the pH electrode). All the temperatures are reported to ±0.1 °C accuracy. The solid lines in Figs. 1–6 represent the computer least-squares fits of the data to the respective functions. There is uncertainty in the literature[6–9,11] about the pK_a value of HCN, but in all the calculations this acid dissociation constant has been taken as 9.0,[8] as has also been determined potentiometrically at 25 °C and $I = 1.0$ mol dm^{-3} in this study.

Results

Previous research has shown that: (*i*) $[MO(OH_2)(CN)_4]^{n-}$ is the only protonated species of the dioxotetracyano-complexes of Mo^{IV}, W^{IV}, Tc^V and Re^V which is reactive towards monodentate substitution, *i.e.* no replacement of the hydroxide ligand in the $[MO(OH)(CN)_4]^{(n+1)-}$ complexes was observed for all the systems studied;[1] (*ii*) for the molybdenum(IV) and some other complexes studied, protonated forms of different nucleophiles, *i.e.* HN_3[12] and more specifically HCN,[5–9] can act as monodentate ligands. These observations, coupled with the fact that $[WO(OH_2)(CN)_4]^{2-}$ (pK_a = 7.8[1]) reacts with cyanide at pH values below the pK_{a1} value of HCN (= 9.0)[8], enables the construction of Scheme 1 for the ligation of $[WO(OH_2)(CN)_4]^{2-}$ by CN$^-$–HCN.



$$\begin{tikzcd}
CN^- + [WO(OH_2)(CN)_4]^{2-} \arrow[r, shift left, "K_1{,}k_1"] \arrow[d, shift right, "-H^+"'] & {[WO(CN)_5]^{3-}} \arrow[l, shift left, "k_{-1}"] \arrow[d, shift right, "-H^+"'] & \text{(a)} \\
HCN + [WO(OH_2)(CN)_4]^{2-} \arrow[u, shift right, "{+H^+,\ K_{aHCN}}"'] \arrow[r, shift left, "K_2{,}k_2"] & {[WO(NCH)(CN)_4]^{2-}} \arrow[l, shift left, "k_{-2}"] \arrow[u, shift right, "{+H^+,\ K_{aNCH}}"'] & \text{(b)}
\end{tikzcd}$$

Scheme 1

The HCN in the $[WO(NCH)(CN)_4]^{2-}$ complex is assumed to be nitrogen bonded[13–16] as has been verified for the $[MoO(NCH)(CN)_4]^{2-}$ ion *via* a crystal structure determination.[5] The effect of possible isomerization is not addressed separately in this system and is assumed to be incorporated in the K_{aNCH} value. It is, however, reasonable to assume that isomerization is rapid since no deviation from the first-order kinetics was observed. This is in agreement with the rapid isomerization observed for cobalt(III), *i.e.* $[Co(CN)_5(NC)]^{3-} \longrightarrow [Co(CN)_6]^{3-}$, $k_{iso} = 0.2$ s^{-1}, even though the normal substitution reactions of cobalt(III) are very slow.[13]

The rate law according to Scheme 1 is given by equation (3)

$$\text{Rate} = k_1[W(OH_2)][CN^-] + k_2[W(OH_2)][HCN] - k_{-1}[W(CN)] - k_{-2}[W(NCH)] \quad (3)$$

where $[W(OH_2)]$, $[W(CN)]$ and $[W(NCH)]$ represent the concentrations of $[WO(OH_2)(CN)_4]^{2-}$, $[WO(CN)_5]^{3-}$ and $[WO(NCH)(CN)_4]^{2-}$ respectively. Before integration of the rate equation, the total concentration of the tungsten(IV) reactant, $[W^{IV}]_{tot} = [WO(OH_2)(CN)_4{}^{2-}] + [WO(OH)(CN)_4{}^{3-}]$, and that of the products, $[W(CN)]_{tot} = [WO(CN)_5{}^{3-}] + [WO(NCH)(CN)_4{}^{2-}]$, were incorporated into equation (3). The definitions of the first acid dissociation of $[WO(OH_2)(CN)_4]^{2-}$, K_{a1}, as well as the acid dissociation constant of HCN, K_{aHCN}, and that of the co-ordinated hydrogen cyanide, K_{aNCH}, were also included. Expressions for the pseudo-first-order rate constant, k_{obs}, were consequently obtained upon integration of the rate law ($[CN^-]$, $[CN^-]_{tot} \gg [W]_{tot}$) in terms of the total cyanide concentration, $[CN^-]_{tot} = [CN^-] + [HCN]$, equation (4). The solid line in Fig. 1 represents the least-squares fit of k_{obs} *vs.* pH by equation (4) (constant

$$k_{obs} = \frac{(k_1K_{aHCN}/[H^+]) + k_2}{\{1 + (K_{a1}/[H^+])\}\{1 + (K_{aHCN}/[H^+])\}}[CN^-]_{tot} + \frac{k_{-2} + (k_{-1}K_{aNCH}/[H^+])}{\{1 + (K_{aNCH}/[H^+])\}} \quad (4)$$

$[CN^-]_{tot} = 0.050$ mol dm^{-3}). Preliminary values obtained from this fit are as follows: $k_1 = 1.2$ dm^3 mol^{-1} s^{-1}, $k_{-1} = 3.6 \times 10^{-2}$ s^{-1}, $k_2 = 8.1$ dm^3 mol^{-1} s^{-1}, $k_{-2} = 7.1$ s^{-1}, and p$K_{aNCH} = 5.9$. More accurate values, in excellent agreement with these, were obtained as described below by simplifying equation (4) under carefully selected experimental conditions.

