Cyanide Exchange on $Tl(CN)_4^-$ in Aqueous Solution Studied by ^{205}Tl and ^{13}C NMR Spectroscopy

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Dynamics of cyanide exchange between $Tl(^{13}CN)_4^-$ and $^{13}CN^-$ was studied by means ^{205}Tl and ^{13}C NMR. The rate law consists of two parts: $w = k_{CN}[Tl(CN)_4^-][CN^-] + k_{OH}[Tl(CN)_4^-][CN^-][OH^-]$ with $k_{CN} = 9.7(\pm0.4) \times 10^6$ $\text{M}^{-1}\text{s}^{-1}$ and $k_{OH} = 5.4(\pm0.4) \times 10^{10}$ $\text{M}^{-2}\text{s}^{-1}$. It was shown that the exchange between the two cyano species can be studied, not only by ^{13}C NMR, but also by ^{205}Tl NMR using the heteronuclear carbon–thallium scalar coupling as an indicator, despite the fact that only one Tl site is present in the system. The reaction mechanism is discussed in terms of an associative interchange mechanism, I_A. Penetration of the incoming cyanide ion into the coordination sphere of $Tl(CN)_4^-$ and $Tl(CN)_4(OH)^-$ is suggested to be the rate-determining step for the two parallel reactions paths. Possible reasons for the strong labilizing effect of the cyanide ligand is discussed in the light of thermodynamic and structural data. The possibility of detection of an exceptional exchange reaction, namely cyanide exchange between two $Tl(CN)_4^-$ entities by a direct encounter was theoretically settled, but found to be too slow to be detected.

Introduction

Recently, the formation of strong complexes between Tl^{III} and cyanide, $Tl(CN)_n^{3-n}$, $n = 1-4$, was established, and their stability constants determined.[1] A detailed multimethod study was published on the structure, symmetry, and coordination numbers of chloro, bromo, and cyano Tl^{III} complexes in aqueous solution.[2] In the monocyano complex, Tl^{III} is six-coordinate, $TlCN(OH_2)_5^{2+}$. In the second complex, *trans*-$TlCN_2(OH_2)_4^+$, the thallium ion retains the six-coordination; the Tl−CN bond length is almost the same as in the first complex, 2.11 Å, and Tl−O is 2.42 Å, that is 0.2 Å longer than in the hydrated thallium(3+) ion, $Tl(OH_2)_6^{3+}$. Upon the formation of the third complex, $Tl(CN)_3(OH_2)$, the coordination number decreases to four and the symmetry is C_{3v} with Tl−C 2.15 Å and Tl−O 2.42 Å. The fourth complex is tetrahedral with the Tl−C bond length equal to 2.19 Å.

The dynamics of the ions of group-13 elements in solution has not been well studied, because of the difficulty of monitoring the reactions.[3−8] The dynamic properties of thallium(III) are not well known. The kinetics of complex formation with semixylenol orange and 4-(2-pyridylazo)resorcinol were studied by stopped-flow methods.[9,10] The complex $Tl(OH)^{2+}$ was found to be the active species in complex formation kinetics. Lincoln et al. reported a lower limit of the pseudo-first-order rate constant of the Cl^- ligand substitution on the $TlCl_6^{3-}$ complex.[11] There are only four recent papers dealing in detail with the ligand exchange of hydrated complexed thallium(III) ions in chemical equilibrium. In these papers,[12−14] high-field ^{205}Tl NMR spectroscopy was established as a powerful tool for elucidating exchange paths using line-shape analysis and two-dimensional exchange spectroscopy (2D EXSY).[15] Three types of exchange paths were identified for thallium(III) cyanide complexes.[14] The first path is a ligand "self-exchange" between complexes with no net chemical change, for example according to Equation (1).

$$Tl(^*CN)(CN)^+ + Tl(CN)_3 \xrightleftharpoons{k_{23}} Tl(^*CN)(CN)_2 + Tl(CN)_2^+ \qquad (1)$$

The second path is the common anation (or complex formation) reaction of thallium(III) complexes, e.g. according to Equation (2).

$$Tl(CN)_2^+ + CN^- \xrightleftharpoons{k'_{23}} Tl(CN)_3 \qquad (2)$$

The third path is a ligand substitution according to Equation (3).

$$Tl(^*CN)(CN)^+ + HCN \xrightleftharpoons[k_{HCN,2}]{k_{2,HCN}} Tl(CN)_2^+ + H^*CN \qquad (3)$$

Rate constants for all dominating ligand exchange pathways were determined (see Table 1). The first type of reaction, according to Equation (1), is a very rarely encountered kind of ligand exchange, related to the inner-sphere electron transfer as far as the ligand-bridged transition state is concerned.[16−18] This exchange pattern dominates at low ligand/metal ratios, and the reason why it is observable at all is the very low free-ligand concentration due to the strong complex formation. Taking into account the effect of different ligands and the activation parameters, a dissociatively activated interchange process was suggested to oper-

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Table 1. Kinetic parameters for some exchange reactions of Tl^{III} halide and cyanide complexes in aqueous solution at 298 K; details for the rate-determining step (r.d.s.) are also given

Reaction	Determined rate constant, k_{ij}	Rate constant for r.d.s./s^{-1}, k_{ij}/K_{os}	Leaving/exchanging group	Ref.
$Tl(CN)_3 + Tl(CN)_4^- \rightleftarrows Tl(CN)_4^- + Tl(CN)_3$	$444\ \text{M}^{-1}\text{s}^{-1}$	1500	CN^-	[14]
$Tl(CN)_2^+ + Tl(CN)_4^- \rightleftarrows 2\ Tl(CN)_3$	$712\ \text{M}^{-1}\text{s}^{-1}$	500	CN^-	[14]
$Tl(CN)_2^+ + Tl(CN)_3 \rightleftarrows Tl(CN)_3 + Tl(CN)_2^+$	$161\ \text{M}^{-1}\text{s}^{-1}$	500	CN^-	[14]
$Tl^{3+} + Tl(CN)_2^+ \rightleftarrows 2\ Tl(CN)^{2+}$	$4.1\ \text{M}^{-1}\text{s}^{-1}$	900	CN^-	[14]
$Tl(CN)_2 + CN^- \rightleftarrows Tl(CN)_3$	$3.9\ \times 10^9\ \text{M}^{-1}\text{s}^{-1}$	1.1×10^{10}	H_2O	[14]
$Tl(CN)_3 + CN^- \rightleftarrows Tl(CN)_4^-$	$4.5\times10^8\ \text{M}^{-1}\text{s}^{-1}$	1.5×10^9	H_2O	[14]
$Tl(^*CN)(CN)^+ + CN^- \rightleftarrows Tl(CN)_2^+ + {}^*CN^-$	$6\times10^9\ \text{M}^{-1}\text{s}^{-1}$	4×10^9	CN^-	[14]
$Tl(^*CN)(CN)_3^- + CN^- \rightleftarrows Tl(CN)_4^- + {}^*CN^-$	$9.7\times10^6\ \text{M}^{-1}\text{s}^{-1}$	1.3×10^8	CN^-	this work
$Tl(^*CN)(CN)_3^- + CN^- (+OH^-) \rightleftarrows Tl(CN)_4^- + {}^*CN^-$	$5.4\times10^{10}\ \text{M}^{-2}\text{s}^{-1}$	–	CN^-	this work
$Tl(^*Cl)(Cl)_{i-1}^{(3-i)} + Cl^- \rightleftarrows Tl(Cl)_i^{(3-i)} + {}^*Cl^-$		10^6	Cl^-	[11]

ate for bromide and chloride in reactions according to Equation (1), i.e. after the encounter of the two complexes and formation of an outer-sphere complex, the leaving of a water ligand from the first coordination sphere of Tl^{III} is the rate-determining step. However, for the cyano Tl^{III} complexes $Tl(CN)_n(OH_2)_m{}^{3-n}$, the ligand "self-exchange" was found to be much slower than for the halide systems; hence, breaking of the Tl−CN bond, which is about 0.3 Å shorter than the Tl−halide bond, was suggested to be the rate-determining step.[14]

