Nitrosyl–Nitrite Interconversion in Pentacyanoruthenate(II) Complexes

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The nucleophilic addition of OH^- to $[Ru(CN)_5(NO)]^{2-}$ leads to the *N*-bonded pentacyanonitroruthenate(II) ion ($\lambda_{max} = 320$ nm, $\varepsilon = 3850$ dm^3 mol^{-1} cm^{-1}). The stoichiometry is 2:1 ($[OH^-]:[Ru]$) and the equilibrium formation constant is 4.4×10^6 dm^6 mol^{-2} (25 °C, $I = 1$ mol dm^{-3}). A kinetic study of the forward reaction showed that it is first order in the concentration of each reactant, with $k = 0.95$ dm^3 mol^{-1} s^{-1} (25 °C, $I = 1$ mol dm^{-3}), $\Delta H^\ddagger = 57.3 \pm 3.3$ kJ mol^{-1} and $\Delta S^\ddagger = -54.0 \pm 4.5$ J K^{-1} mol^{-1}. The mechanism involves two consecutive attacks by OH^-, the first being rate determining. The reaction product decays by an aquation process, leading to $[Ru(CN)_5(H_2O)]^{3-}$ and free NO_2^-. The rate constant for the dissociation reaction of $[Ru(CN)_5(NO_2)]^{4-}$ is $k_{-N} = 2.00 \times 10^{-4}$ s^{-1} (25 °C, $I = 1$ mol dm^{-3}). In the formation reaction, both nitrite (*O*-bound) and nitro (*N*-bound) linkage isomers are formed, with k_O and k_N being 0.23 and 0.15 dm^3 mol^{-1} s^{-1} respectively (25 °C, $I = 1$ mol dm^{-3}). The *O*-bound isomer isomerizes slowly to the thermodynamically more stable *N*-bound isomer. The kinetic and thermodynamic parameters have been analysed by comparison with the chemistry of the complexes $[Fe(CN)_5(NO)]^{2-}$ and $[Fe(CN)_5(NO_2)]^{4-}$.

Transition-metal nitrosyl complexes have been thoroughly studied from the structural point of view.[1] The strength of the M–NO bond accounts for the general lack of reactivity towards ligand interchange in these complexes. In contrast, the electrophilic reactivity of co-ordinated NO with different nucleophiles is well recognized and has been widely explored.[2–4]

One of the best studied among these addition reactions is the attack of OH^- on the $[Fe(CN)_5(NO)]^{2-}$ ion, forming the pentacyanonitroferrate(II) ion.[5,6] Other six-co-ordinated complexes of Ru^{II} and Os^{II} containing the nitrosyl ligand behave in a similar way, although kinetic data are not available.[3,4] A preliminary test showed that the $[Ru(CN)_5(NO)]^{2-}$ ion reacted with OH^-.[7]

A kinetic and equilibrium study of the addition reaction of OH^- to $[Ru(CN)_5(NO)]^{2-}$ is reported here. The rates of both the dissociation and formation reactions of the pentacyanonitroruthenate(II) ion were also measured. The importance of acid–base equilibria in co-ordinated NO^+–NO_2^- systems has been emphasized,[8] as far as they provide the initial stage for the reductive ($6e^-$) process in which NO^+ can be converted into NH_3 (model for the nitritoreductase enzyme).

Experimental

The complex $Na_2[Ru(CN)_5(NO)]\cdot 2H_2O$ was obtained as described previously.[7] Doubly distilled water, previously degassed by argon flushing, was employed. Other chemicals were of analytical grade. The electronic spectra, equilibrium and kinetic measurements were obtained with a Shimadzu UV-210A spectrophotometer.

In the study of the addition reaction (1), the solutions contained an initial concentration of $[Ru(CN)_5(NO)]^{2-}$ of *ca.* 1×10^{-4} mol dm^{-3} and an excess of free nitrite ion (3×10^{-2} mol dm^{-3}), with I up to 1 mol dm^{-3} (KCl). The pH of the medium was adjusted for each experiment by diluting standard solutions of NaOH. The absorption coefficient of the $[Ru(CN)_5(NO_2)]^{4-}$ ion, ε_{RuNO_2}, was obtained by measuring the absorption at 320 nm at pH > 12.5, at which equilibrium (1) is totally shifted to the right.

