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Kinetics and Mechanism of Complex Formation between 1-(2-Hydroxyphenyl)-3,5-diphenylformazan and Ammineaquonickel(II) Complexes

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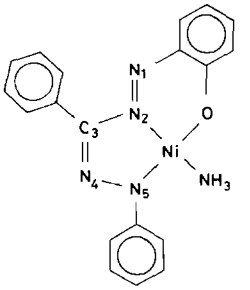
A kinetic study is reported on the reaction between nickel(II) perchlorate and the tridentate ligand 1-(2-hydroxyphenyl)-3,5-diphenylformazan, resulting in two linkage isomers, in ammonia ammonium perchlorate buffers in an ethanol–water (50 wt.%) mixture. The medium dependence of the rate law and the isomer product ratio were analysed on the basis of the Eigen–Wilkins mechanism. The first step of the two-ring chelate coordination seems to be the formation of the Ni(II)–phenoxide bond, followed by a rate-determining Ni(II)–N ring closure.

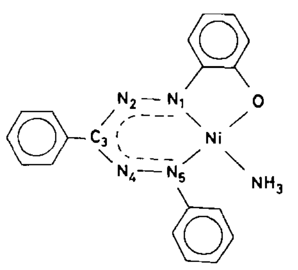
The isomer rearrangement reaction gave information on the decomposition of the complex. The pH dependence of the rate of decomposition indicates the closure of the first ring to be rate-determining.

Introduction

A previous kinetic study of complex formation between copper(II) and 1-(2-hydroxyphenyl)-3,5-diphenylformazan in an ammoniacal ethanol–water mixture has brought evidence for a stepwise coordination of the tridentate ligand to the metal ion [1]. In this reaction the existence of an intermediate of supposedly reduced denticity of the formazan was proved both kinetically and spectrophotometrically. Unfortunately isolation of the intermediate did not succeed. However in the analogous reaction of nickel(II) we could isolate an intermediate (A) which in contrast to the more stable isomeric form (B) [2, 3] has a five-membered formazan ring.



A



B

In a view of the known structure of the nickel(II) intermediate [4] it seemed of interest to study the mechanism of complex formation between nickel(II) and the 1-(2-hydroxyphenyl)-3,5-diphenylformazan and subsequently reconsider the copper(II) reaction in the light of the results obtained. This study, again conducted in an ammoniacal 50 wt.% ethanol–water mixture at 25.0 °C, is reported here.

Experimental

Chemicals

The preparation of 1-(2-hydroxyphenyl-3,5-diphenylformazan (H_2Fo), ammine[1-(2-hydroxyphenyl)-3,5-diphenylformazanato]nickel(II) (isomer A) and ammine[1-(2-hydroxyphenyl)-3,5-diphenylformazanato]nickel(II) (isomer B) have been described [3].

Ethanol–water mixtures (50 wt.%) were prepared as described earlier [1]. All other chemicals were of reagent grade.

Properties of Complexes in Solution

In contrast with the copper intermediate [1] the nickel isomer A does not add nickel(II) or copper(II) when treated with an excess of the metal salts. The more extensive hydrolysis of $Cu(H_2O)_6^{2+}$ compared to $Ni(H_2O)_6^{2+}$ [5] and the fact that in the medium employed in this study no hydrolysis takes place for $Cu(NH_3)_x(H_2O)_{6-x}^{2+}$ [1] justifies to neglect hydrolysis in $Ni(NH_3)_x(H_2O)_{6-x}^{2+}$ complexes.

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Kinetic Runs

The same medium was used as for the analogous copper(II) reactions; the same preventions against air-oxidation were taken [1].