The anation reactions according to Equation (2) dominate the exchange for higher complexes and the rate of reaction depends on the entering ligand. Therefore, an associatively activated rate-determining step was proposed for both halide and cyanide complexes, where the entering ligand labilizes the coordinated water.

Also, it has been possible to determine the rate constants for the ligand substitution reaction according to Equation (3) on $Tl(CN)_2^+$ by means of ^{13}C NMR.[14] Two parallel reaction paths were identified, one with formal contribution of HCN and the other with CN^-. If the common Eigen−Wilkins-type reaction mechanism is assumed for the reaction path, with contribution of CN^-, then the incoming cyanide ion would have to labilize the bonded cyanide ion with 7 orders of magnitude in first-order rate constant units. This was judged to be less probable, and an alternative mechanism was suggested with the participation of HCN, which proceeded by deprotonation of the transition state.[14] In order to provide more confidence to the mechanism of the ligand substitution process according to Equation (3), additional experimental support was needed.

For the present study, the system $Tl(^{13}CN)_4^-/^{13}CN^-$ in aqueous media was selected. The usual tool for studying the chemical exchange in this system would be ^{13}C NMR, because (i) ^{13}C enrichment provides short measurement time and (ii) there are two exchanging carbon sites. Thus, basic conditions for a dynamic study of such an exchange reaction are fulfilled.[19] The convenient ^{205}Tl NMR [high natural abundance of the NMR active isotope(s), high NMR sensitivity, spin 1/2] can principally not be used in this case because only one chemical environment of Tl^{III} is present.

However, different magnetic thallium sites occur due to the scalar ^{205}Tl-^{13}C coupling, resulting in five signals in the ^{205}Tl NMR spectrum with an intensity ratio of 1:4:6:4:1. In the current paper it is shown that this fact makes the detection of the cyanide exchange possible by means of ^{205}Tl NMR. An additional advantage is provided by the fact that in ^{205}Tl NMR the observed line shape and the transfer of longitudinal magnetization is not affected by other exchange reactions in which the cyanide ion takes part; therefore, evaluation of the rate constants is more facile.

Results and Calculations

Determination of pH

Since knowledge of the pH is vital for the studied system, and the experiments had to be performed in a small volume, the NMR technique was the most straightforward way of measuring the pH. At first, 7 mM phosphate solution was prepared in the same medium as the real experiments. The pH was read using a pH meter with combined glass electrode (its internal solution contained NaCl instead of KCl in order to avoid the precipitation of $KClO_4$), and the chemical shift of the ^{31}P signal was determined. The pH was corrected according to Irving's method,[20] and from the dependence of ^{31}P NMR chemical shift vs. pH the actual pK values (protonation constants) and chemical shift values for the different protonated forms of phosphate were determined. For the actual ionic medium, the following values were obtained: $K_1 = (1.9\pm0.2)\times10^{11}$, $K_2 = (3.4\pm0.4)\times10^6$; $\delta(PO_4^{3-}) = 6.2\pm0.05$, $\delta(HPO_4^{2-}) = 3.47\pm0.06$, $\delta(H_2PO_4^-) = 0.7\pm0.03$. These values were then used for the determination of the actual $\log K_{HCN} = 9.9\pm0.2\ \text{M}^{-1}$, which is in good agreement with the literature.[21] The latter stability constant was used for calculation of proton exchange rate constants between HCN and CN^-, which affects the ^{13}C NMR dynamics strongly.[22]

1D NMR Line-Shape Analysis

Some representative ^{205}Tl NMR and ^{13}C NMR spectra as a function of pH are shown in Figures 1 and 2, together

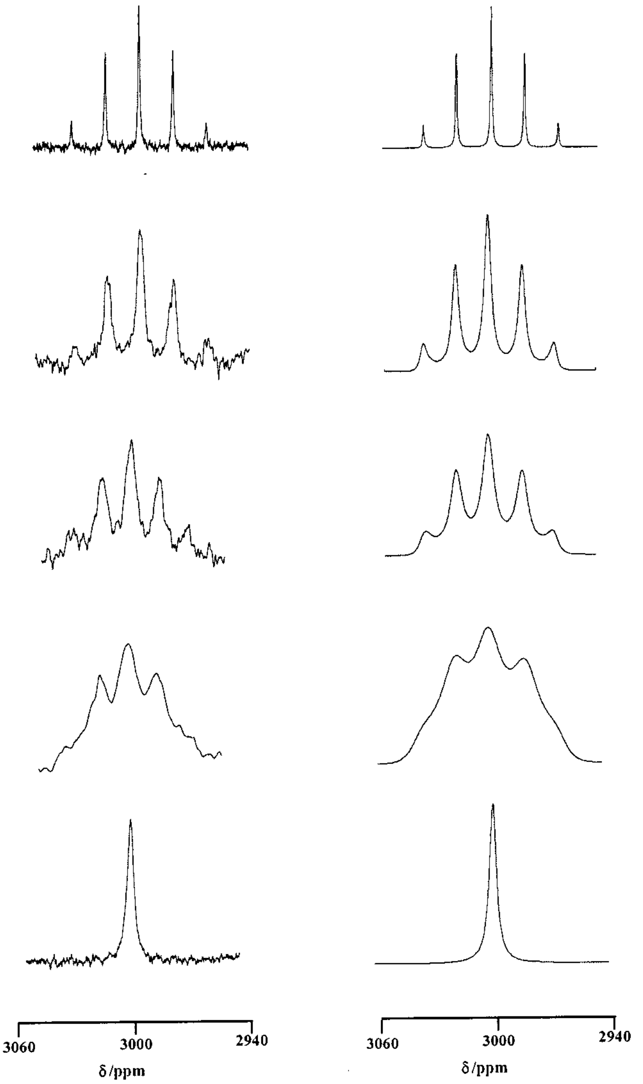


Figure 1. Measured and calculated ^{205}Tl NMR spectra of a solution where $[Tl^{3+}]_{tot}$ = 0.0504 M and $[CN^-]_{tot}$ = 0.135 M as a function of pH; from top to bottom: pH = 6.08 and k_{obs} = 176 s^{-1}, pH = 6.77 and k_{obs} = 861 s^{-1}, pH = 6.98 and k_{obs} = 1400 s^{-1}, pH = 7.16 and k_{obs} = 2120 s^{-1}, pH = 9.15 and k_{obs} = 18400 s^{-1}