Table 1 Absorption coefficients (ε)[a] from mixtures of $[Ru(CN)_5(NO)]^{2-}$ and $[Ru(CN)_5(NO_2)]^{4-}$ at different $[OH^-]$, 25.0 °C, $I = 1$ mol dm^{-3} (NaCl) and $[NO_2^-] = 5 \times 10^{-3}$ mol dm^{-3}

$10^5[Ru]$	$10^4[OH^-]$		
mol dm^{-3}		ε/dm^3 mol^{-1} cm^{-1}	$10^4(\varepsilon_{RuNO_2} - \varepsilon)[OH^-]^2$ [b]/ mol dm^{-3} cm^{-1}
8.3	1.9	570	1.1
8.3	5.4	2200	4.7
6.6	7.2	2650	6.3
5.8	9.5	3103	6.8
5.6	13.0	3393	7.6

[a] Measured at λ = 320 nm. [b] See text for explanation of the calculation procedure.

$$[Ru(CN)_5(NO)]^{2-} + 2\,OH^- \overset{K_1}{\rightleftharpoons} [Ru(CN)_5(NO_2)]^{4-} + H_2O \quad (1)$$

For the determination of the equilibrium constant, K_1, measurements were made at different pH values and total ruthenium concentrations, as detailed in Table 1. A graphical computational procedure was employed,[9] K_1 being determined from the slope of ε *vs.* $(\varepsilon_{RuNO_2} - \varepsilon)[OH^-]^2$, where ε is the apparent absorption coefficient of each mixture; K_1 is in fact an equilibrium quotient, which uses concentrations instead of

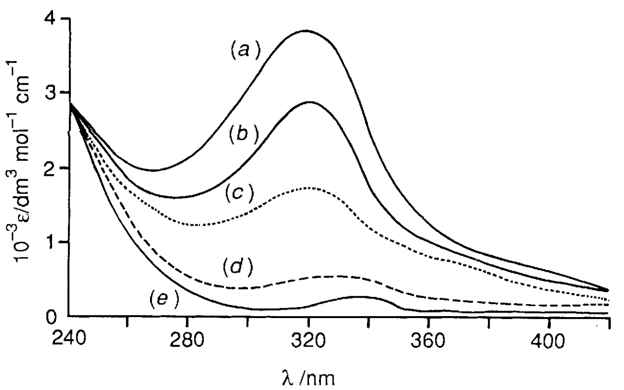

Fig. 1 Electronic spectra of $[Ru(CN)_5(NO_2)]^{4-}$ at pH 13.0 (*a*) and $[Ru(CN)_5(NO)]^{2-}$ at pH 7.0 (*e*). Spectra (*b*), (*c*) and (*d*) show different mixtures of both ions at intermediate pH 11.0, 10.5 and 9.8, respectively. $[Ru]_{total} = 5 \times 10^{-5}$, $I = 1$ mol dm^{-3} (KCl). The optical and reference cell contained nitrite solutions (5×10^{-3} mol dm^{-3})

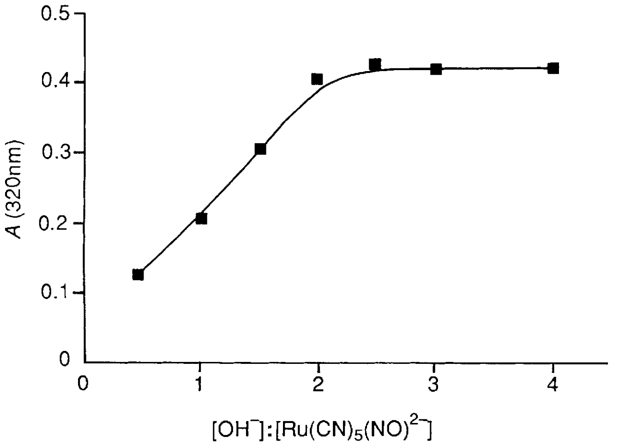

Fig. 2 Plot of absorbance at 320 nm against the mole ratio $[OH^-]:[Ru(CN)_5(NO)^{2-}]$ at $I = 1.0$ mol dm^{-3} (KCl)

activities. For the sake of reasonable comparisons, the experimental conditions (particularly the ionic strength) were kept identical with those used in the previous work[5] with $[Fe(CN)_5(NO)]^{2-}$. We also checked our own data for the latter system and excellent agreement was obtained with Swinehart's reported value for K_1.[5] The kinetics of the addition reaction was studied by measuring the increase in absorbance of the product in the range pH 11.4–13.0 (25 °C). From measurements at different temperatures (10–40 °C), pH 11.5, the activation parameters were calculated through Eyring plots and least-squares treatment of the data. In all of the experiments, pseudo-first-order conditions were used and good linear traces (up to three half-lives) were obtained by plotting $\ln(A_\infty - A_t)$ *vs.* t, where A_t is the absorbance at 320 nm. The second-order rate constant at 25 °C was computed from the slope of the linear plot of k_{exptl} *vs.* $[OH^-]$ [see data in Table 2(*a*)].