The fast complex formation reactions between the formazan and the nickel(II) ion were followed spectrophotometrically by mixing equimolar quantities of both reactants in the equipment used for the rearrangement reactions in the copper(II) system (method B of ref. 1). The concentration of both reactants was 7.0×10^{-5} mol dm^{-3}. The reaction rate was independent of the wavelength (15,000–27,000 cm^{-1}). Second-order rate-constants were calculated from the measured absorbance (at 18,000 cm^{-1}) against time using the computer program LSKIN II [6]. Fits were better than 2%.

The slow rearrangement reactions were measured with a Beckman Acta CIII spectrophotometer. The reaction rates were independent of the complex concentration (varied between $(0.4–1.6) \times 10^{-4}$ mol dm^{-3}) and the wavelength used. The complex concentration in the reported rate measurements was 10^{-4} mol dm^{-3}. The reactions with no added excess formazan were followed at 18,400 cm^{-1} or 19,600 cm^{-1}. The medium dependence of the formazan dependent reaction path was measured at a formazan concentration of 5.0×10^{-5} mol dm^{-3}. The wavelength used for these experiments was 15,000 cm^{-1}. First-order rate constants were calculated using the computer program LSKIN I [7].

All reactions studied go to completion. The reactions were performed at (25.0 ± 0.1) °C and an ionic strength of 0.10 mol dm^{-3}.

Results and Discussion

Complex Formation

Under conditions of equimolar concentrations of formazan (henceforth denoted as H_2Fo) and nickel(II) the formation of the mixed product follows a second-order rate-law. By varying the pH of the ammonia buffer medium and using the analysis method described for the copper(II) reaction [1] we proved that only the monoanionic form HFo^- (in which the phenolic proton is split off) of the formazan participates in the second-order complex formation reaction:

$$\text{rate} = k(\text{obsd}) \cdot [HFo^-] \cdot [Ni]_{\text{total}} \qquad (1)$$

in which k(obsd) can be calculated from the experimental rate data by using the spectrophotometrically determined value (0.043 ± 0.003) of the acid dissociation constant of the formazan [1].

In the buffer medium employed nickel(II) is present in the form of mixed ammineaquocomplexes $Ni(NH_3)_x(H_2O)_{6-x}^{2+}$ [8]. Principally each of these may be active in complex formation. An exact analysis of the contribution of each complex to the overall rate can only be given when all relevant stepwise formation constants of the ammine complexes are known. As this is not the case for ethanol–water mixtures we started the analysis by using in a first approximation the known aqueous values [8]. Performing this analysis from eqn. (1) of reference [1] (but including the hexaammine complex) we found that under the present experimental conditions only the triammine and tetraammine complexes are engaged in complex formation.

We may then use the simplified rate equation:

$$\text{rate} = k_3 \cdot [Ni(NH_3)_3(H_2O)_3^{2+}] \cdot [HFo^-] + k_4 \cdot [Ni(NH_3)_4(H_2O)_2^{2+}] \cdot [HFo^-] \qquad (2)$$

In order to understand the relation between the two reaction routes and the two reaction products it is illuminating to look at the equilibrium between the ammine complexes concerned:

$$Ni(NH_3)_3(H_2O)_3^{2+} + NH_3 \underset{k_4^{H_2O}}{\overset{k_3^{NH_3}}{\rightleftharpoons}} Ni(NH_3)_4(H_2O)_2^{2+} + H_2O$$

This equilibrium may be complicated by the appearance of mixed $H_2O–C_2H_5OH$ complexes, without however changing the essential features of the mechanism. It is very well established [9, 10] that nickel(II) complex formation reactions follow the Eigen–Wilkins mechanism in which the dissociatively activated rate-determining entry of the incoming ligand is preceded by a relatively rapid outer-sphere pre-equilibrium. Using this concept we may put in an obvious notation:

$$k_3^{NH_3} = K_{OS,3}^{NH_3} \cdot k_3^{Ni-OH_2} \qquad (3)$$

$$k_n = K_{OS,n}^{HFo^-} \cdot k_n^{Ni-OH_2} \; (n = 3, 4) \qquad (4)$$

Now the product ratio P of the two isomeric complexes formed in the reaction is a straightforward function of the ammonia concentration (and independent of pH). From Table I it is clear that:

$$P = \left\{\frac{[A]}{[B]}\right\}_{\text{product}} = f \cdot [NH_3] \qquad (5)$$

with $f \simeq 1$ mol^{-1} dm^3.