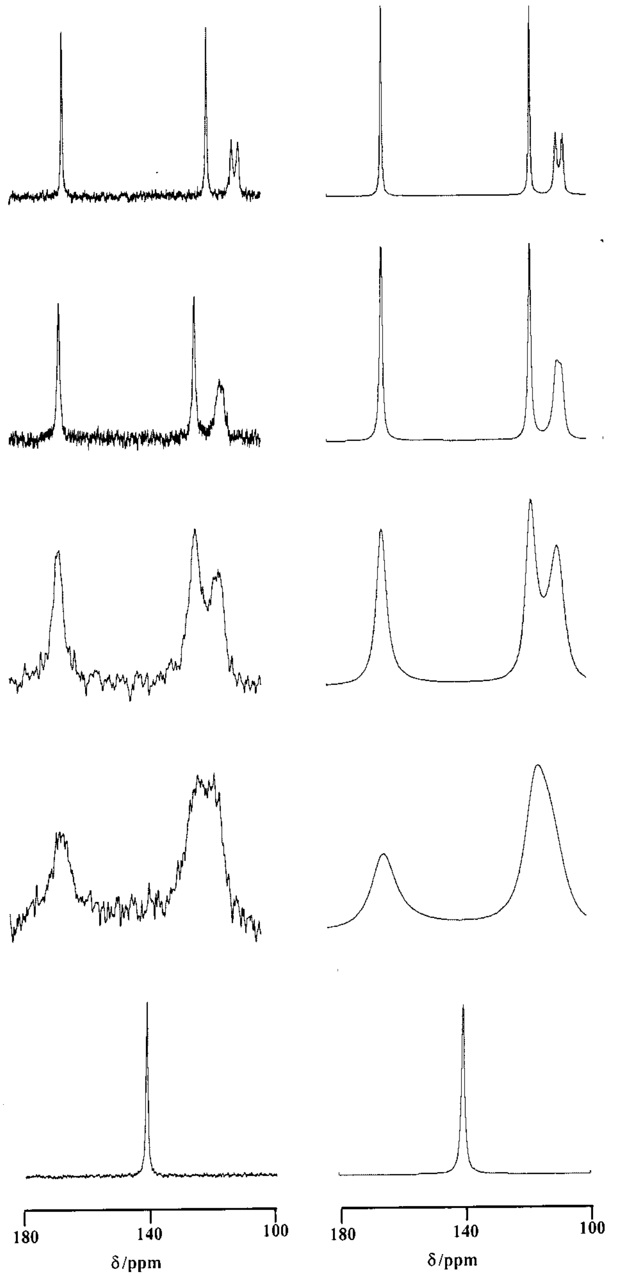


Figure 2. Measured and calculated ^{13}C NMR spectra of a solution in which $[Tl^{3+}]_{tot}$ = 0.0504 M and $[CN^-]_{tot}$ = 0.135 M as a function of pH; from top to bottom pH = 5.53, 6.08, 6.98, 7.16, and 9.82 (see text for details)

with the calculated spectra. It is apparent that complete band-shape analysis had to be used for both ^{205}Tl NMR and ^{13}C NMR.

The simulation of the spectra was made according to Equation (4) given by Reeves and Shaw[23,24] where V is the function of the frequency variable, **P** is the column vector of molar fractions (1/15,4/15,6/15,4/15,1/15 in the thallium pentet), and **C** is a matrix, Equation (5).

$$V = const\,\mathbf{C}^{-1}\,\mathbf{P} \tag{4}$$

$$\mathbf{C} = \mathbf{R}_2 + \mathbf{w}\,\varepsilon\,\mathbf{w} \tag{5}$$

$\mathbf{R_2}$ is the complete relaxation matrix given as a sum of diagonal matrix of the reciprocal relaxation times $\mathbf{T_{2i}}$ and rate matrix **K**, which contains the pseudo-first-order rate constants. $\boldsymbol{\varepsilon}_2 = \mathbf{R}_2^{-1}$, and $\mathbf{w_i}$ is the diagonal matrix of chemical shifts in frequency units. In this case, the creation of the $\mathbf{R_2}$ rate matrix is crucial. It was written in the form for ^{205}Tl NMR [Equation (6)]; k_{obs} is the pseudo-first-order rate constant for all processes that result in exchange of transverse magnetisation between the spin-labelled Tl sites, defined in the usual way from the rate of the exchange reaction $w/[Tl(CN)_4^-]$.[19]

$$\mathbf{K} = \begin{array}{ccccc} -4k_{obs} & k_{obs} & 0 & 0 & 0 \\ 4k_{obs} & -4k_{obs} & 2k_{obs} & 0 & 0 \\ 0 & 3k_{obs} & -4k_{obs} & 3k_{obs} & 0 \\ 0 & 0 & 2k_{obs} & -4k_{obs} & 4k_{obs} \\ 0 & 0 & 0 & k_{obs} & -4k_{obs} \end{array} \tag{6}$$

Construction of the rate matrix was made as follows (see Appendix for details). The thallium sites in the ^{205}Tl NMR spectra are observed as five peaks because of the ^{13}C scalar coupling, which can simply be modelled by the spin states α and β of ^{13}C(N) around the thallium ion. The five peaks are Tl(α,α,α,α), Tl(α,α,α,β), Tl(α,α,β,β), Tl(α,β,β,β), and Tl(β,β,β,β) with the intensities according to the probability of existence of each species.[25,26] An exchange reaction, using simplified symbols for the species present, can therefore be written according to Equation (7).

$$\mathrm{Tl}(4\alpha) + \mathrm{CN}(\beta) \xrightleftharpoons{k_{4\alpha,3\alpha}} \mathrm{Tl}(3\alpha 1\beta) + \mathrm{CN}(\alpha) \qquad (7)$$

Taking into account the ratio of the concentrations of the different forms, and the fact that the rate is the same in both directions, the matrix **K** can be constructed. The principle of microscopic reversibility is fulfilled because the sum of the columns gives 0, while for the off-diagonal elements of the matrix $p_i k_{ij} = p_j k_{ji}$ (where p_i is the ith element of vector **P** and k_{ij} is an element of matrix **K** in ith line and jth column).

In contrast to the apparent simplicity of the rate matrix for ^{205}Tl NMR, the situation for ^{13}C NMR is more complicated both from a kinetic and a spectroscopic point of view. The species H^{13}CN (doublet at δ = 112.7, $^1J_{\text{H-C}}$ = 270 Hz) exchanges with CN$^-$, causing line broadening in their signals. The cyanide ions exchange between the free cyanide ion and Tl(^{13}CN)$_4^-$ causing an additional broadening of the signals of the participating sites. Moreover, the species Tl(^{13}CN)$_4^-$ appears in the ^{13}C NMR spectrum as four signals; although the chemical shift is δ = 142.75, the isotopomers containing ^{205}Tl and ^{203}Tl, respectively, have different coupling constants to ^{13}C, resulting in two pairs of doublets.[1] The exchange system therefore requires a 7×7 matrix with rate constants for exchange between Tl(CN)$_4^-$ and CN$^-$/HCN, and HCN and CN$^-$. The latter exchange is known from the literature.[22] After a considerable effort the rate matrix could be constructed [see Appendix and Equation (8)]; $k_{\text{HCN}}^{\text{H}}$, k_{CN}^{H} are the rate constants of the proton exchange between HCN and CN$^-$; k_{HCN} and k_{CN} are the rate constants of cyanide exchange between Tl(CN)$_4^-$ and HCN/CN$^-$, respectively. Half of the isotopomer ratios of ^{203}Tl and ^{205}Tl, are represented as r_3 (0.295/2) and r_5 (0.705/2), respectively, while the division factors 2 are due to the spin-spin coupling. The diagonal elements (Σ) were set up so that the sum of each column is zero.