The equilibrium constant for reaction (2), K_2^N, was calculated by performing independent kinetic experiments leading to k_N and k_{-N} values for the formation and dissociation reactions of the *N*-bonded isomer, respectively. The value of k_N was obtained by first measuring the increase in absorbance at 320 nm, after mixing solutions of the $[Ru(CN)_5(H_2O)]^{3-}$ ion[10,11] (5×10^{-4} mol dm^{-3}) with solutions of the nitrite ion [(2–10) $\times 10^{-3}$ mol dm^{-3}] at pH 12.0, 25.0 °C and $I = 1$ mol dm^{-3}. The treatment of the data [Table 2(*b*)] was the same as described for the addition reaction. The second-order rate constant so obtained, k_{2nd}, reflects the formation of a mixture of *N*- and *O*-bonded isomers (see below), *i.e.* $k_{2nd} = k_N + k_O$; if the fraction of each isomer formed, f_N or f_O, is known, individual values for k_N and k_O can be calculated, as $k_N = (k_N + k_O)f_N$. As will be shown later, f_N can be estimated from the dissociation rate experiments. The value of k_{-N} was obtained from two kinds of independent experiments. In the first, the $[Ru(CN)_5(NO_2)]^{4-}$ ion was formed by mixing $[Ru(CN)_5(NO)]^{2-}$ with OH^- (pH 12.5); when the addition reaction had gone to completion, 0.5 mol dm^{-3} pyrazine (pyz) was added and the increase in absorbance at 370 nm {maximum for the $[Ru(CN)_5(pyz)]^{3-}$ ion}[10] was measured at 25.0 °C. Pseudo-first-order rate constants, k_{exptl}, were obtained as described above. In dissociation-rate studies with $[M(CN)_5L]^{n-}$ complexes, a non-linear dependence of k_{exptl} on the 'scavenger' ligand concentration is usually found; for sufficiently high values of the latter, kinetic saturation is attained and k_{exptl} reaches a constant value; this can be equated to k_{-L}, the dissociation rate constant for the ligand L.[11] Our results (L = *N*-bonded NO_2^-) agree with the general picture, pyrazine acting as the scavenger ligand for the $[Ru(CN)_5(H_2O)]^{3-}$ intermediate. In the second procedure, $[Ru(CN)_5(NO_2)]^{4-}$ was formed after the reaction of $[Ru(CN)_5(H_2O)]^{3-}$ (*ca.* 10^{-4} mol dm^{-3}) with NO_2^- (5×10^{-3} mol dm^{-3}); pyrazine was added to the latter solution and the kinetics was followed at 370 nm, as in the previous experiment. Three runs were performed by varying the delay time of addition of pyz after the mixing of the $[Ru(CN)_5(H_2O)]^{3-}$ and NO_2^- solutions. The first run was done 30 min after mixing (*i.e.* the estimated time for completion of the formation reaction) and two additional runs were done with delay times of 1 and 4 h. For all three runs the plots of $\ln(A_\infty - A_t)$ *vs.* t were curved, suggesting the onset of two processes with different time-scales. A good linear behaviour was obtained for times higher than about 10 min, with k_{exptl} having the same value as obtained in the experiment corresponding to the dissociation of $[Ru(CN)_5(NO_2)]^{4-}$ (previously formed by way of the addition reaction). By extrapolating data from the above mentioned linear region to zero time, an estimation of the concentration of initial Ru^{II} which generated the slower process was obtained. Thus, the concentration of initial Ru^{II} which reacted with pyz at a higher rate could also be estimated. These calculations showed that the fraction of slowly reacting Ru^{II} relative to the total initial Ru^{II} increased with increasing delay time in the addition of pyz to the mixture of $[Ru(CN)_5(H_2O)]^{2-} + NO_2^-$.