As will be clear in the following this result can be explained by assuming that the tetraammine complex will form isomer A and the triammine will form B. Then

$$P = \frac{k_4}{k_3} \times \frac{k_3^{NH_3}}{k_4^{H_2O}} \cdot [NH_3] \qquad (6)$$

TABLE 1. Summarized Kinetic Results of the Complex Formation Reaction between 1-(2-Hydroxyphenyl)-3,5-diphenylformazan and Ammineaquonickel(II) Complexes in 50 wt.% Ethanol–Water Mixtures at 25.0 ± 0.1 °C and an Ionic Strength of 0.10 mol dm^{-3}.

$[NH_3]$ mol dm^{-3}	q[a]	k(obsd)[b] mol^{-1} dm^3 s^{-1}	k(calc)[c] mol^{-1} dm^3 s^{-1}	p[d]
2.50	4	3.02×10^2	3.07×10^2	2.33
2.00	1	5.32×10^2	5.13×10^2	1.86
1.50	8	1.05×10^3	1.01×10^3	1.22
1.25	2	1.62×10^3	1.55×10^3	1.00
1.00	2	2.57×10^3	2.64×10^3	0.85
0.75	2	4.47×10^3	5.19×10^3	0.67
0.50	5	1.11×10^4	1.24×10^4	0.47
0.25	6	3.10×10^4	3.00×10^4	0.28

[a] q is the number of independent experiments performed at one ammonia concentration. [b] k(obsd) is the mean value of the observed rate constants. [c] k(calc) from eqn. (9) using the parameter values given in the text. [d] p = product ratio isomer A/isomer B.

Combining eqns. (5) and (6) gives

$$\frac{k_3}{k_4} \times \frac{k_4^{H_2O}}{k_3^{NH_3}} \simeq 1 \text{ mol}^{-1} \text{ dm}^3 \tag{7}$$

Combining eqns. (3), (4) and (7) with the supposed equality $K_{OS,3}^{HFo^-} = K_{OS,4}^{HFo^-}$ gives that the numerical value of the quotient

$$\frac{k_4^{Ni-NH_3}}{k_4^{Ni-OH_2}} \text{ equals } K_{OS,3}^{NH_3} \text{ (in units mol}^{-1} \text{ dm}^3\text{);}$$

$K_{OS,3}^{NH_3}$ is calculated from an electrostatic model (Fuoss [11, 12]) to be 0.32 mol^{-1} dm^3 (a = 500 pm).

The outcome of this analysis in which we tentatively have equated

$$k_3 = \frac{k_4 k_3^{NH_3}}{k_4^{H_2O} f} = \frac{k_4 K_4}{f} \tag{8}$$

(K_4 is the fourth stepwise formation constant of the Ni^{2+}–NH_3 system; f = 1 mol^{-1} dm^3) seems to be reasonable.

Continuing the treatment of the rate data, eqn. (8) gives a simplification of eqn. (1) of ref. 1 to (f = 1 mol^{-1} dm^3)

$$\text{k(obsd)} = \frac{k_3 \cdot (1 + f[NH_3])}{1 + K_4[NH_3] + K_4K_5[NH_3]^2 + K_4K_5K_6[NH_3]^3} \tag{9}$$

Equation (9) was fitted to the data presented in Table I using a weighted least-squares computerized analysis. Under the condition of non-negative parameter values the best fit yielded that the $K_4[NH_3]$ and $K_4K_5[NH_3]^2$ contributions are negligible within the experimental error.