At pH values *ca.* 6, where $[H^+] \gg K_{aHCN}$, K_{a1}, equation (4) simplifies to (5). Fig. 2 illustrates the dependence of the pseudo-first-order rate constant on the total cyanide concentration (primarily in the form of HCN) at pH 5–7 (lower values could not be studied due to the small effective equilibrium constant, see Figs. 2 and 5). It is clear that the increase in k_{obs} is primarily a result of the increase of the intercept, *i.e.*, the reverse rate

$$k_{obs} = k_2[CN^-]_{tot} + \frac{k_{-2} + (k_{-1}K_{aNCH}/[H^+])}{\{1 + (K_{aNCH}/[H^+])\}} \quad (5)$$

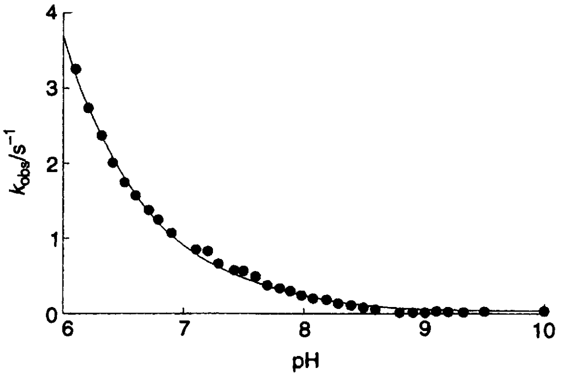


Fig. 1 pH Dependence of the pseudo-first-order rate constant at 25 0 °C, $[W^{IV}]_{tot} = 5.0 \times 10^{-3}$ mol dm^3, $I = 1.0$ mol dm^3 (KNO_3) and $[CN^-]_{tot} = 0.050$ mol dm^3

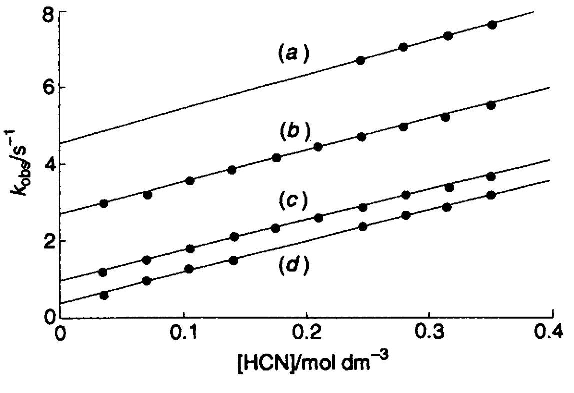


Fig. 2 Dependence of the pseudo-first-order rate constant at pH (*a*) 5.5, (*b*) 6.0, (*c*) 6.5 and (*d*) 7.0, at 25.0 °C, $[W^{IV}]_{tot} = 5.0 \times 10^{-3}$ mol dm^{-3} and $I = 1.0$ mol dm^{-3} (KNO_3)

Table 1 Kinetic and equilibrium data at different temperatures, $[\mathrm{W^{IV}}]_{\mathrm{tot}} = 5.0 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} (KNO$_3$)

T/°C	Constant	
25.0	$k_1{}^a$/dm^3 mol^{-1} s^{-1}	1.0(3)
16.0		0.40(6)
8.0		0.17(3)
25.0	$k_{-1}{}^a$/s^{-1}	$1.0(2) \times 10^{-3}$
16.0		$4(1) \times 10^{-4}$
8.0		$1.5(3) \times 10^{-4}$
—	$\Delta H^\ddagger(k_1)$/kJ mol^{-1}	90(5)
—	$\Delta S^\ddagger(k_1)$/J K^{-1} mol^{-1}	12(20)
25.0	$k_2{}^b$/dm^3 mol^{-1} s^{-1}	9(1)
15.0		2.9(1)
6.0		1.1(1)
25.0	$k_{-2}{}^b$/s^{-1}	8.0(2)
15.0		3.2(2)
6.0		1.1(1)
—	$\Delta H^\ddagger(k_2)$/kJ mol^{-1}	69(3)
—	$\Delta S^\ddagger(k_2)$/J K^{-1} mol^{-1}	$-5(10)$
25.0	K_1/dm^3 mol^{-1}	$1.0(2) \times 10^{3\,c}$
		$1.1(1) \times 10^{3\,d}$
25.0	K_2/dm^3 mol^{-1}	$1.0(2)^e$
		$1.2(2)^f$
25.0	pK_{aNCH}	$5.8(3)^g$
13.0	$\Delta V^\ddagger$/cm^3 mol^{-1}	$-28(2)^h$