The nature of the products present in the solution at different times after mixing $[Ru(CN)_5(H_2O)]^{3-}$ with NO_2^- was investigated by inducing the formation of precipitates through addition of a nickel(II) salt. The precipitates were isolated and dried, and IR spectra obtained in KBr disks, on a Perkin-Elmer 580B instrument, for freshly prepared (precipitated 30 min after mixing) and aged samples (24 h).

Results and Discussion

When solutions of $[Ru(CN)_5(NO)]^{2-}$ are made alkaline (pH > 10) a product absorbing at 320 nm is observed (Fig. 1); the transformation is reversible when HCl is added to pH 6–7. A spectrophotometric titration shows that the stoichiometry of the reaction corresponds to a 1:2 ratio for $[Ru(CN)_5(NO)]^{2-}$: OH^-, as shown by the plot in Fig. 2. From the position and intensity (ε = 3850 dm^3 mol^{-1} cm^{-1}) of the band, as well as from comparisons with reactions of other nitrosyl complexes,[5,6] the process is described by equation (1). The position of the absorbance maximum for the pentacyanonitroruthenate(II) ion is shifted to higher energy, as compared to $[Fe(CN)_5(NO_2)]^{4-}$ and $[Ru(NH_3)_5(NO_2)]^{+}$,[5,12] in agreement with the behaviour of other $[Ru(CN)_5L]^{n-}$ complexes.[10,13] This similarity and the intensity of the bands suggest a 'metal-to-ligand' charge-transfer (m.l.c.t.) transition. As in $[Fe(CN)_5(NO)_2]^{4-}$,[14] the *N*-bound nitrite isomer is proposed to be the product of reaction (1).

The $[Ru(CN)_5(NO_2)]^{4-}$ ion is not stable; a slow decay of the band at 320 nm (*k ca.* 10^{-4} s^{-1}, 25 °C) is observed, with final

Table 2 Experimental pseudo-first-order rate constants at 25 °C and I = 1 mol dm^{-3} (KCl)

(*a*) Addition reaction (1)^a		(*b*) Formation reaction of the isomer mixture (5)^b	
$10^4 k_{exptl}$/s^{-1}	10^4[OH$^-$]/mol dm^{-3}	$10^3 k_{exptl}$/s^{-1}	10^3[NO$_2^-$]/mol dm^{-3}
0.2	0.2	0.90	2.5
1.0	1.0	1.92	5.0
3.1	2.8	2.85	7.5
6.2	6.3	3.78	10.0
9.2	8.8		

^{a} $[Ru(CN)_5(NO)]^{2-} = 1 \times 10^{-4}$, $[NO_2^-] = 3 \times 10^{-2}$ mol dm^{-3}. ^{b} $[Ru(CN)_5(H_2O)]^{3-} = 5 \times 10^{-4}$ mol dm^{-3}, pH 12.0.

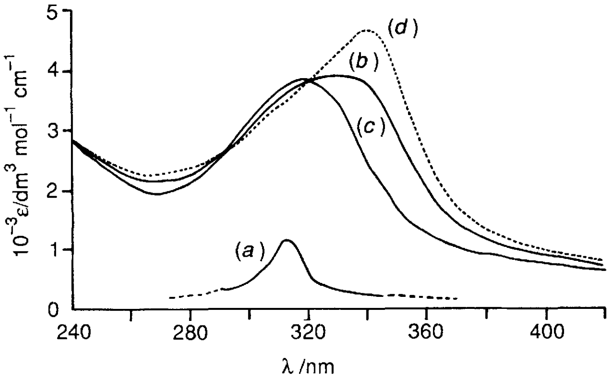

Fig. 3 Electronic spectra of (*a*) $[Ru(CN)_5(H_2O)]^{3-}$, (*b*) the mixture obtained at the end of the rapid reaction of $[Ru(CN)_5(H_2O)]^{3-}$ with excess of NO_2^-, (*c*) the final stable product obtained 24 h after mixing the reactants, assigned as $[Ru(CN)_5(NO_2)]^{4-}$, and (*d*) calculated spectrum of $[Ru(CN)_5(ONO)]^{4-}$ (see text)

peaks appearing at 306 and 280 nm. The stability is greatly enhanced if reaction (1) is carried out in the presence of excess of nitrite ion. These observations suggest that an additional equilibrium (2) must be taken into account. The spectral

$$[Ru(CN)_5(NO_2)]^{4-} + H_2O \underset{k_N}{\overset{k_{-N}}{\rightleftharpoons}} [Ru(CN)_5(H_2O)]^{3-} + NO_2^- \quad (2)$$

changes in the spontaneously decaying solutions are consistent with the formation of $[Ru(CN)_5(H_2O)]^{3-}$;[7,10] free NO_2^- was also detected by means of Ilosva's test.[15] As will be shown later, k_{-N} and k_N could be determined under suitable conditions.