For the remaining constants the calculation resulted in:

$$k_3 = 3.3 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}; K_4K_5K_6 = 24 \text{ mol}^{-3} \text{ dm}^9.$$

The value 24 for the product $K_4K_5K_6$ may be compared to the aqueous Bjerrum value [8] of 55.

In order to evaluate the results obtained we rewrite eqn. (4) as

$$k_3 = p \cdot K_{OS,3}^{HFo^-}(\text{calc}) \cdot k_3^{Ni-OH_2} \tag{10}$$

in which $K_{OS,3}^{HFo^-}$(calc) is the value for the outer-sphere constant calculated from the electrostatic (Fuoss) model [11, 12] and p is a factor correlating the stability constant of the outer-sphere complex lying on the path of the reaction with the one of the electrostatic model [13].

$k_3^{Ni-OH_2}$ may be equated to the rate constant of the nickel–water bond rupture in the triammine complex [10, 14] for which the aqueous value of 2.5×10^6 s^{-1} (25 °C) is available [15]. By lack of better we shall use this value here, although a slight increase of the rate constant is expected on going from water to our 50 wt.% ethanol–water mixture [14].

Taking the usual value (500 pm) for the distance of closest approach, presumably between the phenolic O$^-$ of the formazan and Ni^{2+}, $K_{OS}^{HFo^-}$(calc) becomes 4.9 mol^{-1} dm^3. Putting the other known parameter values in eqn. (10) gives $p = 2.7 \times 10^{-3}$, which is rather low, but not completely unexpected in view of the values observed for similar systems [16].

Now it is well known that when water is replaced from a coordination sphere which already contains a large number of nitrogen donor atoms, the straightforward Eigen–Wilkins mechanism may change to the so-called sterically controlled substitution [9] with rate-determining ring-closure, resulting in a decrease of the overall rate. Our results therefore can also be interpretated on the basis of a rate-determining Ni–N ring-closure, while the formation and rupture of the Ni–O$^-$ bond is a fast pre-equilibrium.

Rearrangement of Isomer A to Isomer B

The rearrangement reaction obeys a first-order rate-law. The resulting (pseudo) first-order rate-constant was found to be a linear function of the excess formazan concentration:

$$\text{k(obsd)} = k^0 + k^1 \cdot [H_2Fo]_{\text{total}} \tag{11}$$

The medium dependence of the formazan independent part of the rate constant was investigated by

TABLE II. Formazan Independent Part of the Rate Constant for the Rearrangement Reaction Isomer A → Isomer B as a Function of the Ammonia and the Ammonium Perchlorate Concentration.[a]

$[NH_3]$ mol dm^{-3}	$[NH_4^+]$ mol dm^{-3}	$10^5 \cdot k^0_{obsd.}$ s^{-1}	$10^5 \cdot k^0_{calc.}$[b] s^{-1}	$[NH_3]$ mol dm^{-3}	$[NH_4^+]$ mol dm^{-3}	$10^5 \cdot k^0_{obsd.}$ s^{-1}	$10^5 \cdot k^0_{calc.}$[b] s^{-1}
2.50	0.100	4.72	4.59	1.50	0.080	1.74	1.81
2.50	0.083	4.09	3.87	1.50	0.050	1.15	1.18
2.50	0.060	3.08	2.91	1.50	0.030	0.73	0.77
2.50	0.050	2.67	2.49	1.30	0.100	1.82	1.80
2.50	0.040	2.26	2.07	1.15	0.100	1.53	1.50
2.50	0.030	1.78	1.65	1.00	0.100	1.21	1.21
2.50	0.020	1.33	1.23	1.00	0.060	0.72	0.75
2.50	0.010	0.79	0.81	1.00	0.050	0.60	0.63
2.25	0.100	4.16	3.97	1.00	0.030	0.39	0.41
2.00	0.100	3.34	3.36	1.00	0.020	0.26	0.29
2.00	0.080	3.05	2.74	0.85	0.100	0.86	0.93
2.00	0.060	2.17	2.12	0.75	0.100	0.71	0.76
2.00	0.050	1.84	1.81	0.75	0.050	0.37	0.40
2.00	0.030	1.20	1.18	0.75	0.030	0.23	0.25
2.00	0.020	0.79	0.87	0.60	0.100	0.48	0.53
2.00	0.010	0.44	0.56	0.50	0.050	0.19	0.20
1.75	0.100	2.78	2.78	0.50	0.030	0.12	0.13
1.50	0.100	2.21	2.22	0.40	0.100	0.31	0.26