[a] From equation (7), k_1 = slope ($K_{a1}/[\mathrm{H^+}]$) in Fig. 3, pH 10.5. [b] From equation (5), k_2 = slope, k_{-2} from intercept, in Fig. 2 [pH 7.0, k_2 = 9.0(2); 6.5, 8.9(5); 6.0, 8.6(7); and 5.5, 9.3(4) dm^3 mol^{-1} s^{-1}]. [c] Kinetically, $K_1 = k_1/k_{-1}$. [d] From Fig. 5(*a*), equation (9) at pH 10.0. [e] Kinetically, $K_2 = k_2/k_{-2}$. [f] From equation 10, average at pH 6.0, 6.5 and 7.0. [g] Least-squares fit by equation (8), Fig. 4. [h] Reaction between $[\mathrm{WO(OH_2)(CN)_4}]^{2-}$ and F$^-$, data in Table 2.

constants [second term in equation (5)], and that the kinetics at these pH values is adequately described by equation (5). The average value of k_2 can be obtained from the slope of the lines in Fig. 2 and is reported in Table 1.

At pH between 10.5 and 11 where $[\mathrm{H^+}] \ll K_{\mathrm{aHCN}}$ and K_{a1}, equation (4) simplifies to (6). Fig. 3 shows the dependence of

$$k_{\mathrm{obs}} = \frac{k_1[\mathrm{H^+}][\mathrm{CN^-}]_{\mathrm{tot}}}{K_{a1}} + \frac{k_{-2} + (k_{-1}K_{\mathrm{aNCH}}/[\mathrm{H^+}])}{\{1 + (K_{\mathrm{aNCH}}/[\mathrm{H^+}])\}} \qquad (6)$$

k_{obs} on the total cyanide concentration (primarily in the form of CN$^-$ ions) at pH 10.0–11.0. The value for k_1 obtained from the slope [equation (6)] (pH 10.5), upon incorporation of [H$^+$] and K_{a1}, is given in Table 1. The values at pH 10.0 (large contribution of the HCN path) and 11.0 (small slope, large uncertainty) were not used.

The contribution of the reverse path to the total pseudo-first-order rate constant, given by equations (5) and (6), is at lower pH values primarily a function of the acid dissociation constant of the co-ordinated HCN, *i.e.* K_{aNCH}. Assuming a pK_{aNCH} *ca.* 6 [as obtained from the preliminary fit of data in Fig. 1 by equation (4), see above], equation (6) can be simplified even further $\{k_{-1} > k_{-2}[\mathrm{H^+}]/K_{\mathrm{aNCH}}$, as confirmed by the similarity in the intercepts of the lines (pH 10.5 and 11) in Fig. 3$\}$, giving expression (7) for the first-order rate constant (pH *ca.* 11). At

$$k_{\mathrm{obs}} = \frac{k_1[\mathrm{H^+}][\mathrm{CN^-}]_{\mathrm{tot}}}{K_{a1}} + k_{-1} \qquad (7)$$

high pH values (> 10) equation (7) may be used to obtain values for the forward and reverse rate constants for the CN$^-$ pathway (k_1 and k_{-1} in Scheme 1) from the intercepts of the lines in Fig. 3. The k_{-1} value thus obtained is reported in Table 1.

The pH dependence of the intercept at lower pH values [see equation (4)] is given by equation (8), with the contribution of k_{-1} being relatively small at pH < 7 ($k_{-1} \ll k_{-2}$, see Table 1)

$$\mathrm{Intercept} = \frac{k_{-2} + (k_{-1}K_{\mathrm{aNCH}}/[\mathrm{H^+}])}{\{1 + (K_{\mathrm{aNCH}}/[\mathrm{H^+}])\}} \qquad (8)$$

since the intercept is primarily determined by k_{-2}. This pH dependence is shown in Fig. 4 [the least-squares fit of the intercept *vs.* pH using equation (8) gives the solid line], from which a fairly accurate pK_a value for the co-ordinated HCN can be determined, see Table 1. A more accurate definition of the complete curve in Fig. 4 is restricted by the decrease in the reaction yield at pH < 6.5. From this result, *i.e.* pK_{aNCH} = 5.8, k_{-2} values at the different pH values could be calculated, and the average is reported in Table 1.