The equilibrium constant for reaction (1) was 4.4 × 10^6 dm^6 mol^{-2} (25 °C, I = 1 mol dm^{-3}, KCl) slightly higher than that found for the similar reaction with pentacyanoferrate(II), 1.5 × 10^6 dm^6 mol^{-2}.[5] It is however significantly lower than the values found for OH$^-$ addition to $[Ru(bipy)_2Cl(NO)]^{2+}$, (bipy = 2,2′-bipyridine), $[Os(terpy)(bipy)(NO)]^{3+}$ (terpy = 2,2′:6′,2″-terpyridine) and $[Ru(terpy)(bipy)(NO)]^{3+}$ (1.6 × 10^9, 7.0 × 10^{10} and 2.1 × 10^{23} dm^6 mol^{-2} respectively).[16] In the latter systems, if we compare with pentacyanonitrosylmetalates, the π-back bonding from the metal to NO (and thus, the electron density at N) are lower; a higher affinity is expected therefore for the formation of the respective nitro-complexes (see below).

Kinetic Analysis of the Addition Reaction (1).—The forward reaction (1) is first order in the concentration of each of the reactants [Table 2(*a*)]. The same rate law was found with $[Fe(CN)_5(NO)]^{2-}$,[5,6] and thus the mechanism in equations (3)

$$[Ru(CN)_5(NO)]^{2-} + OH^- \overset{k_3}{\rightleftharpoons} [Ru(CN)_5(NO_2H)]^{3-} \quad (3)$$

$$[Ru(CN)_5(NO_2H)]^{3-} + OH^- \overset{k_4}{\rightleftharpoons} [Ru(CN)_5(NO_2)]^{4-} + H_2O \quad (4)$$

and (4) can be postulated, the first step (3) being rate-determining. The value of k_3 is 0.95 dm^3 mol^{-1} s^{-1} (25.0 °C, I = 1 mol dm^{-3}, KCl). Activation parameters for (3) ($\Delta H_3^\ddagger$ = 57.3 ± 3.3 kJ mol^{-1}, $\Delta S_3^\ddagger$ = −54.0 ± 4.5 J K^{-1} mol^{-1}) compare reasonably well with values for the reaction of $[Fe(CN)_5(NO)]^{2-}$ with OH$^-$. The value of k_3 for the latter reaction was 0.55 dm^3 mol^{-1} s^{-1}.[5] The comparison of k_3 for both pentacyanonitrosylmetalates parallels the previously shown trend for K_1, *i.e.* the higher affinity for reaction (1), compared to the similar reaction for the iron compound, appears to be mainly determined by the higher electrophilic reactivity of the {Ru–NO} moiety. The nucleophilic attack of hydrazine on $[Ru(CN)_5(NO)]^{2-}$ is also slightly faster.[17]

The higher value of k_3 for $[Ru(CN)_5(NO)]^{2-}$ is rather unexpected if a correlation of k_3 with the NO stretching frequency is assumed to hold. As pointed out by Bottomley,[2] nitrosyl complexes with high ν_{NO} will have the lowest electron density at the N atom and may behave as electrophiles; this is certainly the case for a group of complexes with ν_{NO} ranging from *ca.* 1860 to 2000 cm^{-1},[2] including both pentacyanonitrosylmetalates (ν_{NO} 1945, Fe; 1926 cm^{-1}, Ru).[7] The electrophilic reactivity of coordinated NO$^+$ seems to be mainly influenced by the back-bonding ability of the metal centre towards NO$^+$, which in turn depends on the bonding properties of other ligands in the coordination sphere (see above); however, when comparing two complexes with very similar electronic structure, and only minor differences in k_3 and ν_{NO}, we should hardly expect a strict correlation between these parameters. Other factors probably influence the nucleophilic reactivity of OH$^-$; the higher k_3 value for $[Ru(CN)_5(NO)]^{2-}$ may be related to the softer character of the ruthenium complex[10] (London forces and polarizability effects contribute positively to the nucleophilic rates).[18] The higher radius[7] (and lower charge density) of the $[Ru(CN)_5(NO)]^{2-}$ ion could also favour a higher rate for the OH$^-$ addition. Unfortunately, no kinetic data are available for the reaction of $[Ru(NH_3)_5(NO)]^{3+}$ with OH$^-$; the $[Ru(NH_3)_5(NO_2)]^+$ is formed by two parallel pathways, that involving deprotonation of ammonia being predominant.[12]

