KINETICS OF LIGAND SUBSTITUTION REACTION: NICKEL(II)-TRIETHYLENETETRAMINEHEXAACETATE WITH CYANIDE IONS

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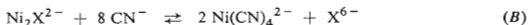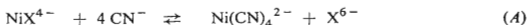
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The kinetics and mechanism of the reactions of nickel(II)-triethylenetetraminehexaacetate chelates with cyanide ions were examined. Similarly as in the reaction of the nickel(II)-EDTA chelate, the formation of mixed complexes with cyanide and triethylenetetraaminehexaacetic acid was verified. The transition between nickel(II)-triethylenetetraminehexaacetate chelates and nickel(II)-cyanide complex is kinetically controlled by the presence of three cyanide ions around one nickel atom in the chelate molecule.

The formation of tetracyanatonickelate(II) ions is slower in the presence of EDTA[1,2] compared with the reaction of hydrated nickel(II) ions with cyanide[3] or with the reaction of nickel(II)-polyamine complexes with cyanide[4]. For the reaction of nickel(II)-EDTA chelate with cyanide ions the formation of the mixed complex Ni–(EDTA)–(CN) is typical, while the formation of stable mixed complexes was not observed in the study of the reaction of iminodiacetate or N-methyliminodiacetate nickel(II) chelates with cyanide[5].

In the present paper the kinetics of the formation and dissociation of tetracyanatonickelate(II) ions are examined in the presence of triethylenetetraminehexaacetic acid (H_6X). Because nickel(II) ions form with H_6X 1 : 1 and 2 : 1 molar ratio metal to ligand chelates[4], the studied ligand substitution process is expected to proceed according to the reactions

$$NiX^{4-} + 4 CN^- \rightleftarrows Ni(CN)_4^{2-} + X^{6-} \qquad (A)$$

$$Ni_2X^{2-} + 8 CN^- \rightleftarrows 2 Ni(CN)_4^{2-} + X^{6-} \qquad (B)$$

under the proposal that the reaction products are identical in both cases.

EXPERIMENTAL

Apparatus and reagents. The concentration of the $Ni(CN)_4^{2-}$ was measured with the ultraviolet spectrophotometer Unicam SP 800 (Unicam Instr., England) with a thermostated cell compartment. pH values of the solutions examined were measured with a glass electrode using the Radiometer PHM—25 (Denmark). The H_6X solution was prepared from the r.g. chemical (Dojin Pharmaceutical Laboratories, Japan) and standardized by visual titration with standard zinc solution[6]. The solution of nickel(II) chloride was prepared from the r.g. chemical (Merck,

Darmstadt, Germany) and standardized by an amperometric titration with H_6X reagent[7]. Sodium cyanide solutions were standardized with nickel. The constant ionic strength of the measured solutions was adjusted by the addition of sodium perchlorate. All solutions used (sodium hydroxide, buffers) were prepared from r.g. chemicals and kept CO_2 free.

Procedure. Similarly as in the papers of Margerum and coworkers[1-3] this study was based on the spectrophotometric determination of the concentration of tetracyanatonickelate(II) ion in dependence on time. On Fig. 1 the spectrum of $Ni(CN)_4^{2-}$ is shown and also the spectra of $Ni(CN)_4^{2-}$ formed at a typical rate during the reaction of nickel(II) H_6X chelate with cyanide. The absorbance was read at 268 nm, where $Ni(CN)_4^{2-}$ exhibited a high maximum, while the adsorbance of the reagent and of the nickel(II) chelate are minimum. The spectra on Fig. 1 show two isosbestic points under the conditions when respective spectral scans were made in dependence on time. This phenomenon may indicate a transition from a set of reactants in rapid equilibrium to a set of products without the formation of any intermediates. The concentration

$$[Ni(CN)_4^{2-}] = A_t - A_0/a(\varepsilon_{Ni(CN)_4} - \varepsilon_0) \qquad (1)$$

of $Ni(CN)_4^{2-}$ was determined from the absorbance data using the expression (1), where a is the cell length; A_t the sum of the adsorbance of $Ni(CN)_4^{2-}$ complex and the adsorbance of all other complex species formed, such as $NiX(CN)^{5-}$; A_0 is the initial adsorbance at zero time. The molar absorptivity of $Ni(CN)_4^{2-}$, $\varepsilon_{Ni(CN)_4}$, was equal to 11 330, and the molar absorptivity of the reaction mixture ε_0 varied from 20 to 100. Equation (1) is valid only when the cyanide concentration was constant during the rate measurement and therefore an excess of cyanide was used. The concentration of the nickel(II) chelates during the course of the reactions studied was calculated from the spectrophotometric data using equation (1) and one of the following expressions:

$$[NiX^{4-}]_T = C_{Ni} - [Ni(CN)_4^{2-}], \qquad (2)$$

$$[Ni_2X^{2-}]_T = 0.5(C_{Ni} - [Ni(CN)_4^{2-}]), \qquad (3)$$

where C_{Ni} is the total concentration of nickel and $[NiX^{4-}]_T$ is the sum of the concentrations of all nickel(II) chelates ($NiX^{4-} + NiX(CN)^{5-} + NiX(CN)_2^{6-} \ldots$) present in the system studied prior to the rate step; similarly $[Ni_2X^{2-}]_T$ is the sum of the concentrations of all nickel(II) chelates ($Ni_2X^{2-} + Ni_2X(CN)^{3-} + Ni_2X(CN)_2^{4-} + \ldots$).

RESULTS

The Kinetics of Forward Reaction of the Binuclear Nickel(II) Chelate with Cyanide Ions

H_6X formed 1 : 1 and 2 : 1 metal to ligand ratio chelates with nickel(II) ions. The stability constants of these chelates differ significantly; $\log K(NiX^{4-}) = 18.1$, $\log K(NiX^{4-} + Ni^{2+} \rightleftarrows Ni_2X^{2-}) = 32.4$ (see[10]). For the treatment of the kinetic data presented in this study it is very important to know which type of nickel(II) chelate is present in the system studied, at zero time. In their study, connected with the determination of the stability constants of H_6X chelates, Bohigian and Martell[8] neglected the existence of the binuclear nickel chelate in the system containing equimolar amounts of nickel and the reagent. As shown[9], such an approximation led,

however, to calculation of less accurate values of the equilibrium constants. According to Harju[9,10] it can be concluded that, in solutions in which the molar ratio of nickel to the ligand is 1 : 1, the binuclear chelate predominates at pH below approx. 6. In alkaline solutions the relative amount of the 2 : 1 nickel chelate decreases but remains measurable. When, on the other hand the molar ratio, metal : ligand = 2 : 1, the formation of the 1 : 1 chelate is minimum in the pH interval 8 − 10. Therefore the rate of the reaction of the binuclear nickel(II) chelate with cyanide ions was first examined.

When sodium cyanide was added to a solution of Ni_2X^{2-} chelate, an instantaneous increase of absorbance was observed. This phenomenon led to the proposal that some type of mixed chelate Ni— X—CN was formed prior to the rate determining step. The results of the rate measurements gave a linear dependence of $\log [Ni_2X^{2-}]_T$ vs time, indicating pseudo-first order dependence on $[Ni_2X^{2-}]_T$. The corresponding values of the pseudo-first order rate constant k_0 are summarized in Table I. A dependence of the log value of the observed rate constant k_0 on the logarithm of the total cyanide concentration is a line with slope equal to 2. On the basis of the given results, fast formation of a mixed ligand chelate $Ni_2X(CN)_2^{4-}$ was supposed. The mixed

FIG. 1

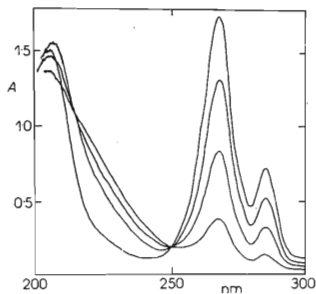UV Spectra Recorded During the Reaction of NiX^{4-} Chelate with Sodium Cyanide

1 cm cell; $C_{Ni} = 1 . 10^{-4}$M; $C_{CN} = 1.5 . 10^{-2}$M; 24°C. 1 spectrum of $Ni(CN)_4^{2-}$; 2 spectrum obtained 1.5 min after mixing of NiX^{4-} with cyanide; 3 as 2, 6.5 min after mixing; 4 as 2, 17 min after mixing.
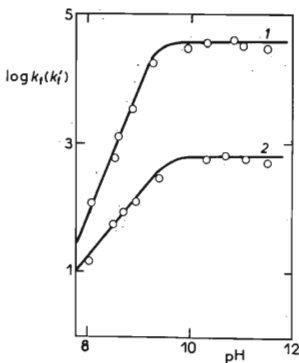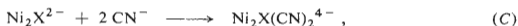
FIG. 2