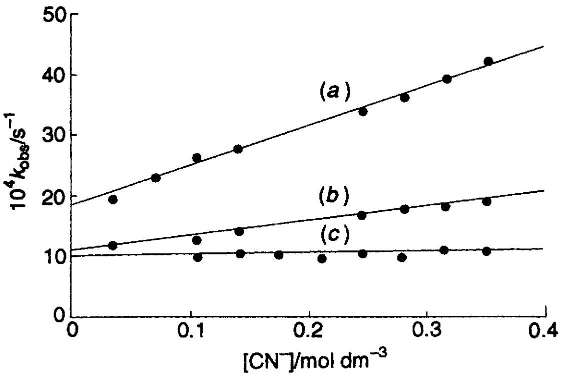


Fig. 3 Dependence of the pseudo-first-order rate constant at pH (*a*) 10.0, (*b*) 10.5 and (*c*) 11.0; other conditions as in Fig. 2

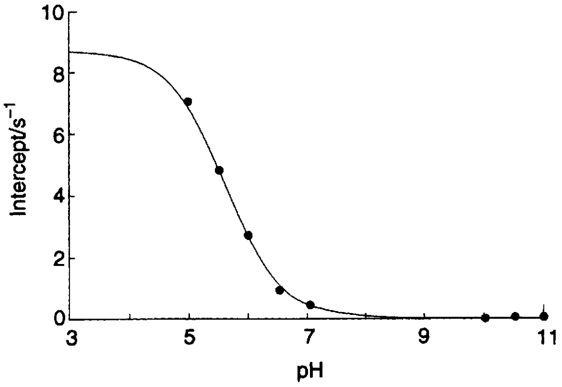


Fig. 4 pH Dependence of the *y*-intercept [equations (5) and (6)] at 25.0 °C, $[\mathrm{W^{IV}}]_{\mathrm{tot}} = 5.0 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^3 (KNO$_3$) and $[\mathrm{CN^-}]_{\mathrm{tot}} = 0.050$ mol dm^3

The equilibrium constants for both the HCN and CN$^-$ pathways were also determined spectrophotometrically by selecting appropriate pH values and incorporating the relevant K_a values. At high pH (10.0) where $[\mathrm{H^+}] \ll K_{a1}$, $[\mathrm{CN^-}] \approx [\mathrm{CN^-}]_{\mathrm{tot}}$, the CN$^-$ pathway dominates the absorbance dependence on [CN$^-$] for this system, and upon incorporation of Beer's law, mass balance, the definition of K_1 (k_1/k_{-1}) and K_{a1}, the relationship between absorbance data and K_1, described by equation (9), is obtained. The K_1 value, obtained from a least-squares fit of the absorbance *vs.* [CN$^-$] data, using equation (9), shown in Fig. 5(*a*), is reported in Table 1. In equations (9) and (10) A_{m} and A_{m1} represent the absorbance

$$A = \frac{A_{\mathrm{m}}(1 + K_{a1}/[\mathrm{H^+}]) + (A_{\mathrm{m1}}K_1[\mathrm{CN^-}])}{\{1 + (K_{a1}/[\mathrm{H^+}]) + K_1[\mathrm{CN^-}]\}} \qquad (9)$$

$$A = \frac{A_{\mathrm{m}} + A_{\mathrm{m1}}K_2[\mathrm{HCN}]\{1 + (K_{\mathrm{aNCH}}/[\mathrm{H^+}])\}}{1 + K_2[\mathrm{HCN}]\{1 + (K_{\mathrm{aNCH}}/[\mathrm{H^+}])\}} \qquad (10)$$

contributions due to the substituted and unsubstituted complexes respectively.

At pH values where $[H^+] \gg K_{aHCN}$ (pH < 7.5) and [HCN] = $[CN^-]_{tot}$, the HCN pathway dominates and the absorbance dependence on [HCN] for this system, and the relationship between absorbance data and K_2, is described by equation (10). The results, obtained from a least-squares fit of the absorbance *vs.* [HCN], shown in Fig. 5(*b*)–(*d*), to equation (10), are reported in Table 1. A temperature-dependence study was undertaken to determine the activation parameters for both the HCN (pH 6.5) and CN^- (pH 10.5) pathways. The rate constants are given in Table 1. The temperature dependence of the pK_a values of the tungsten(IV) complexes was assumed to be negligible compared to that of the other parameters.[1i]

In order to gain more information on the mechanism of substitution in these complexes in general, we opted to study the high-pressure kinetics of some of the reactions known to date, see Fig. 6. In the case of the reaction between $[WO(OH_2)(CN)_4]^{2-}$ and CN^-–HCN, the following inherent systematic limitations were experienced. (*i*) The reaction rate at lower pH values (*ca.* 5), was too rapid to monitor by even rapid stopped-flow techniques, the effect of pressure on the pK_{aNCH} value [and consequently on the intercept (equation (5)] is not known, and finally, the overall reaction yield at around these pH values is very low. (*ii*) At higher pH the rate expression is a function of the $[WO(OH_2)(CN)_4]^{2-}$ concentration and is therefore pK_{a1} dependent, and since the pressure dependence thereupon is not known, the possibility to study this reaction by high-pressure kinetics is consequently eliminated. Similar limitations hold for all the substitution reactions by monodentate nucleophiles for the tungsten(IV) complex, except for F^- ions. Since it has been shown previously that the reaction between $[WO(OH_2)(CN)_4]^{2-}$ and F^- (as in the case of HCN) shows a significant deviation from the linear free-energy relation, compared to the reactions with py, N_3^-, and NCS^- ions[1d], see Fig. 6, information on this reaction would provide additional insight on the mechanism as a whole. It was consequently decided to study the effect of high pressure on the reaction with F^-.