Kinetic Analysis of the Formation and Dissociation Reactions (2) *of the Pentacyano-nitro- and -nitrito-ruthenate*(II) *Ion.*—When the $[Ru(CN)_5(H_2O)]^{3-}$ ion [Fig. 3(*a*)] is mixed with excess of nitrite ion a broad band develops, centred at *ca.* 330 nm [spectrum (*b*)]; the rate of this process is first order in the concentration of each of the reactants, and a second-order rate constant, k_{exptl} = 0.38 dm^3 mol^{-1} s^{-1} [25.0 °C, I = 1 mol dm^{-3}, see Table 2(*b*)] was calculated. For longer time spans, the band at 330 nm shifts gradually to a new band at 320 nm, with nearly equal intensity [spectrum (*c*)]. The position and intensity of the latter band are exactly the same as those obtained with the product of reaction (1). Moreover, the rate of the slow process is not dependent on the nitrite concentration. The results can be explained according to reaction (5), with formation of a mixture

$$[Ru(CN)_5(H_2O)]^{3-} + NO_2^- \xrightarrow[-H_2O]{k_{exptl}} f_N[Ru(CN)_5(NO_2)]^{4-} + f_O[Ru(CN)_5(ONO)]^{4-} \quad (5)$$

of *N*-bonded (nitro) and *O*-bonded (nitrito) isomers. A similar process, followed by a slower isomerization reaction, has recently been studied by mixing $[Ru(CN)_5(H_2O)]^{3-}$ with 4- or 3-cyanopyridine;[19] the rapid formation of the mixture of *N*-bound pyridine and -nitrile isomers is followed by the slower conversion of the latter into the more thermodynamically stable *N*-pyridine isomer. In the present case, the electronic spectral

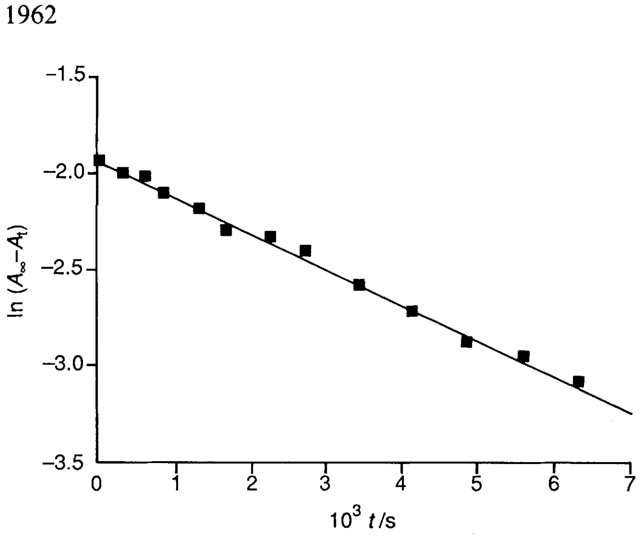

Fig. 4 Plot of $\ln(A_\infty - A_t)$ against time for the dissociation reaction of $[Ru(CN)_5(NO_2)]^{4-}$ at pH 12.5, [pyz] = 0.5 mol dm^{-3} (KCl), and 25.0 °C. The ion $[Ru(CN)_5(NO_2)]^{4-}$ was generated from $[Ru(CN)_5(NO)]^{2-}$ + OH^-

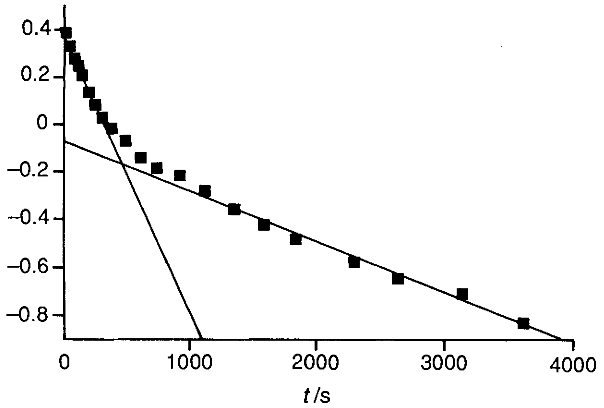

Fig. 5 Plot of $\ln(A_\infty - A_t)$ against time for the dissociation of the mixture of isomers obtained after mixing $[Ru(CN)_5(H_2O)]^{3-}$ (1.0×10^{-4} mol dm^{-3}) and NO_2^- (5.0×10^{-3} mol dm^{-3}) (see Experimental section) at [pyz] = 0.5 mol dm^{-3}, I = 1 mol dm^{-3} (KCl) and 25.0 °C