Dependence of the Formation Rate Constants, k_f and k_f', on pH at 24°C and I 0.10

Dependence of the rate constant: 1 k_f'; 2 k_f.

ligand chelate is further transformed to $Ni(CN)_4^{2-}$ according to the reactions

$$Ni_2X^{2-} + 2\,CN^- \longrightarrow Ni_2X(CN)_2^{4-}, \tag{C}$$

$$Ni_2X(CN)_2^{4-} + 6\,CN^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2\,Ni(CN)_4^{2-} + X^{6-}. \tag{D}$$

The rate equation of the rate determining step was formulated as

$$d[Ni_2X^{2-}]/dt = k_0[Ni_2X^{2-}]_T = k_f[Ni_2X(CN)_2^{4-}]\,[CN]_T^2 \tag{4}$$

where $[CN]_T$ is defined as

$$[CN]_T = C_{CN} - 2[Ni_2X(CN)_2^{4-}]. \tag{5}$$

In equation (5) C_{CN} is the total concentration of cyanide. If the stability constant of the mixed ligand chelate $Ni_2X(CN)_2^{4-}$, defined by the expression

$$K_{Ni_2X(CN)_2}^{CN} = [Ni_2X(CN)_2^{4-}]/[Ni_2X^{2-}]\,[CN]_T^4, \tag{6}$$

is introduced into equation (4), a rate equation of the following form is obtained

$$-d[Ni_2X^{2-}]/dt = k_f^*[Ni_2X^{2-}]\,[CN]^4, \tag{7}$$

where $k_f^* = K_{Ni_2X(CN)_2}^{CN} \cdot k_f$.

To verify the validity of equation (4), the dependence of the initial velocity v_i on the total concentration of cyanide was tested. In this case the term $[CN]_T$ in equation (4) was replaced by the term C_{CN}, because neglect of $[Ni_2X(CN)_2^{4-}]$ resulted in a small error (Eq. (5)), under conditions when cyanide was presented in a relatively large excess over nickel. The dependence $\log v_i$ vs $\log C_{CN}$ is a straight line with slope equal to 3·9, which indicates the validity of equation (4).

The rate measurements carried out at various pH values (pH 7—12) show that the reaction velocity depends on pH up to approx. 9·5. At pH values higher than the dissociation constant of hydrocyanic acid (pK_{HCN}^H 9·32) the reaction velocity was found constant, as shown on Fig. 2 (curve 2). The slight decrease of the reaction velocity at pH 11—12 was due to hydrolysis of cyanide ions. The value of the constant, k_f, decreased when the hydrogen ion concentration was increased below pH 8; the slope of the dependence $\log k_f$ vs. pH was found to be equal to one (Fig. 2, line 2). The temperature dependence of the rate constant is as follows: $k_f (C_{Ni}$ 1·5 . 10^{-4}M; C_{CN} 1·5 . 10^{-2}M; pH 10·6; I 0·10):

$t, °C$:	14	24	46
k_f, mol^{-2} min^{-1} . 10^{-2}:	4·11	6·78	15·40

This dependence followed the Arrhenius expression. The corresponding value for the activation energy E was found to be 7.75 kcal mol^{-1} at I 0.10. Examination of the influence of ionic strength on the reaction velocity of the nickel(II) chelate with cyanide ions showed a great rate increase with increased ionic strength.

Kinetics of the Forward Reaction of the NiX^{4-} Chelate with Cyanide Ions

In spite of the fact that the $1:1$ molar mixture of nickel(II) ions and H_6X must contain some comparable amount of the binuclear nickel(II) chelate, the preliminary kinetic measurements carried out with this mixture similarly as described in the previous section gave reproducible results. Therefore, all the measurements described were repeated with the $1:1$ nickel to ligand mixture. During these experiments a small but instantaneous increase of absorbance was again observed when sodium cyanide was added to the mixture of nickel(II) ions and TTHA. The concentration of the nickel(II) chelate, decreasing during the course of reaction (A), was calculated according to equations (1) and (2). The results of these measurements gave a linear dependence of log $[NiX^{4-}]_T$ vs time, thus indicating pseudo first order in $[NiX^{4-}]_T$ of the reaction studied. The values of the first order rate constant k'_0 are summarized in Table II. Under identical conditions the reaction velocity is higher than in the case of the Ni_2X^{2-} chelate. The dependence of the observed first order rate constant k_0 on total cyanide concentration is a straight line with slope equal to 3.0. The ob-

TABLE I

Formation Rate Constant for the Reaction of the Ni_2X^{2-} Chelate with Cyanide
I 0.10; pH 10.6; $24°C$.