The reaction of $[WO(OH_2)(CN)_4]^{2-}$ with F^- ions[17] is given in equation (11), which, since the pH was selected to be *ca.* 5.5–6.0, can be simplified to include only the $[WO(OH_2)(CN)_4]^{2-}$

$$[WO(OH_2)(CN)_4]^{2-} + F^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [WO(F)(CN)_4]^{3-} \quad (11)$$

ion as reactant. At pH ≈ 6, $[WO(OH_2)(CN)_4]^{2-}$ is the only tungsten(IV) complex in solution (pK_{a1} = 7.8), and the high-pressure dependence of the K_a constants of the metal complex and HF would have little effect on the concentration of the reactive species in solution. It was shown previously[17] that at $[F^-] = 0.25$ mol dm^{-3} the contribution of the reverse pathway in equation (11) (k_{-1}) is only 3% of the observed rate constant. Under these conditions, the pressure dependence of only the forward rate constant can thus be determined. The effect of high pressure on the reaction between $[WO(OH_2)(CN)_4]^{2-}$ and F^- was therefore investigated and the results are given in Table 2. A least-squares analysis of the data using the appropriate function, as reported before,[1a] yielded the volume of activation (Table 1) for this substitution process.

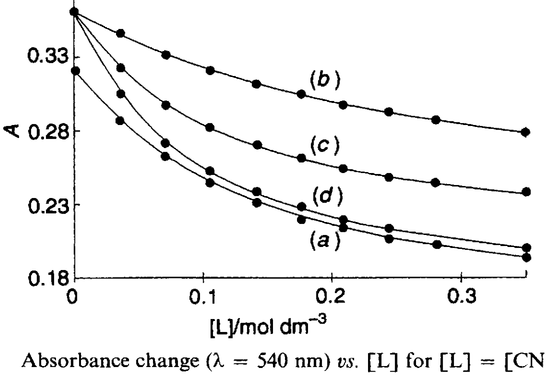


Fig. 5 Absorbance change (λ = 540 nm) *vs.* [L] for [L] = $[CN^-]_{tot}$ at pH 10.0 (*a*) and [L] = [HCN] at pH 6.0 (*b*), 6.5 (*c*) and 7.0 (*d*), at 25.0 °C, $[W^{IV}]_{tot} = 5.0 \times 10^{-3}$ mol dm^{-3} and $I = 1.0$ mol dm^{-3} (KNO_3)

Discussion

The pentacyanooxotungstate(IV) complex has been obtained previously and is well characterized, and a recent crystal structure determination showed it to be isostructural with the corresponding molybdenum(IV) complex.[14,18,19] Reactions with HCN as nucleophile were also described previously in aqueous systems containing, $[MoO(OH_2)(CN)_4]^{2-}$,[5] [Rh(tpps)$(OH_2)_2$] [H_2tpps = 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin],[7] different nickel(II) complexes,[6] aquacobalamin[8] and thallium(III) systems.[9] It was found that CN^- ions may react more rapidly than HCN,[7] but the opposite also holds true.[8] It is assumed that HCN co-ordinates to the metal centre *via* the nitrogen as has recently been crystallographically verified by the structure determination of the corresponding molybdenum(IV) complex, $[MoO(NCH)(CN)_4]^{2-}$.[5] Further evidence in support of this comes from different structure determinations such as those of $[(NH_3)_5CoNCCo(CN)_5]\cdot H_2O$[15] (indicating that CN^- can act as an ambidentate ligand, *i.e.* co-ordinate with either the carbon or nitrogen atom), $[Co(NH_3)(cacac)]Cl[ClO_4]\cdot 2H_2O$ (cacac = 3-cyanoacetylacetonate),[18] $[N(PPh_3)_2]_2[MoO(CN)_4(NCMe)]$[14] and the existence of dimeric $[(NC)_6W–NC–W(CN)_6]^-$ and trimeric $[(NC)_7W–CN–W(CN)_7–CN–W(CN)_7]^{6-}$ ions.[20]

The fact that HCN does co-ordinate in these systems poses a question regarding its behaviour once co-ordinated. According to Scheme 1, acid dissociation of the co-ordinated HCN results in an almost simultaneous isomerization to the carbon-co-ordinated cyano complex (see above). It might be anticipated

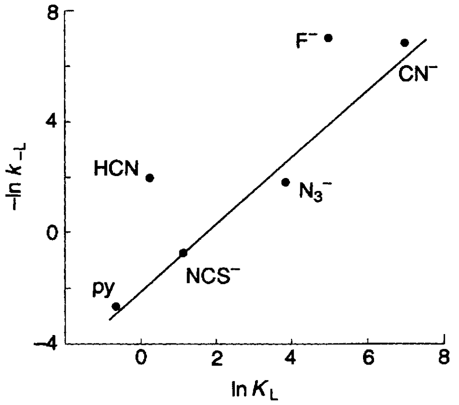


Fig. 6 Free-energy relationship between ln k_{-L} and ln K_L, for the reaction [(a) in Scheme 1] between $[WO(OH_2)(CN)_4]^{2-}$ and entering ligands L [pyridine (py), HCN, F^-, N_3^-, NCS^- and CN^- ions]