evidence strongly suggests that the nitro-isomer is the final stable product.*

Direct evidence for the isomerization reaction was obtained through IR measurements (see Experimental section); in addition to characteristic peaks at 2090 and 550 cm^{-1} (C–N and Ru–C stretching respectively), well defined absorptions were found in three different regions, namely at 1470–1400, 1100 and 835 cm^{-1}. While the intensity of the bands at 1470–1400 and 835 cm^{-1} increases for the aged sample, the band at 1100 cm^{-1} decreases. This is entirely consistent with previous results and interpretation of the nitrito–nitro isomerization reaction for pentaamminecobalt(III) complexes.[20] The first group of bands is assigned to ν_{asym}- + ν_{sym}-(NO_2), although $\nu_{N=O}$(ONO) is also expected in this region; the increase in intensity is however consistent with the nitrito–nitro conversion, because the absorption coefficient of $\nu_{asym}(NO_2)$ is higher than that of $\nu_{N=O}$(ONO). The bands at 1100 and 835 cm^{-1} are characteristic of ν_{N-O}(ONO) and $\delta(NO_2)$ absorptions, respectively, and therefore their decrease and increase are also good evidence for the proposed isomerization process. We do not have any direct evidence for the mechanism of the latter; while an intramolecular process has been postulated in the cobalt(III) system,[21] an intermolecular path seems to be involved in the isomerization of nitrile-bound cyanopyridine (CN-py) in $[Fe(CN)_5(CN\text{-}py)]^{3-}$ [22] and $[Ru(CN)_5(CN\text{-}py)]^{3-}$ [18] complexes.

The calculated values for k_N and k_O (individual formation rate constants for each isomer) were 0.15 and 0.23 dm^3 mol^{-1} s^{-1}, respectively. A similar value was found for the entry of a mononegatively charged ligand, the nicotinate ion, into $[Ru(CN)_5(H_2O)]^{3-}$.[11] The formation reactions in $[Fe^{II}(CN)_5L]^{n-}$ and $[Ru^{II}(CN)_5L]^{n-}$ systems are usually interpreted in terms of an ion-pair dissociative interchange mechanism[11] [equations (6) and (7)]. Accordingly, k_{exptl}, the second-order experimental

$$[Ru(CN)_5(H_2O)]^{3-} + L \xrightleftharpoons{K_{ip}} \{[Ru(CN)_5(H_2O)]^{3-}, L\} \quad (6)$$

$$\{[Ru(CN)_5(H_2O)]^{3-}, L\} \underset{k_{H_2O}}{\overset{k_{-H_2O}}{\rightleftharpoons}} [Ru(CN)_5L]^{3-} + H_2O \quad (7)$$

rate constant, is sensitive to the charge of the ligand L through the value of the ion-pair equilibrium constant, K_{ip}. In this mechanism, $k_{exptl} = K_{ip}k_{-H_2O}/(1 + K_{ip}k_{-H_2O})$; if $K_{ip}k_{-H_2O} \ll 1$, a simplified relation holds, $k_{exptl} = K_{ip}k_{-H_2O}$, where k_{-H_2O}, the rate of loss of water from the metal centre in the ion pair, is roughly independent of the type (and charge) of the ligand L. Higher values for k_{exptl} have been measured in formation reactions of $[Ru(CN)_5L]^{n-}$ complexes with neutral and monopositive ligands L, if compared with negatively charged ones.[11]

The values of k_N and k_O are of the same order as the value previously quoted for the iron complex (0.46 dm^3 mol^{-1} s^{-1}),[5] a striking result because formation reactions of $[Ru(CN)_5L]^{n-}$ complexes are known to be significantly slower than those of the iron(II) analogues.[11] A more reasonable value of k_2 = 42 dm^3 mol^{-1} s^{-1} was obtained later by Asperger and co-workers[23] for the formation of $[Fe(CN)_5(NO_2)]^{4-}$, in good correspondence with the presently reported value for the ruthenium analogue.