Kinetic Analysis

First, the ^{205}Tl NMR spectra were analysed by giving different values for k_{obs} in Equation (6), and comparing the calculated line shapes to the experimental ones. In this way a set of pseudo-first-order rate constants was obtained and analysed as a function of pH (cf. Figure 3). The two models according to Equation (9) could describe the cyanide exchange at constant cyanide concentration.

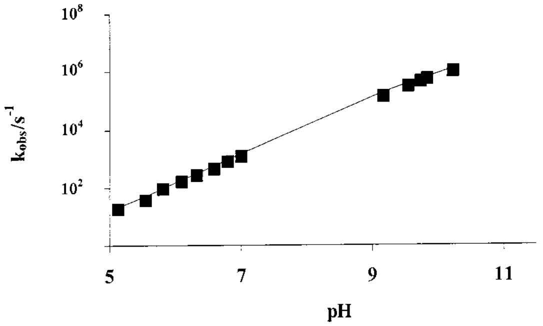


Figure 3. The dependence of the pseudo-first-order rate constants on the [H$^+$] concentration (squares); the line represents the best fit according to Equation (10b) with k_{CN} = (9.7±0.4)×10^6 M^{-1}s^{-1} and k_{OH} = (5.4±0.4)×10^{10} M^{-2}s^{-1}

$$w = k_{\text{CN}}[\text{CN}^-][\text{Tl(CN)}_4^-] + k_{\text{OH}}[\text{OH}^-][\text{Tl(CN)}_4^-] \qquad (9a)$$

or

$$w = k_{\text{CN}}[\text{CN}^-][\text{Tl(CN)}_4^-] + k_{\text{OH}}[\text{OH}^-][\text{CN}^-][\text{Tl(CN)}_4^-] \qquad (9b)$$

Taking into account the facts that w/[Tl(CN)$_4^-$] equals k_{obs} and K_{HCN} = [HCN]/[H$^+$][CN$^-$], the dependencies on the pH are according to Equation (10), where K_w is the water ion product and T_{CN} is the total concentration of the uncomplexed cyanide.

$$k_{obs} = \frac{k_{OH}K_w + (k_{OH}K_{HCN}K_w + k_{CN}T_{CN})[\text{H}^+]}{(1 + K_{HCN}[\text{H}^+])[\text{H}^+]} \qquad (10a)$$

$$k_{obs} = \frac{k_{OH}T_{CN}K_w + k_{CN}T_{CN}[\text{H}^+]}{(1 + K_{HCN}[\text{H}^+])[\text{H}^+]} \qquad (10b)$$

In order to distinguish between the two possibilities [Equations (9a) and (9b)], the line width was also measured in a solution that had ten times lower free cyanide concentration. At the same pH the line width decreased with a factor of about ten, which shows that the rate Equation (9b) is operative. The results of the least-squares fitting are shown in Figure 3, and the calculated rate constants are:

$$\mathbf{K} = \begin{array}{ccccccc}
\Sigma & 0 & \frac{1}{2}k_{HCN}[\text{HCN}] & \frac{1}{2}k_{HCN}[\text{HCN}] & \frac{1}{2}k_{HCN}[\text{HCN}] & \frac{1}{2}k_{HCN}[\text{HCN}] & k_{CN}^{H} \\
0 & \Sigma & \frac{1}{2}k_{HCN}[\text{HCN}] & \frac{1}{2}k_{HCN}[\text{HCN}] & \frac{1}{2}k_{HCN}[\text{HCN}] & \frac{1}{2}k_{HCN}[\text{HCN}] & k_{CN}^{H} \\
k_{HCN}r_5[\text{Tl}] & k_{HCN}r_5[\text{Tl}] & \Sigma & 0 & 0 & 0 & k_{CN}r_5[\text{Tl}] \\
k_{HCN}r_3[\text{Tl}] & k_{HCN}r_3[\text{Tl}] & 0 & \Sigma & 0 & 0 & k_{CN}r_3[\text{Tl}] \\
k_{HCN}r_3[\text{Tl}] & k_{HCN}r_3[\text{Tl}] & 0 & 0 & \Sigma & 0 & k_{CN}r_3[\text{Tl}] \\
k_{HCN}r_5[\text{Tl}] & k_{HCN}r_5[\text{Tl}] & 0 & 0 & 0 & \Sigma & k_{CN}r_5[\text{Tl}] \\
2\times k_{HCN}^{H} & 2\times k_{HCN}^{H} & k_{CN}[\text{CN}] & k_{CN}[\text{CN}] & k_{CN}[\text{CN}] & k_{CN}[\text{CN}] & \Sigma
\end{array} \qquad (8)$$

$k_{CN} = (9.7\pm0.4)\times10^6\ \text{M}^{-1}\text{s}^{-1}$ and $k_{OH} = (5.4\pm0.4)\times10^{10}\ \text{M}^{-2}\text{s}^{-1}$.

In order to further verify the rate constants determined by ^{205}Tl NMR these were introduced into the rate matrix of ^{13}C NMR [Equation (8)], and the proton exchange rate constants were taken from the literature.[22] Then, ^{13}C NMR spectra were simulated (Figure 2, right side); good agreement was found considering that the literature values were obtained for a different ionic medium. The largest deviation in the line widths was generally below 10%.

Similarly to the recently established existence of the ligand "self-exchange" between complexes, e.g. $Tl(CN)_3$ and $Tl(CN)_4^-$,[14] it was now considered that cyanide exchange can also occur between two $Tl(CN)_4^-$ species according to Equation (11).

$$Tl(^{*}CN)_4^- + Tl(CN)_4^- \overset{k_{4,4}}{\rightleftharpoons} Tl(CN)_4^- + Tl(^{*}CN)_4^- \tag{11a}$$

Use of the short notations introduced above, and considering an encounter of two thallium complexes with different spin states of ^{13}C yields Equation (11b).

$$Tl(4\alpha) + Tl(3\alpha\beta) \overset{k_{4,4}}{\rightleftharpoons} Tl(3\alpha\beta) + Tl(4\alpha) \tag{11b}$$