Table 2 Observed rate constant k_{obs} as a function of pressure for the reaction between $[WO(OH_2)(CN)_4]^{2-}$ and F^-, pH 5.5, I = 1.0 mol dm^{-3} (KNO_3), 13.0 °C and $[F^-]$ = 0.25 mol dm^{-3}

P/bar	k_{obs}/s^{-1}
300	$4.5(7) \times 10^{-3}$
500	$6.1(2) \times 10^{-3}$
700	$7.6(1) \times 10^{-3}$
900	$1.11(3) \times 10^{-2}$
1100	$1.43(5) \times 10^{-2}$

that the combination of this dissociation/isomerization results in a pK_a value for the co-ordinated HCN that is more acidic than that of the free acid in aqueous solution. Co-ordination of HCN *via* the nitrogen atom to an electrophilic [(hard tungsten(IV) metal centre)] moiety is expected to weaken the H–C bond, resulting in a stronger acid. As a result of higher stability constants for the $[WO(L)(CN)_4]^{n-}$ complexes compared to that of the corresponding $[MoO(L)(CN)_4]^{n-}$ ions, the stability constant for the $[WO(NCH\text{-}N)(CN)_4]^{2-}$ complex (stronger W–NCH bond) is also expected to be larger than that of the molybdenum(IV) complex. This is indeed the case, *i.e.* the pK_a value of the *N*-bonded HCN in $[MoO(NCH)(CN)_4]^{2-}$ is lower compared to that of free HCN (9.0),[8] and furthermore decreases from 7.8 to 5.8 for Mo^{IV} and W^{IV} respectively, in direct correlation with the stability constants for monosubstituted $[MO(L)(CN)_4]^{n-}$ complexes for these two metal centres.[2a]

Since the effective equilibrium constant at lower pH values is primarily governed by the pK_a value of the co-ordinated HCN [see equations (5) and (6)], the reaction yield at around these values was too low for a complete definition of the intercept *vs.* pH function [Fig. 4, equation (8)]. The reaction for the tungsten(IV) system could indeed be monitored closer to the pK_{aNCH} than for the corresponding molybdenum(IV) system (and therefore a more accurate determination of pK_{aNCH} was possible) but is still limited as a result of the rapid decrease in reaction yield at low pH.

When considering the reaction between $[WO(OH_2)(CN)_4]^{2-}$ and HCN–CN$^-$ in the present study, it is clear that the reverse rate constants (*i.e.* hydrolysis) differ by more than two orders of magnitude compared to only a five times difference in the second-order rate constant for the aqua substitution for the CN$^-$ and HCN pathways. This is in agreement with a dissociative mechanism. The five times increase in reaction rate with HCN (compared to that with CN$^-$) observed in this study might be attributed to the better association ability of HCN, being a neutral entity, and experiencing less electrostatic repulsion than the negatively charged CN$^-$ ion during the rate-determining step. Slightly increased rates were also observed for both W^{IV} (py compared to N_3^- and NCS$^-$, 6, 4.1 and 2.9 dm^3 mol^{-1} s^{-1} at 25 °C respectively) and Re^V (ref. 2) (for the neutral nucleophiles thiourea and hydrazoic acid, between 2 and 10 times larger rate constants than for the reaction with NCS$^-$) when neutral incoming nucleophiles were used.

The activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) are in general not very accurate indicators of the specific mechanism.[21] In this case even more so, since the accuracy of the k_1 (CN$^-$ path) value is linked to pK_{aHCN}, and since there is an uncertainty therein, also with respect to temperature, a similar uncertainty is introduced in the rate constant. The interpretation of the parameters with respect to the type of mechanism was therefore not attempted and is not discussed further. However, in previous studies a dissociative mechanism for the reactions between $[WO(OH_2)(CN)_4]^{2-}$ and monodentate nucleophiles, and for aqua substitution in the $[MO(OH_2)(CN)_4]^{n-}$ complexes in general, was postulated based on different experimental results. Firstly, the large *trans* influence of the oxide ligand as observed in the metal–aqua bond distance in $[MO(OH_2)(CN)_4]^{n-}$, as well as the mode of distortion (displacement of the central metal atom by 0.3 Å towards the oxo from the plane formed by the four cyano carbon atoms), will promote a dissociative activation.[1] Secondly, more convincing evidence of such an activation stems from the fact that for the reaction between $[WO(OH_2)(CN)_4]^{2-}$ and N_3^- ions a $\Delta V^\ddagger = +10.2$ cm^3 mol^{-1} was obtained. Thirdly, the free-energy relationship between K_1 and k_{-1} (Scheme 1) given in Fig. 6 suggest that the reactions with pyridine, N_3^-, NCS$^-$ and CN$^-$ ions (this study) all indeed proceed *via* a dissociative mechanism. A similar mechanism is thus anticipated for the reaction with CN$^-$–HCN.