The dissociation of the nitro-ligand from the $[Ru(CN)_5(NO_2)]^{4-}$ ion was studied as in previous work with related systems.[11] The value of k_{-N} was found to be 2.00×10^{-4} s^{-1} (25.0 °C, I = 1 mol dm^{-3}) when $[Ru(CN)_5(NO_2)]^{4-}$ had been generated through the addition reaction (see Fig. 4); this value is consistent with $k_{-NO_2} = 7.7 \times 10^{-3}$ s^{-1} for the $[Fe(CN)_5(NO_2)]^{4-}$ ion;[5] k_{-L} values from a series of $[Ru(CN)_5L]^{n-}$ complexes are about 20–30 times lower than the corresponding values for $[Fe(CN)_5L]^{n-}$ ions, as discussed elsewhere.[11] In both $M(CN)_5L$ series, k_{-NO_2} shows an intermediate value between k_{-NH_3} and k_{-pyz}.[13] The higher value for k_{-NH_3} is related to the absence of π interactions in the Ru–N bond; this is in contrast with the accepted bonding picture of Ru^{II} with pyz.[10,11] We conclude that some degree of π interaction exists between Ru^{II} and the π-antibonding orbital associated with the N-bound nitro-ligand.

As pointed out in the Experimental section, a biphasic plot was obtained in the dissociation kinetic study when the $[Ru(CN)_5(NO_2)]^{4-}$ ion was generated from the reaction of $[Ru(CN)_5(H_2O)]^{3-}$ with nitrite (Fig. 5). Upon addition of pyrazine, the more rapid process (k *ca.* 10^{-3} s^{-1}) seems to reflect the decay of the $[Ru(CN)_5(ONO)]^{3-}$ O-bound isomer, while the lower value of k, 2.00×10^{-4} s^{-1}, corresponds to the dissociation of the N-bound isomer (see above). When pyrazine is added 30 min after mixing $[Ru(CN)_5(H_2O)]^{3-}$ and NO_2^- (see Experimental section), the rapidly decaying product accounts for about 60% of total Ru^{II}, close to the value expected on statistical grounds. Moreover, when pyrazine is added 1 and 4 h after the formation of the mixture, f_O decreases to 40 and 29%, respectively. This is further evidence that the proposed nitrito–nitro isomerization process is taking place, as in the $[Co(NH_3)_5(NO_2)]^{2+}$ system.[21]

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* From data obtained through spectra (*b*) and (*c*), the spectrum of the pure $[Ru(CN)_5(ONO)]^{4-}$ isomer could be calculated [spectrum (*d*)], since the fraction of each isomer was determined independently. The shift to lower energy for O- *vs.* N-bound nitrite is reasonable if the bands are assigned to d–d transitions; however, a m.l.c.t. character may be present from intensity considerations in both cases. The shift is still understandable if a higher electron affinity is assumed for the O- compared to the N-bound ligand.

The value of the equilibrium formation constant for reaction (2), $K_2^N = k_N/k_{-N} = 7.5 \times 10^2$ dm^3 mol^{-1} (25.0 °C, I = 1 mol dm^{-3}) can be compared with the values previously found for other $[Ru(CN)_5L]^{n-}$ and $[Fe(CN)_5L]^{n-}$ complexes.[11] The negative charge and poor π-acceptor ability of the nitro-ligand contribute to a low stability of the pentacyanonitroruthenate ion; if compared, for instance, with other uncharged and stronger π acceptors, such as substituted pyridine and pyrazine ligands. From the estimated values for k_O and k_{-O}, K_2^O attains an even lower value, 2.3×10^2 mol^{-1} dm^3, giving sense to the isomerization reaction. The lower stability for the nitrito-isomer stems mainly from its higher rate of dissociation, k_{-O}, compared to that for the nitro-isomer; *O*-bonded ligands are known to dissociate faster than *N*-bonded ligands {*cf.* H_2O *vs.* NH_3 in $[M(CN)_5L]^{n-}$ complexes[13]}; thus, a lower σ-bonding strength accounts for the higher rate of dissociation of the nitrito-isomer. In addition, a lower extent of π interaction could also be postulated for the latter compound.

Equilibrium (2) is also affected by further thermal decomposition of $[Ru(CN)_5(H_2O)]^{3-}$, leading most probably to $[Ru(CN)_6]^{4-}$ and Ru^{2+}(aq) ions.[11]

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