[a] Initial $[A] = 1.0 \times 10^{-4}$ mol dm^{-3}; $I = 0.10$ mol dm^{-3}; t = 25.0 ± 0.1 °C; in 50 wt.% ethanol–water; measured at 18,400 cm^{-1} an 19,600 cm^{-1}. [b] From eqn. (12) and the parameter values given in the text.

performing reactions at different ammonia and ammonium perchlorate concentrations. The results are in Table II. Plots of k^0 *versus* $[NH_4^+]$ gave straight lines with non-zero intercepts proportional to $[NH_3]^2$. Plots of $k^0 \cdot [NH_3]^{-1}$ *versus* $[NH_3]$ showed straight lines at low ammonia concentrations but a saturation effect at high ammonia concentrations. In the absence of ammonia no reaction took place. These features suggest to express k^0 as

$$k^0 = \frac{k_1^0 \cdot [NH_3]^2 \cdot [NH_4^+]}{1 + a[NH_3]} + k_2^0[NH_3]^2 \qquad (12)$$

A computerized weighted least-squares fitting of eqn. (12) to the values in Table II gives:

$k_1^0 = (2.15 \pm 0.15) \times 10^{-4}$ mol^{-3} dm^9 s^{-1};

$k_2^0 = (6.2 \pm 2.0) \times 10^{-7}$ mol^{-2} dm^6 s^{-1};

$a = (0.88 \pm 0.20)$ mol^{-1}.

The formazan-dependent part of the rearrangement reaction was studied at excess formazan concentration. The value of k^1 (eqn. (11)) was calculated by substracting the formazan independent part (eqn. (12)) from the overall rate.

The medium dependence of k^1 is given in Table III. Studying the pH dependence of k^1 at a constant ammonia concentration proved the involvement of both the neutral formazan and the anion in the rate equation. Both species give a medium-independent contribution but only the anion showed an additional contribution, inversely proportional to $[NH_3]$. Therefore the rate constants of Table III were subjected to a least-squares fitting on the basis of eqn. (13)

$$k^1[H_2Fo]_{total} = k_1^1[H_2Fo] + k_1^2[HFo^-] + k_1^3[HFo^-][NH_3]^{-1} \qquad (13)$$

giving: $k_1^1 = (0.31 \pm 0.30)$ mol^{-1} dm^3 s^{-1};

$k_1^2 = (3.03 \pm 0.10)$ mol^{-1} dm^3 s^{-1};

$k_1^3 = (0.75 \pm 0.07)$ s^{-1}.

As seen from Table III the fit is satisfactory.

Conclusion

The preceding section has brought indications that in the formation reaction of the [1-(2-hydroxyphenyl)-3,5-diphenylformazanato]nickel(II) complexes the rate-determining step is either the formation of the Ni–O (phenoxide) bond or ring-closure (presumably of the second nitrogen donor) preceded by a fast equilibrium coordination between ammine-aquonickel(II) complexes and the phenoxidic oxygen. In this reaction the triammine gives the stable end-product isomer B, whereas the tetraammine gives the intermediate isomer A. It is interesting to note that for the analogous formation reaction of nickel(II) with 1-(2-carboxyphenyl)-3,5-diphenylformazan only the triammine is reactive and no intermediate is formed [17].