A comparison of the two oxo complexes known to date (of W^{IV} and Mo^{IV}) which accept an HCN ligand, and that of the only known nitrido aqua complex reacting similarly, *i.e.* $[ReN(OH_2)(CN)_4]^{2-}$,[22] is possible, revealing some interesting features (see Table 3). One striking observation is that an almost linear relationship exists between both the k_2 {HCN co-ordination, *i.e.* 9, 900 and 3900 dm^3 mol^{-1} s^{-1}; formation of the *N*-bonded $[MX(NCH)(CN)_4]^{2-}$ complex} and the k_1 values {CN$^-$ co-ordination, *i.e.* 1.15, 170 and 8100 dm^3 mol^{-1} s^{-1}; formation of the $[MX(CN)_5]^{3-}$ complex} *vs.* pK_{a1} values (7.8, 9.9 and 11.5) for W^{IV}, Mo^{IV} and Re^V.[4] This is independent of oxide or nitride ligand, and depends only on the basicity of the M–X core, *i.e.* $(M{=}O)^{2+}$ or $(M{\equiv}N)^{2+}$, as manifested by the co-ordination ability of an aqua ligand *trans* thereto. These relationships are in direct agreement with a dissociative mechanism. A second interesting point is that the decrease in the pK_{aNCH} values follows the same trend as that of the pK_{a1} values of 7.8 and 9.8 for the $[MO(OH_2)(CN)_4]^{2-}$ complexes of W^{IV} and Mo^{IV} respectively. This is actually expected since a similar effect of the metal core on H_2O (as manifested in the pK_{a1} value) is anticipated for the HCN moiety.

Fig. 6 shows that the reactions of HCN and F$^-$ ions (although in general agreement when comparing the hydrolysis and anation steps) do not fit the relationship well. The reaction of HCN however is too rapid to study by high-pressure kinetics, but the activation volume of the reaction with F$^-$ can be determined (see Results section). The value of -28 cm^3 mol^{-1} obtained from the high-pressure study is unexpectedly negative and largely so, and is interpreted that in the case of F$^-$ the mechanism of activation changes to one where association plays a major part. This is not totally unexpected considering that the strong point charge of the F$^-$ ion (*i.e.* extremely strong hard base) that will favour interaction with the hard acid W^{IV}. What is however rather surprising is the magnitude of the negative activation volume, which in principle suggests that the mechanism changes to a purely associative activation. This cannot be explained at present and further research on extended systems of this type is necessary. Some evidence of association being of importance has recently been obtained for the oxygen-

Table 3 Comparative kinetic and equilibrium data for the molybdenum(IV),[5] tungsten(IV) and rhenium(V)[22] systems at 25 °C, I = 1.0 mol dm^{-3}

Constant[a]	$[WO(OH_2)(CN)_4]^{2-}$	$[MoO(OH_2)(CN)_4]^{2-}$	$[ReN(OH_2)(CN)_4]^{2-}$
pK_{a1}	7.8	9.8	11.5
K_2/dm^3 mol^{-1}	1.0	3	*b*
$k_2{}^c$/dm^3 mol^{-1} s^{-1}	9	900	3900
$k_{-2}{}^c$/s^{-1}	8	300	*b*
K_1/dm^3 mol^{-1}	1100	95	600
$k_1{}^c$/dm^3 mol^{-1} s^{-1}	1.15	170	8100
$k_{-1}{}^c$/s^{-1}	0.0011	1.8	12
pK_{aNCH}	5.8	7.6	7.5

[a] Standard deviations not reported but vary between *ca.* 5 and 10%. [b] Not determined. [c] Calculated at 25 °C.

exchange reactions in $[\mathrm{MO(OH)(CN)_4}]^{(n+1)-}$ [23] complexes and also in the molecular oxygen addition to the $[\mathrm{MO(CN)_5}]^{3-}$ complexes of molybdenum(IV) and tungsten(IV)[19]. A possibility worth considering which is in favour of the mechanism changing to an associative type stems from the fact that $\mathrm{F^-}$ is known to form strong hydrogen bonds and can in principle form a W–OH–H–F entity, resulting in an effective increase in the $\mathrm{W{-}OH_2}$ bond strength and the formation of a complex which very much resembles $[\mathrm{MO(OH)(CN)_4}]^{(n+1)-}$,[17,23] undergoing substitution *via* an associative type of mechanism. If dissociation is limited, as mentioned above, it is expected that association might become important since the 16-electron metal complex will be susceptible to additional nucleophilic attack. Examples of complexes with increased co-ordination number for these metal centres are the well-known $[\mathrm{W(CN)_8}]^{4-}$ and $[\mathrm{Mo(CN)_8}]^{4-}$,[1] rendering associative mechanisms in these systems very probable. Further mechanistic studies which include detailed high-pressure kinetic investigations on a variety of nucleophiles and all the metal centres of these types of complexes is currently in progress to clarify and correlate the mechanism as a function of all relevant parameters.

Acknowledgements

Financial support by the South African Foundation for Research and Development and the Research Fund of the University of the Orange Free State is gratefully acknowledged.