C_{Ni} M . 10^{-4}	C_{CN} M . 10^{-2}	k_0 min^{-1} 10^2	$k_f = k_0/(C_{CN})^2$ mol^{-2} min^{-1} 10^{-2}
1.00	0.90	5.77	7.12
1.00	2.00	27.7	6.93
1.00	1.60	17.3	6.76
1.50	0.72	3.46	6.67
1.50	1.60	17.3	6.76
1.50	2.25	34.1	6.74
1.50	1.02	6.93	6.66
0.50	0.90	4.97	6.14
0.50	0.42	1.12	6.36
5.00	4.20	11.9	6.76
5.00	2.1	30.1	6.83
		Average:	6.70

tained results led to the formulation of the corresponding rate equation

$$d[Ni(CN)_4^{2-}]/dt = k_0[NiX^{4-}]_T = k_f[NiX(CN)^{5-}][CN]_T^3, \qquad (8)$$

where
$$[CN]_T = C_{CN} - [NiX(CN)^{5-}]. \qquad (9)$$

When the stability constant K_{NiXCN} of the mixed nickel chelate $NiX(CN)^{5-}$ was defined as

$$K_{NiXCN} = [NiX(CN)^{5-}]/[NiX^{4-}][CN]_T \qquad (10)$$

and the term $[NiX(CN)^{5-}]$ was expressed by equation (10) and introduced into equation (8), the resulting rate equation was transformed into

$$d[Ni(CN)_4^{2-}]/dt = k_f K_{NiXCN}[NiX^{4-}][CN]_T^4. \qquad (11)$$

As shown on Fig. 2, the dependence of logarithm of the rate constant k'_f on pH had a similar shape as the similar dependence corresponding to the reactions of the binuclear chelate with cyanide ions. One exception was, however, found: in the region below pH 8 the log k'_f vs pH dependence is linear with slope equal to two.

Similarly as described above, the dependence of the initial velocity v'_i on the total concentration of cyanide was tested and it was found that the dependence of log v'_i vs log C_{CN} is a line with slope equal to 3·9. The temperature dependence of the rate constant k'_f was found to follow the Arrhenius expression and similarly as in the reaction of the binuclear chelate it was observed that the reaction velocity v'_i increased with increased ionic strength.

TABLE II
Formation Rate Constant for the Reaction of the NiX^{4-} Chelate with Cyanide
pH 10·6; I 0·10; 24°C.

C_{Ni} M . 10^{-4}	C_{CN} M . 10^{-2}	k'_0 min^{-1} . 10^2	$k'_f = k'_0/(C_{CN})^3$ mol^{-3} min^{-1} 10^{-4}
1·00	0·50	0·59	4·72
1·00	0·95	4·07	4·75
1·00	1·30	9·89	4·50
1·00	1·75	23·1	4·31
1·50	0·75	1·82	4·31
1·50	1·40	13·9	5·07
1·50	2·02	34·7	4·21
1·50	2·50	69·3	4·44

Kinetics of the Reverse Reaction

It has been observed that the reverse reaction proceeded only in the presence of a relative high excess of H_6X. The rate of the reverse reaction depends linearly on the concentration of $Ni(CN)_4^{2-}$ and on the concentration of H_6X and is suppressed by the presence of cyanide ions. The reverse reaction was found to be first order with respect to $Ni(CN)_4^{2-}$ and the rate equation was formulated as

$$-d[Ni(CN)_4^{2-}]/dt = k_{0,r}[Ni(CN)_4^{2-}] = k_r[Ni(CN)_4^{2-}][X^{6-}] . \qquad (12)$$

The dependence between the observed reverse rate constant $k_{0,r}$ and the concentration of H_6X was determined from the plot of log $k_{0,r}$ vs log C_{H_6X}. This plot was a line with slope equal to 0·9. The experimentally determined values of the rate constants $k_{0,r}$ and k_r are presented in Table III. The comparison with the reaction of tetracyanatonickelate(II)ions with EDTA shows that the reverse reaction involving H_6X is faster[1].