If this reaction were to occur, then it would be possible to study it by both ^{13}C and ^{205}Tl NMR because of the scalar coupling present in these systems.[25] A solution sample was prepared, suitable for detection of such a reaction, i.e. pH and cyanide concentration was kept as low as possible in order to slow down the exchange paths described by Equations (9a) and (9b). However, pH could not be decreased below a certain value, in order to avoid the exchange between $Tl(CN)_3$ and $Tl(CN)_4^-$. The composition of the sample was: $[Tl^{3+}]_{tot} = 0.0434$ M, $[^{13}CN^-]_{tot} = 0.1816$ (in 3.0 M $NaClO_4$), and the pH was carefully regulated to 6.5 as monitored by ^{31}P NMR. Both ^{205}Tl and ^{13}C NMR spectra were recorded for this sample in order to assure that no significant amount of $Tl(CN)_3$ was present. In order to determine the exchange rate matrix in a facile way, ^{205}Tl NMR 2D-EXSY experiments were run on the sample using mixing times of 4 ms and 8 ms. Cross peaks were detected (cf. Figure 4), indicating chemical exchange between the magnetically labelled spin sites of $Tl(CN)_4^-$. A quantitative analysis resulted in the rate matrices for 4 ms mixing time [Equation (12a)] and for 8 ms mixing time [Equation (12b)].[27]

$$\begin{matrix} 136.9 & 45.8 & - & - & - \\ 183.5 & 44.1 & 64.1 & - & - \\ - & 96.1 & 59.2 & 84.5 & - \\ - & - & 56.3 & 34.4 & 172.4 \\ - & - & - & 43.1 & 125.9 \end{matrix} \tag{12a}$$

$$\begin{matrix} 80.1 & 26.8 & - & - & - \\ 107.2 & -6.3 & 53.6 & - & - \\ - & 80.4 & -13.0 & 74.1 & - \\ - & - & 49.4 & -2.9 & 119.2 \\ - & - & - & 29.8 & 39.6 \end{matrix} \tag{12b}$$

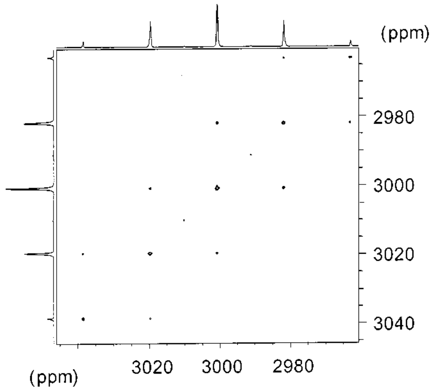


Figure 4. ^{205}Tl 2D EXSY of $Tl(^{13}CN)_4^-$ aqueous solution with mixing time 4 ms; T = 298 K; ^{12}C satellites are also visible at δ = 2990 and 3010

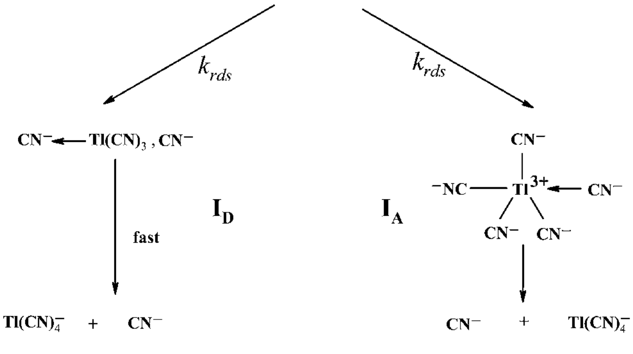
The matrix elements denoted by "–" have no real meaning and have been removed. Also, the diagonal elements are not the real ones because we did not use zero mixing time for the calculation.[27] Then, using the rate constants determined above from the 1D NMR spectra, the rate matrix was calculated [Equation (12c)].

$$\begin{matrix} -120 & 30 & 0 & 0 & 0 \\ 120 & -120 & 60 & 0 & 0 \\ 0 & 90 & -120 & 90 & 0 \\ 0 & 0 & 60 & -120 & 120 \\ 0 & 0 & 0 & 30 & -120 \end{matrix} \tag{12c}$$

Good agreement can be recognized in the off diagonal elements of the matrices [Equation (12)]. Therefore, no further detectable parallel reaction path is needed to describe the system, even at very small cyanide excess. Thus, it can be concluded that NMR makes it possible to detect the otherwise undetectable exchange reactions according to Equation (11), if they match the NMR criteria (lifetime comparable to the NMR relaxation times) and kinetic criteria (high enough exchange rate).

Discussion

For the ligand substitution process according to Equation (13) the rate Equation (14) was found.



Scheme 1

$$Tl(CN)_4^- + {}^*CN^- \underset{k_{CN,4}}{\overset{k_{4,CN}}{\rightleftharpoons}} Tl({}^*CN)(CN)_3^- + CN^- \qquad (13)$$

$$w = k_{4,CN}[CN^-][Tl(CN)_4^-] + k_{OH}[OH^-][CN^-][Tl(CN)_4^-] \qquad (14)$$

In Equations (13) and (14) the notation of the rate constant is $k_{4,CN}$ (instead of k_{CN}), i.e. the same as in our earlier papers on the same or related subject.[12−14]. Usually, the Eigen−Wilkins-type mechanism[28] is used to describe such reactions according to Scheme 1.

During the first, generally fast step an ion pair is formed for which the stability constant can be estimated using the Fuoss equation, by considering only the electrostatic interactions.[28] For the present case this stability constant $K_{os}(-1,-1)$ is 0.074, from which the rate constant of the rate-determining step can be calculated as $k_{rds} = k_{4,CN}/K_{os} = 1.3\ 10^8\ s^{-1}$. There are two parallel paths according to Scheme 1. If the rate of dissociation of a CN^- ligand determines the exchange rate, the path is a dissociative interchange I_D. If the incoming cyano ligand forces out one of the complexed ligands, the process is an associative interchange I_A (or limiting associative A, if a complex with a higher coordination number can be detected).

The hitherto reported rate constants concerning pertinent ligand exchange reactions in chemical equilibrium have been collected (cf. Table 1) and can be helpful for suggesting the mechanism of the presently studied reaction. In the case of a "self-exchange" reaction, when one cyanide ion goes from one metal ion to another (see Table 1, first four lines), it was found that the rupture of a Tl−C bond is a slow process with rate constant of a few hundred s^{-1}.[14] For complex formation reactions (Table 1, lines 6−7) these rate constants are several orders of magnitude larger, because the bottle-neck of these reactions is the rupture of the $Tl-OH_2$ bond activated by the entering ligand, or sometimes the diffusion.[29] These rate constants are equally high for the thallium(III) halide and cyanide complexes, and larger than the estimated water exchange rate.[12] Therefore, it was concluded that an associatively activated process I_A operates. There was some doubt about this, because no pronounced entering ligand effect was found when comparing the chloride, bromide, and cyanide complexes. However, this was attributed to the fact that these complex formation reactions had a rate close to the diffusion control limit; therefore, the differences cannot be observed.[14]

In the case of ligand substitution reactions of $Tl(CN)_2^+$ [Equation (3)] it was difficult to characterise the mechanism: rupture of the Tl−C bond must occur in any case because of the symmetric nature of the reaction according to Equation (3). However, the calculated rate constant of the rate-determining step was also found to be much higher than those found for the ligand exchange between complexes, according to Equation (1).[14] This was surprising, and an alternative mechanism was suggested in the case of $Tl(CN)_2^+$ with participation of HCN (rather than CN^-).[14] In the present work, another rate constant has been determined for ligand substitution, e.g. on $Tl(CN)_4^-$, with an equally fast rate-determining step. A probable explanation is that the incoming cyanide ion coordinates, forming a transition state where the complexes are highly labile. Therefore, an associative interchange or associative mechanism is supposed to be operative.