References

1 (*a*) J. G. Leipoldt, S. S. Basson and A. Roodt, *Adv. Inorg. Chem.*, 1993, **40**, 241; (*b*) J. G. Leipoldt, S. S. Basson, A. Roodt and W. Purcell, *Polyhedron Report Number 44*, 1992, **11**, 2277; (*c*) A. Roodt, J. G. Leipoldt, E. A. Deutsch and J. C. Sullivan, *Inorg. Chem.*, 1992, **31**, 1080; (*d*) A. Roodt, J. G. Leipoldt, S. S. Basson and I. M. Potgieter, *Transition Met. Chem.*, 1988, **13**, 336; (*e*) A. Roodt, J. G. Leipoldt, S. S. Basson and I. M. Potgieter, *Transition Met. Chem.*, 1990, **15**, 439; (*f*) I. M. Potgieter, S. S. Basson, A. Roodt and J. G. Leipoldt, *Transition Met. Chem.*, 1988, **13**, 209; (*g*) W. Purcell, A. Roodt, S. S. Basson and J. G. Leipoldt, *Transition Met. Chem.*, 1989, **14**, 224; (*h*) W. Purcell, A. Roodt, S. S. Basson and J. G. Leipoldt, *Transition Met. Chem.*, 1989, **14**, 369; (*i*) W. Purcell, A. Roodt and J. G. Leipoldt, *Transition Met. Chem.*, 1991, **16**, 339.

2 (*a*) A. Roodt, S. S. Basson and J. G. Leipoldt, *Polyhedron*, 1994, **13**, 509; (*b*) I. M. Potgieter, S. S. Basson, A. Roodt and J. G. Leipoldt, *Inorg. Chem.*, 1987, **26**, 57; (*c*) A. Samotus, A. Kanas, W. Glug and J. Szklarzewicz, *Transition Met. Chem.*, 1991, **16**, 614.

3 A. Roodt, J. G. Leipoldt, L. Helm and A. E. Merbach, *Inorg. Chem.*, 1992, **31**, 2864.

4 A. Roodt, J. G. Leipoldt, L. Helm and A. E. Merbach, *Inorg. Chem.*, 1994, **33**, 140.

5 J. P. Smit, W. Purcell, A. Roodt and J. G. Leipoldt, *Polyhedron*, 1993, **12**, 2271; *J. Chem. Soc., Chem. Commun.*, 1993, 1389.

6 G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, 1968, **7**, 2230; 1969, **8**, 1125; E. J. Billo, *Inorg. Chem.*, 1973, **12**, 2783.

7 P. Hambright and R. Langley, *Inorg. Chim. Acta*, 1987, **137**, 209.

8 W. W. Reenstra and W. P. Jencks, *J. Am. Chem. Soc.*, 1979, **101**, 5780.

9 G. Batta, I. Bányai and J. Glazer, *J. Am. Chem. Soc.*, 1993, **115**, 6782.

10 J. G. Leipoldt, S. S. Basson, A. Roodt and I. M. Potgieter, *Transition Met. Chem.*, 1986, **11** 323.

11 D. Dobos, *Electrochemical Data*, Elsevier, London, 1975, ch. 3, p. 105.

12 W. Purcell, A. Roodt and J. G. Leipoldt, *Transition Met. Chem.*, 1991, **17**, 339.

13 J. H. Epenson and J. P. Birk, *J. Am. Chem. Soc.*, 1965, **87**, 3280; J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, 1965, **87**, 3002.

14 H. Arzoumanian, M. Pierrot, F. Ridouane and J. Sanchez, *Transition Met. Chem.*, 1991, **16**, 422.

15 B.-C. Wang, W. P. Schaefer and R. E. Marsh, *Inorg. Chem.*, 1971, **10**, 1492.

16 R. J. Balahura, G. Ferguson, A. Johnson and G. L. Ruhl, *Polyhedron*, 1986, **5**, 2075.

17 J. G. Leipoldt, S. S. Basson, A. Roodt and I. M. Potgieter, *S. Afr. J. Chem.*, 1986, **39**, 179.

18 K. Wieghardt, G. Backes-Dahman, W. Holzbach, W. J. Swiridoff and J. Z. Weiss, *Z. Anorg. Allg. Chem.*, 1983, **499**, 44.

19 J. P. Smit, A. Roodt, W. Purcell, J. G. Leipoldt, A. Oscarsson and L. I. Elding, unpublished work.

20 B. Sieklucka, R. Dziembaj and S. Witkowski, *Inorg. Chim. Acta*, 1991, **187**, 5.

21 J. G. Leipoldt, W. Purcell and H. Meyer, *Polyhedron*, 1991, **10**, 1379.

22 L. J. Damoense, W. Purcell and J. G. Leipoldt, *Transition Met. Chem.*, 1994, **19**, 619.

23 A. Roodt, J. G. Leipoldt, L. Helm, A. Abou-Hamdan and A. E. Merbach, *Inorg. Chem.*, in the press.

Received 23*rd August* 1994; *Paper* 4/05144K