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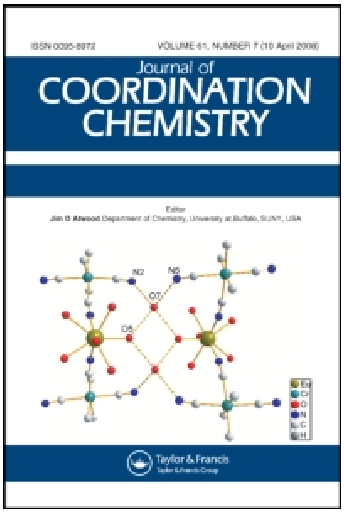

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SHORT COMMUNICATION

Kinetics of Ligand Substitution Reactions: An Observation on Reaction of Nickel(II) Triethylene Tetramine Hexaacetate with Cyanide Ion

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The kinetics and mechanism of reaction between NiTTHA (where TTHA = triethylene tetramine hexaacetic acid) and cyanide ion at pH = 10.6; temp = 24°C and $\mu = 0.1$ M studied earlier by Stara and Kopanica has been reinterpreted in the light of investigations of aminocarboxylatonickel(II) reactions with cyanide ion under similar conditions.

KEY WORDS: Cyanide kinetics triethylenetetraminehexaacetatonickel, Kinetics cyanide triethylenetetraminehexacetatonickel, Nickel triethylenetetraminehexaacetate kinetics cyanide, Triethylenetetraminehexaacetatonickel kinetics.

Stara and Kopanica[1] have reported their results on the rates of the following substitution reaction:

$$\mathrm{Ni(TTHA)^{4-} + 4CN^- \rightleftharpoons Ni(CN)_4{}^{2-} + TTHA^{6-}}$$

at pH = 10.6, temp = 24°C, $\mu = 0.1$ M. The forward rate was measured in presence of excess cyanide and reverse rate in presence of excess ligand TTHA. They have observed first order dependence in $\mathrm{NiL^{2-n}}$ (L = TTHA) and third order in cyanide for forward reaction. They also observed first order dependence in $\mathrm{Ni(CN)_4{}^{2-}}$ and first order in $\mathrm{L^{-n}}$ for reverse reaction. Without being explicit they have suggested the following steps for this reaction:

$$\mathrm{Ni(TTHA)^{4-} + CN^- \overset{K_1}{\rightleftharpoons} Ni(TTHA)(CN)^{5-}\ (fast)} \qquad (1)$$

$$\mathrm{Ni(TTHA)(CN)^{5-} + 3CN^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ni(CN)_4{}^{2-} + TTHA^{6-}\ (r.d.s.)} \qquad (2)$$

This view does not appear to be correct. Although they observed and reported that the rate of reverse reaction is suppressed by the presence of cyanide ions, the cyanide ion dependence is not reflected in the reverse rate expression formulated by them and given below:

$$-\frac{d[\mathrm{Ni(CN)_4{}^{2-}}]}{dt} = k'_{\mathrm{obsd}}\,[\mathrm{Ni(CN)_4{}^{2-}}]\ \text{(in presence of excess ligand)}$$

$$= k_r\,[\mathrm{Ni(CN)_4{}^{2-}}]\,[\mathrm{TTHA^{6-}}] \qquad (3)$$

Our experiments[2] on DTPA (diethylenetriamine-penta-acetic acid) and 1,2-PDTA (1,2-diamino-propanetetra-acetic acid) reaction under similar conditions show that first 30% of the reverse reaction follows roughly pseudo first order kinetics ($\mathrm{L^{n-}}$ in large excess). But later points do not show even a remote fit. They fit very well into the rate expression (5) which is the integrated form of Eq. (4) and which, unlike expression (3), explicitly shows inverse cyanide dependence.