TABLE III

Reverse Rate Constant for the Reaction of $Ni(CN)_4^{2-}$ with H_6X
$[Ni(CN)_4^{2-}] = 3\cdot3 \cdot 10^{-6}$M; pH 10·6; $I = 0\cdot10$; 24°C.

C_{H_6X} M . 10^{-3}	$k_{0,r}$ min^{-1} . 10^7	$k_r = k_{0,r}/C_{H_6X}$ mol^{-1} min^{-1} . 10^5
1·65	0·278	1·68
0·82	0·156	1·90
5·80	1·0	1·72
1·0	0·165	1·65
8·2	1·40	1·71

DISCUSSION

Both studied reactions *A* and *B* involved the displacement of multidentate ligand with monodentate ligands and also the conversion of the octahedral chelate to a squareplanar complex. According to Kolski and Margerum[7] the formation of $Ni(CN)_4^{2-}$ is rapid ($k_f \approx 10^{19}$) and its dissociation very slow ($k_d \approx 10^{-4}$). On the other hand, no quantitative data connected with the rate of formation and dissociation of Ni(II)-H_6X chelates are known up to now. The results obtained by titration with H_6X as titrant[5], however, showed the sluggish nature of the nickel(II) chelates of H_6X.

These findings may lead to the conclusion that the velocity of both reactions studied depended mostly on the rate of H_6X dissociation. The experimental results presented above, however, suggest that cyanide does not accelerate the dissociation of H_6X and that the rate controlling factor is the attachment of CN^- groups around the nickel atom in the chelate molecule. This statement verifies the observed effect of hydroxide ion concentration on the rate of the studied reactions (in the pH range above 9) and also the finding that the rate terms (Eqs (4) and (8)) are valid in the pH interval from $7 - 11.5$. Also the pronounced jump observed at zero time during the examination of the reaction of $Ni(CN)_4^{2-}$ with H_6X suggest the existence of a rapid equilibrium between $Ni(CN)_4^{2-}$ and the reagent prior to the rate determining step. The proposed mechanism for the reaction of Ni_2X^{2-} chelate with cyanide is expressed by reactions (C) and (D) and the attachment of three cyanide ions around the nickel atom appears to be rate controlling factor, similarly as in the case of the reaction of Ni-EDTA chelate with cyanide[1].

There is no possibility of determining experimentally the stability constants of the products of the fast reaction (C), because no experimental data were obtained under conditions when the measurement was carried out at 1 : 1 molar ratio of Ni_2X^{2-} chelate and cyanide. This was due to the fact that the reaction studied proceeds only in the presence of a large excess of cyanide. In the case of the reaction of nickel EDTA chelate with cyanide, when the ratio Ni-EDTA : $CN^- = 1$, the spectrophotometric data, however, enabled the determination of the stability of the mixed nickel–EDTA–cyanide chelate[1].

The equilibrium constant K_D corresponding to reaction (D) was defined by the equation

$$K_D = \frac{[Ni(CN)_4^{2-}]^2 [X^{6-}]}{[Ni_2X(CN)_2^{4-}] [CN]^6} = \frac{K^2(Ni(CN)_4^{2-})}{K(Ni_2X) K(Ni_2X(CN)_2)}, \qquad (13)$$

The value of the constant K_D cannot be determined experimentally because it was impossible to determine the concentrations of all components in the equilibrium state. Substitution of the known values of the stability constants $K_{Ni(CN)_4}$ and $K(Ni_2X)$ $(K(Ni(CN)_4) = 10^{30.5}$ and $K(Ni_2X) = 10^{32.4})^{1.9}$ into equation (13) enabled, however, expression of the constant K_D as

$$K_D = 10^{28.6}/K(Ni_2X(CN)_4), \qquad (14)$$

Substitution of the value K_D by the ratio k_f/k_r in equation (14) led to the calculation of the value of the stability constant of the mixed ligand chelate $Ni_2X(CN)_2$. Using the values of the forward and reverse rate constants determined in this study and equation (14), the stability of the mixed-ligand chelate $Ni_2X(CN)_2^{4-}$ was determined by the value $10^{21.6}$. This value is acceptable: it is lower than the stability constant of the binuclear nickel(II)-H_6X chelate and lower than the corresponding constant of the $Ni(CN)_4^{2-}$ complex.

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