TABLE III. Formazan Dependent Part of the Rate Constant for the Rearrangement Reaction Isomer A → Isomer B as a Function of the Ammonia and the Ammonium Perchlorate Concentration.[a]

$[NH_3]$ mol dm^{-3}	$[NH_4^+]$ mol dm^{-3}	$10^4 \cdot k(obsd)$ s^{-1}	$k^1_{obsd.}$ [b] mol^{-1} dm^3 s^{-1}	$k^1_{calc.}$ [c] mol^{-1} dm^3 s^{-1}
1.00	0.100	0.86	1.5	1.4
1.00	0.080	0.90	1.6	1.5
1.00	0.070	0.98	1.8	1.6
1.00	0.050	1.05	2.0	1.9
1.00	0.040	1.06	2.0	2.1
1.00	0.030	1.22	2.4	2.4
1.00	0.020	1.51	3.0	2.7
1.00	0.013	1.53	3.0	3.0
1.00	0.010	1.58	3.1	3.1
2.50	0.100	1.23	1.5	1.9
2.25	0.090	1.25	1.8	1.9
2.00	0.080	1.14	1.7	1.9
1.75	0.070	1.23	2.1	1.9
1.50	0.060	1.10	1.9	2.0
0.80	0.032	1.25	2.4	2.2
0.75	0.030	1.24	2.4	2.2
0.50	0.020	1.25	2.5	2.5
0.40	0.016	1.32	2.6	2.7
0.30	0.012	1.50	3.0	3.0
0.25	0.010	1.58	3.2	3.3

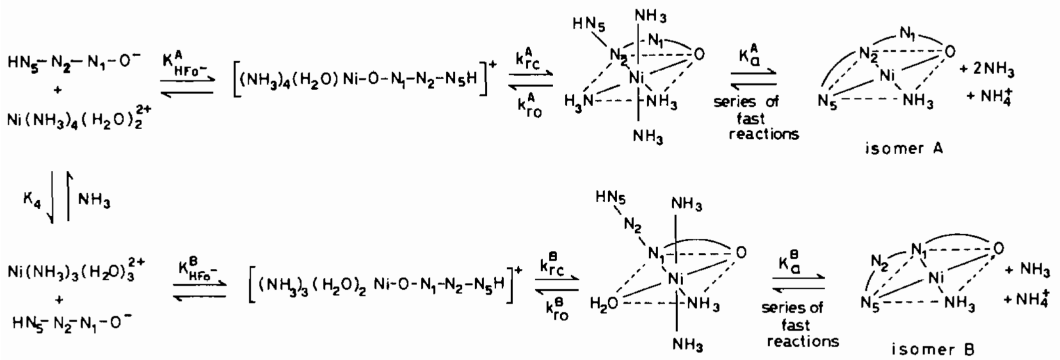
[a] Initial [A] = 1.0×10^{-4} mol dm^{-3}; [Form] = 5.0×10^{-5} mol dm^{-3}; I = 0.10 mol dm^{-3}; t = 25.0 ± 0.1 °C; in 50 wt.% ethanol–water; measured at 15,000 cm^{-1}. [b] k^1 from k(obsd) and applying eqn. (11) with the parameters k_1^0, k_2^0 and a given in the text. [c] k^1 from eqn. (13) with the parameters k_1^1, k_1^2 and k_1^3 given in the text and K_{H_2Fo} = 0.043.

A detailed interpretation of the two reaction routes is hampered by the fact that nothing is known about the relative stability of the isomers of the triammine and the tetraammine. However, it seems reasonable that it is easier for the triammine to give ring-closure at the nitrogen (N_1) in the *cis*-position leading to isomer B followed by rapid formation of the remaining Ni–N_5 bond. Especially if the stable configuration of the tetraammine is a planar structure this type of *cis*-coordination will be blocked and a more removed nitrogen (N_2 or N_5) will coordinate first, leading to the intermediate isomer A.