$$-\frac{d[\mathrm{Ni(CN)_4{}^{2-}}]}{dt} = k'_{\mathrm{obsd}}\,\frac{[\mathrm{Ni(CN)_4{}^{2-}}]}{[\mathrm{CN^-}]}$$

$$= k_r\,\frac{[\mathrm{Ni(CN)_4{}^{2-}}]\,[\mathrm{L^{n-}}]}{[\mathrm{CN^-}]} \qquad (4)$$

$$(A_i - A_t) + A_i \ln\frac{A_t}{A_i} = -\frac{\epsilon.1}{4}\,.\,k'_{\mathrm{obsd}}t \qquad (5)$$

The plot of left hand side of equation number 5 *vs* time gives a straight line and the slope gives the value of k'_{obsd} and so k_r. It may be that these workers did not follow their reaction beyond 30% or ignored the later part of reaction and were led to an erroneous conclusion. It may be noted that Eq. (5) approximates to a first order rate equation at the beginning of reaction that is when $A_t \approx A_i$. According to them step 2 of their scheme will be the rate determining step. This again is in conflict with their statement that a rapid equilibrium exists between $Ni(CN)_4^{2-}$ and the ligand in reverse reaction prior to the rate determining step. Also they have reported that for forward rate a plot of log v_i *vs* log C_{CN} gave a slope equal to 3.9 (~4.0) (they have not shown these plots in the paper under discussion).[1] The initial velocity v_i was presumably estimated from slopes of concentrations – time curves. It would be difficult to differentiate between the slopes of three and four in these initial rate plots and they seem to have erred in this respect. The inverse cyanide dependence observed by us[2] and others[3-6] would bring the rate determining step one step earlier than the last step.

Thus their postulation that a mixed cyanide $NiL(CN)^{1-n}$ is first produced which adds up three cyanide ions to form tetracyanonickelate giving rise to third order dependence of CN^- does not appear to be sound. On the other hand, according to the mechanism postulated by Margerum *et al.*[3-5] and confirmed by us[2] and Pagenkopf[6] for some other aminocarboxylates a third order dependence is interpreted as leading to formation of $NiL(CN)_3^{-(n+1)}$ from NiL^{2-n} followed by rapid addition of the fourth cyanide ion. This eminently plausible mechanism is given here under:

$$NiL^{2-n} + CN^- \overset{K_1}{\rightleftharpoons} NiL(CN)^{(1-n)} \text{ (fast)} \tag{6}$$

$$NiL(CN)^{1-n} + CN^- \overset{K_2}{\rightleftharpoons} NiL(CN)_2^{-n} \text{ (fast)} \tag{7}$$

$$NiL(CN)_2^{-n} + CN^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} NiL(CN)_3^{-(n+1)} \text{ (r.d.s.)} \tag{8}$$

$$NiL(CN)_3^{-(n+1)} + CN^- \overset{K_4}{\rightleftharpoons} Ni(CN)_4^{2-} + L^{-n} \text{ (fast)} \tag{9}$$

The stability constant for $Ni(TTHA)^{4-}$ can be evaluated using the stability constant (β_4) for $Ni(CN)_4^{2-}$ and observed rate constants[1] by the following expression:

$$\frac{\beta_4}{K_{Ni(TTHA)}} = \frac{k_f}{k_r} = K = \frac{4.6 \times 10^4}{1.73 \times 10^{-5}} = 2.66 \times 10^9$$

Hence

$$K_{Ni(TTHA)} = \frac{2.5 \times 10^{30}}{2.66 \times 10^9} = 9.40 \times 10^{20}, \text{ and}$$

$$\log K_{Ni(TTHA)} = 20.97$$

which is very much different from the literature value ($\log K_{Ni(TTHA)} = 18.1$).[7] If they had taken the third step as the rate determining step and evaluated k_r from plots of Eq. (5) they would have got correct value of k_r and $K_{Ni(TTHA)}$.

Lastly, a total of ten aminocarboxylates[2-6] have been shown to follow the proposed mechanism. It appears unlikely that the TTHA should behave differently.

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