In order to interpret the details of the reaction mechanism of the ligand substitution reaction paths the data in Table 1 can be utilised. Let us start with ligand exchange reaction between complexes [Equation (1)]. If we suppose that binuclear complexes are temporarily formed so that the attacking "ligand" is complexed as well, it is difficult to assume any labilizing effect of the incoming reactants. Therefore, the most probable rate-determining step is a rupture of the metal−ligand bond in the transition state containing a ligand in a bridging position. The kinetic stability, i.e. inertness, of these intermediates could well be controlled by the lability of the metal−ligand bond. This interpretation is supported by the similarity of the halide ligands in this so called "self exchange", whereas there is a significant difference between the halide ions and the more covalently bonded cyanide ion. For the species $Tl(CN)_n^{3-n}$ this reaction is slower by a few orders of magnitude compared to that for the thallium(III) halide complexes.

If it is accepted that the ligand "self-exchange" [Equation (1)] mirrors the Tl−CN bond breaking with little external influence then the high rate of ligand substitution [Equation (13)] is unexpected. At this point, the physical/chemical properties of the studied species should be considered. The thermodynamic stability of the thallium cyanide complexes[1] is: $\log K_i = 13.21, 13.39, 8.67$, and 7.44, for $i = 1$ to 4, respectively. The first two Tl^{III} halide complexes are five orders of magnitude stronger, which can serve as an indication for changing of the character of the metal−ligand bond.[31] The first two cyanide complexes show similarity with covalently bonded organometallic Tl^{3+} compounds,[32,33] while $Tl(CN)_3$ and $Tl(CN)_4^-$ show similarity to the usual inorganic ligand coordination mainly by donation of the electrons to the metal ion. This difference can also be discerned in the behaviour of Tl^{III} complexes in organometallic reactions.[33]

The steric arrangement and change of the coordination geometry may play a key role in kinetics and in mechanistic considerations. For the cyano Tl^{III} species, $Tl(CN)_n(OH_2)_{6-n}{}^{n-3}$ ($n = 1$ and 2) in solution, the coordination number is six with equal and very short Tl−CN bond lengths, 2.10−2.11 Å.[2] For $n = 3$ and 4 this bond is significantly longer, 2.15 and 2.19 Å, respectively, and these complexes are both tetrahedral. However, the bond lengths are still 0.2−0.4 Å shorter than the corresponding bonds of the halides.

Ligand substitution kinetic data for cyanide exchange is known for two species only, $Tl(CN)_2(OH_2)_4^{2+}$ [14] and $Tl(CN)_4^-$ (this work). For $Tl(CN)_2(OH_2)_4^{2+}$, after the attack of the incoming cyanide ligand a new species forms as a transition state in which the Tl−CN bond resembles the one in $Tl(CN)_3$, but still with a number of water molecules (probably four) in the first coordination sphere of the thallium ion. Presumably, this Tl−CN bond is more labile due to the much higher coordination number than the one in the thermodynamically stable third complex, namely

$Tl(CN)_3(OH_2)$.[2] With this argument, the fast ligand substitution can be understood.

For $Tl(CN)_4^-$, a transition state species with five-coordination is expected to be labile. Also in this case, the rate of insertion of the entering ligand determines the rate of leaving of the coordinated ligand; therefore, an associative interchange mechanism is probable.

The hydroxide-dependent parallel path also needs some consideration: (i) Such a path is not often encountered in ligand substitution reactions, but if it exists it proceeds by OH^- catalysis and deprotonation of the coordinated ligands.[28] (ii) Hitherto, formation of ternary hydroxo Tl^{3+} cyanide complexes has not been reported, although binary hydroxo complexes with high stability are well known.[30] However, all earlier investigations were made in acidic solution in order to avoid hydrolysis. In Figure 5, relative contributions of the two reaction paths are presented. It can be seen that the contribution of the hydroxide-assisted reaction path starts to be effective for pH > 9.5.

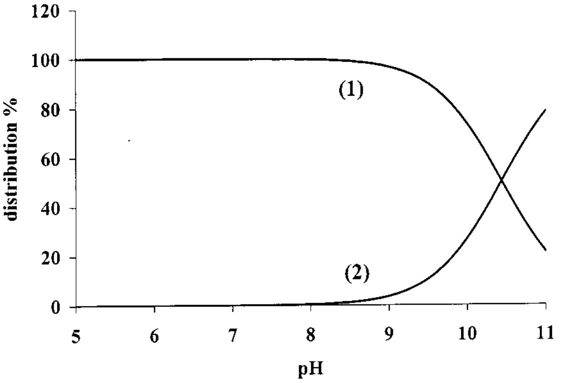


Figure 5. The relative contribution of the two reaction paths, (1) without and (2) with OH contribution, as a function of the pH

A first approximation was to consider both HCN and CN^- as reactive species; however, this was not compatible with the experiments. If $Tl(CN)_3OH^-$ were assumed to be the active species then the rate equation would not have the form of Equation (9b). It is possible that a five-coordinate $Tl(CN)_4OH^{2-}$ acts as kinetically active species which would give a rate equation consistent with the one obtained [Equation (10)]. However, the calculation of the rate-determining step is difficult because the stability constant of the suggested $Tl(CN)_4OH^{2-}$ is not known. In fact, when the pH is increased to > 11 the solution containing Tl^{III} and excess cyanide turns brownish, indicating that in spite of the high stability of the cyanide complexes they can be transferred into (mixed) hydroxo species. In this case, the penetration of the incoming cyanide ion would determine the exchange rate in the same way as discussed above. The limiting associative mechanism, that is the formation of six-coordinate species from $Tl(CN)_4OH^{2-}$, would not be compatible with the experimental findings, namely that a maximum of four cyanide ligands can coordinate to the thallium(III) ion, even at a large cyanide excess.[1] Also, other kinetic data are consistent with the suggested reaction mechanism. Mixed complexes with exceptionally high coordination numbers, for example those between $Tl(edta)^-$ on one side and Cl^-, Br^-, CN^-, and SCN^- on the other side also show high kinetic lability.[34]

In conclusion, two new examples of ligand substitution reactions for cyanothallium(III) complexes were established. The new reactions, similar to the previously described one [Equation (3)], proceed by an associatively activated interchange mechanism.

^{205}Tl NMR was confirmed to be the experimental technique of choice for studies of thallium solution chemistry. In this specific case, due to the magnetic spin labelling it was possible to utilise its power despite the fact that only one thallium-containing species was participating in the chemical process under study.