The preference of the triamminecopper(II) complex for an intermediate structure (no direct formation of the stable isomer B) could then result from the preference of copper(II) for a square coordination, if the intermediate is given a similar structure as the nickel isomer A.

Another possibility is the earlier suggestion [1] that the copper formation reaction leads to an intermediate with a bidentate formazan [1]. This bidentate character of the formazan is borne out by the ability to add a second copper(II). The absence of this coordination made in the present nickel–formazan isomer A could mean that there is a definite difference in structure between the two intermediates.

The rearrangement reaction of the intermediate in the copper(II)-1-(2-hydroxyphenyl)-3,5-diphenylformazan system was found to follow a rate-law similar [1] to the one found for the decomposition of the [1-(2-carboxyphenyl)-3,5-diphenylformazanato]copper(II) complex [17] and was therefore formulated accordingly. It is satisfying that – apart from the saturation term (1 + 0.88 $[NH_3]$) – the present rearrangement reaction of the ammine [1-(2-hydroxyphenyl)-3,5-diphenylformazanato]nickel(II) (isomer A) to isomer B follows the same rate-law, with an additional term also found in the decomposition of the carboxyformazan complex of nickel(II) [17]. The similarity of the values found for the constants a (0.88) in eqn. (12) and f in eqn. (5), describing the product ratio of the two formation paths, makes it reasonable to assume that the slow rearrangement reaction A → B takes the route *via* complete decomposition of complex A, followed by a recombination of nickel(II) and formazan governed by eqn. (2), in a proportion determined by eqn. (5). The medium dependence of the most-important term of the rearrangement rate (eqn. 12) makes it reasonable to assume that the mechanism of decomposition includes a rapid pre-equilibrium between the complex and its protonated form, followed by a rate-determining ring opening. If this mechanism is accepted for the decomposition reaction, microscopic reversibility dictates that in the formation the Ni–N_2 ring closure is also rate determining. The most likely scheme for the complete reaction is than as follows:



HN_5–N_2–N_1–O^- denotes the formazan with its essential donor atoms. In this Scheme the rates of formation and decomposition (rearrangement) are governed by the rate constants k_{rc} and k_{ro} for ring closure and ring opening respectively.

The constants in the reaction Scheme can be combined with the experimental rate constants:

$$k_3(\text{formation}) = K^{B}_{HFo^-} \cdot k^{B}_{rc} = 3.3 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1},$$

$$k_4(\text{formation}) = K^{A}_{HFo^-} \cdot k^{A}_{rc} = 2.5 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1},$$

(using eqn. (8) and the aqueous Bjerrum K_4 value [8]),

$$k^0_1(\text{rearrangement}) = K^{A}_{a} \cdot k^{A}_{ro} = 2.15 \times 10^{-4} \text{ mol}^{-3} \text{ dm}^9 \text{ s}^{-1}.$$

From these the equilibrium constant for the equilibrium

$$Ni(NH_3)_4(H_2O)_2^{2+} + HFo^- \rightleftharpoons A + 2NH_3 + NH_4^+$$ is approximately 10^7.

The small pH independent term $k^0_2[NH_3]^2$ in the rearrangement may refer to Ni–N_2 ring opening without the Ni–N_5 pre-equilibrium, followed by a Ni–N_1 ring closure.

It is reasonable to assume that the difference in stability between the isomers A and B is due to a greater ring tension in A leading to a high value of k^{A}_{ro} compared to k^{B}_{ro}.

Following reference [1] the formazan dependent part of the rearrangement can be described as an attack of the formazan-anion HFo^- or the neutral molecule at the A isomer, whether or not after splitting off the ammonia ligand. Entering and leaving of the formazan will be a synchronous process of bond making and bond breaking at the nickel ion.

Only when the process results in a situation where the formazan is coordinated as in isomer B a net rearrangement is observed.

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