Experimental Section

Preparation and Analysis of Solutions: A ca. 1.2 M aqueous stock solution of $Tl(ClO_4)_3$ in 3.8 M $HClO_4$ was prepared by anodic oxidation of a $TlClO_4$ solution.[30,31] The concentrations of acid and thallium content in the stock solution were determined as described elsewhere.[35] The samples were prepared from the appropriate volume of the stock solution, solutions of 0.3 M $HClO_4$ and 5 M $NaClO_4$, and a weighted amount of solid $Na^{13}CN$ (Cambridge Isotope Laboratories, > 99% ^{13}C enrichment). In order to keep the activity coefficients of the reacting species approximately constant, the total sodium concentration, $[Na^+]_{tot}$, was kept at 3 M. The composition of the samples was determined by quantitative ^{205}Tl and ^{13}C NMR. Some details of sample preparation and analysis were described in a previous paper.[12] The pH dependence of the ^{205}Tl NMR and ^{13}C NMR spectra was recorded by titration of a 1-mL sample with 0.3 M $HClO_4$ (containing the same ionic medium, i.e. 3 M $NaClO_4$) in an NMR tube using a micro syringe, between pH = 7.4 and pH = 5.12. The change of pH was measured by ^{31}P chemical shifts; this "potentiometer" was calibrated by pH potentiometry in independent experiments.[36] The sample contained 7 mM total PO_4^{3-} in different protonated forms. Another 1 mL of the solution was titrated with NaOH in a similar way. In this case, the $^{13}CN/HCN$ signal was also used for checking the pH.

NMR Measurements: All NMR spectra were recorded at a probe temperature of 25±0.5 °C with a Bruker DMX500 spectrometer. The magnetic field was unlocked; field drift was found to be negligible. ^{205}Tl NMR: spectrometer frequency 289.4 MHz, flip angle 90° (12 μs), pulse repetition time of 5 s was found long enough for complete magnetic relaxation. The chemical shifts are reported in ppm toward higher frequency with respect to an aqueous solution of $TlClO_4$ extrapolated to infinite dilution. ^{13}C NMR: spectrometer frequency 125.8 MHz, flip angle ca. 30° (8 μs), relaxation delay was in the range 4−16 s depending on the relaxation rates of the investigated species. The chemical shifts are reported in ppm toward higher frequency with respect to an external water-soluble sodium derivative of TMS. ^{205}Tl 2D-EXSY NMR spectra were recorded with 512 increment experiments, each consisting of 8 scans and with 5 s relaxation delay. Fourier transformations were performed in a 1K×1K data-point matrix with a window function cosine and an SSB = 2 filter. The Fourier transformation, volume integration and other NMR spectroscopic data treatment was performed using a Bruker program package (2D WinNMR®).

APPENDIX

Construction of Rate Matrices for ^{205}Tl NMR

As was found in a previous paper from this laboratory, in an exchange process between two complexed cyano species only one cyanide ligand changes its position.[15] Therefore, only this type of transition is considered. As an example, we choose the process when one cyanide ion goes from $\mathrm{Tl[CN_4(4\alpha)]^-}$ [denoted for the sake of simplicity as Tl(4α)] to $\mathrm{Tl(CN)(3\alpha,1\beta)^-}$ [denoted as Tl(3α)]. The labels in brackets give the concentrations of the various carbon-labelled Tl sites. For example: $\mathrm{Tl[CN_4(4\alpha)]^-}$ has four α-carbon atoms and the concentration is [4α] while for $\mathrm{Tl(CN)(3\alpha,1\beta)^-}$ the notation is [3α]. The rate of exchange from site *i* to *j* is written using pseudo-first-order rate constants (or observed rate constants) k_{ij}, as in Equation (15).

$$w_{43} = w_{34} = k_{43}[4\alpha] = k_{34}[3\alpha] \tag{15}$$

From Equation (15) the most important consequence is the relation between the forward and backward observed rate constants [Equation (16)].

$$k_{34}=k_{43}\frac{[4\alpha]}{[3\alpha]}=\frac{1}{4}k_{43} \tag{16}$$

It is easy to generalize Equations (15) and (16) as Equations (17) and (18).

$$w_{ij} = w_{ji} = k_{ij}[j\alpha] = k_{ij}[i\alpha] \tag{17}$$

$$k_{ij} = k_{ij}([i\alpha]/[j\alpha]) = p_j/p_i \tag{18}$$

From these considerations Equation (19) follows.

$$k_{34} = k_{43}\frac{1}{4}; k_{23} = k_{32}\frac{2}{3}; k_{12} = k_{21}\frac{3}{2}; k_{01} = k_{10}\frac{4}{1}; \tag{19}$$

It is obvious that since all exchanges are identical reactions from a chemical point of view (i.e. one cyano ligand is substituted) they cannot be characterized by four different rate constants. Let us consider that if a Tl(3α,1β) meets $\mathrm{CN^-}$(α) the probability of forming Tl(4α) is one, but if this interaction happens between $\mathrm{CN^-}$(α) and Tl(2α,2β) then this probability is twice as high because there are two cyanide ions with β spin state. Following this consideration up to Tl(4α) we can find a series of relations as in Equation (20).

$$k_{10} = k^{\mathrm{obs}}; k_{01} = 4k^{\mathrm{obs}}; k_{12} = 3k^{\mathrm{obs}}; k_{21} = 2k^{\mathrm{obs}}; k_{23} = 2k^{\mathrm{obs}}; k_{32} = 3k^{\mathrm{obs}}; k_{34} = k^{\mathrm{obs}}; k_{43} = 4k^{\mathrm{obs}} \tag{20}$$

These considerations are a consequent application of microscopic reversibility, therefore the sum of the elements of each column of the rate matrix **K** should be zero provided that the matrix was correctly constructed. It is easy to make mistakes in setting up the rate matrix, especially when the number of elements is large. However, in the test phase of the model, reaching the so called "fast exchange" regime − when only one peak appears − calculation of the chemical shift will be wrong if the matrix setup is not correct, indicating the error. The model calculation was performed so that the k_{obs} values were varied until the band shape of the calculated spectra were identical with the experimental ones. Then, the dependence of the obtained observed rate constant on the pH was analyzed.

Construction of Rate Matrices for ^{13}C NMR

The construction of the ^{13}C rate matrix required somewhat longer, but not more complicated algebra. While for ^{205}Tl NMR we knew that all peaks are determined by one exchange reaction, and as they were side-bands of a main peak they had to behave in exactly the same way, for ^{13}C NMR it is not the case. Still, there are multiplets in the spectrum: Hα and Hβ, Tlα5 and Tlβ5 (for the ^{205}Tl isotope), or Tlα3 and Tlβ3 (for the ^{203}Tl isotope) which behave identically. However, the isotopomers behave as independent species and have different line widths caused by the exchange, because of their different populations. Furthermore, the proton exchange between HCN and $\mathrm{CN^-}$ should also be taken into account. First, we denote the seven signals a follows: Hα and Hβ are HCN doublets; Tlα5 and Tlβ5 are the ^{205}Tl-coupled doublets; Tlα3 and Tlβ3 are the ^{203}Tl-coupled doublets; CN is the signal of the cyanide ion. The concentrations according to the previous paragraph are the notations in brackets, e. g. [Hα] is the concentration of the α-spin-state proton-containing HCN. The task is to find the smallest number of observed rate constants from which we can combine the possible 42 elements of the **K** rate matrix. Take a reaction between $\mathrm{Tl(CN)_4^-}$ (Tlα5) and H(α)CN. According to Equation (15) the Equations (21) and (22) follow.

$$w_{\mathrm{H\alpha\alpha5}} = w_{\mathrm{\alpha5H\alpha}} = k_{\mathrm{H\alpha\alpha5}}[\mathrm{H\alpha}] = k_{\mathrm{\alpha5H\alpha}}[\mathrm{Tl\alpha5}] \tag{21}$$

$$k_{\mathrm{H\alpha\alpha5}} = k_{\mathrm{\alpha5H\alpha}}([\mathrm{Tl\alpha5}]/[\mathrm{H\alpha}]) \tag{22}$$

According to Equations (21) and (22) we can obtain 8 relations between 16 elements of **K**, i. e. exchange between Hα and Tlα5, Tlα3, Tlβ5, Tlβ3; and between Hβ and Tlα5, Tlα3, Tlβ5, Tlβ3. Of course, there is only one chemically determined rate process, namely according to Equation (23).

$$w = k_{\mathrm{HCN}}[\mathrm{HCN}][\mathrm{Tl(CN)4^-}] \tag{23}$$

The rate constant is independent of the spin labelling, therefore Equation (24) follows.

$$w_{\mathrm{H\alpha\alpha5}} = w_{\mathrm{\alpha5H\alpha}} = k_{\mathrm{HCN}}[\mathrm{H\alpha}][\mathrm{Tl\alpha5}] \tag{24}$$

Considering the relation between the concentration of the chemically identical but magnetically labelled species Equation (25) is given, where 0.705 is the isotopic ratio of the ^{205}Tl isotope.

$$w_{\mathrm{H\alpha\alpha5}} = w_{\mathrm{\alpha5H\alpha}} = k_{\mathrm{HCN}}\frac{1}{2}[\mathrm{HCN}]\frac{0.705}{2}[\mathrm{Tl(CN)_4^-}] \tag{25}$$

Therefore, the pseudo-first-order rate constants for the forward and backward reaction is given by Equation (26).

$$k_{\mathrm{H\alpha\alpha5}} = w/\frac{1}{2}[\mathrm{HCN}] = k_{\mathrm{HCN}}\frac{0.705}{2}[\mathrm{Tl(CN)_4^-}] \tag{26a}$$

$$k_{\mathrm{\alpha5H\alpha}} = w/\left(\frac{0.705}{2}[\mathrm{Tl(CN)_4^-}]\right) = k_{\mathrm{HCN}}\frac{1}{2}[\mathrm{HCN}] \tag{26b}$$

Another three pairs of this type of relation is valid for the rest of exchange processes in which H(α)CN is involved [Equation (27) to (29)].

$$k_{\mathrm{H\alpha\alpha3}} = w/\frac{1}{2}[\mathrm{HCN}] = k_{\mathrm{HCN}}\frac{0.295}{2}[\mathrm{Tl(CN)_4^-}] \tag{27a}$$

$$k_{\mathrm{\alpha3H\alpha}} = w/\left(\frac{0.295}{2}[\mathrm{Tl(CN)_4^-}]\right) = k_{\mathrm{HCN}}\frac{1}{2}[\mathrm{HCN}] \tag{27b}$$

$$k_{\mathrm{H\alpha\beta5}} = w/\frac{1}{2}[\mathrm{HCN}] = k_{\mathrm{HCN}}\frac{0.705}{2}[\mathrm{Tl(CN)_4^-}] \tag{28a}$$

$$k_{\mathrm{\beta5H\alpha}} = w/\left(\frac{0.705}{2}[\mathrm{Tl(CN)_4^-}]\right) = k_{\mathrm{HCN}}\frac{1}{2}[\mathrm{HCN}] \tag{28b}$$

$$k_{\mathrm{H\alpha\beta3}} = w/\frac{1}{2}[\mathrm{HCN}] = k_{\mathrm{HCN}}\frac{0.295}{2}[\mathrm{Tl(CN)_4^-}] \tag{29a}$$

$$k_{\mathrm{\beta3H\alpha}} = w/\left(\frac{0.295}{2}[\mathrm{Tl(CN)_4^-}]\right) = k_{\mathrm{HCN}}\frac{1}{2}[\mathrm{HCN}] \tag{29c}$$

Of course, we have four pairs of relations for exchanges where H(β)CN is involved which are exactly the same. Therefore, 16 elements are already determined. Another 8 elements come from the reaction between CN^- and Tlα5, Tlα3, Tlβ5, Tlβ3 [Equations (30) and (31)].

$$w_{CN\alpha5} = w_{\alpha5CN} = k_{CN\alpha5}[CN^-] = k_{\alpha5CN}[\alpha5] \tag{30}$$

$$k_{CN\alpha5} = k_{\alpha5CN}([\alpha5]/[CN^-]) \tag{31}$$

Also here, only one chemical reaction should be taken into account, namely according to Equations (32) and (33).

$$w = k_{CN}[CN^-][Tl(CN)_4^-] \tag{32}$$

$$w_{CN\alpha5} = w_{\alpha5CN} = k_{CN}[CN^-][Tl\alpha5] \tag{33}$$

It is important to note that we consider principally only one reaction path. Of course, there can be many parallel reaction paths, but it principally does not change the final results.

Substitution of the concentrations of the different Tl species into Equation (33) yields Equation (34), which leads to the pseudo-first-order rate constants according to Equations (35) to (38).

$$w_{CN\alpha5} = w_{a5CN} = k_{CN}\left[CN^-\right]\frac{0.705}{2}\left[Tl(CN)_4^-\right] \tag{34}$$

$$w_{CN\alpha5} / \left[CN^-\right] = k_{CN}\,\frac{0.705}{2}\left[Tl(CN)_4^-\right] \tag{35a}$$

$$w_{\alpha5CN} / \frac{0.705}{2}\left[Tl(CN)_4^-\right] = k_{CN}\,\left[CN^-\right] \tag{35b}$$

$$w_{CN\alpha3} / \left[CN^-\right] = k_{CN}\,\frac{0.295}{2}\left[Tl(CN)_4^-\right] \tag{36a}$$

$$w_{\alpha3CN} / \frac{0.295}{2}\left[Tl(CN)_4^-\right] = k_{CN}\,\left[CN^-\right] \tag{36b}$$

$$w_{CN\beta5} / \left[CN^-\right] = k_{CN}\,\frac{0.705}{2}\left[Tl(CN)_4^-\right] \tag{37a}$$

$$w_{\beta5CN} / \frac{0.705}{2}\left[Tl(CN)_4^-\right] = k_{CN}\,\left[CN^-\right] \tag{37b}$$

$$w_{CN\beta3} / \left[CN^-\right] = k_{CN}\,\frac{0.295}{2}\left[Tl(CN)_4^-\right] \tag{38a}$$

$$w_{\alpha5CN} / \frac{0.295}{2}\left[Tl(CN)_4^-\right] = k_{CN}\,\left[CN^-\right] \tag{38b}$$

Since it turned out that the reactions between the magnetically labelled Tl species, e.g. Tlα5 and Tlβ5, do not occur, we do not show how they were introduced into the rate matrix.

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