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Kinetics of the Ligand Exchange Reaction between 1,10-Phenanthroline and Ethylenediaminediacetatonickelate(II)

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Introduction

The exchange of a metal ion between two multidentate ligands has been shown in many cases to be much more rapid than the solvent dissociation rate of the reactant complex [1]. As a result, interesting and unique types of interactions and effects are seen in the mechanism of ligand exchange reactions. Several years ago, the ligand exchange reaction of 1,10-phenanthroline (phen) and $Ni(trien)^{2+}$ was studied [2]. The results showed an initial rapid formation of $Ni(trien)(phen)^{2+}$ followed by a slow displacement of trien by phen. The one proton assisted rate of trien dissociation was about a factor of 200 times larger than the corresponding term for $Ni(trien)^{2+}$. These results showed that the coordinated phen accelerated the dissociation of trien from $Ni(trien)(phen)^{2+}$. It is of interest to investigate the same exchange reaction, shown in eqn. (1) using another tetradentate ligand, ethylenediaminediacetic acid (EDDA). The use of EDDA instead of trien gives a complex with two terminal labile sites unlike trien and is less sterically crowded because of the smaller amount of space required by acetate groups compared to amine groups.

$$Ni(EDDA) + 3phen \rightarrow Ni(phen)_3^{2+} + EDDA^{-2} \quad (1)$$

Experimental

Materials

All chemicals were reagent grade and used without further purification with the exception of EDDA which was recrystallized from water. Solutions of Ni(EDDA) were prepared and standardized as described elsewhere [3]. Boric acid–mannitol was used as the buffer and NaCl was used to control the ionic strength.

Nickel Monophenanthroline

Crystalline nickel monophenanthroline was prepared and analyzed according to procedures previously described [2]. *Anal.* Calcd for $Ni(phen)(H_2O)_2(NO_3)_2$: Ni, 14.7; phen, 45.1. Found: Ni, 15.4, phen, 44.8.

Kinetic Runs

All kinetic runs were made using a Cary Model 14 spectrophotometer by following the increase in absorbance due to the formation of $Ni(phen)_3^{2+}$ at either 343 nm or 508 nm. Kinetic data were obtained over the pH range of 4.54 to 6.55 using a boric acid–mannitol buffer. The pH held constant throughout the reaction. This was demonstrated at several pH values by mixing the reactants and monitoring the pH as the reaction proceeded. The ionic strength was held constant at 0.1 M using NaCl and the temperature was maintained constant at 25.0 ± 0.1 °C.

Stability Constants of Ni(EDDA)(phen)

Data for the calculation of the stability constants for the formation of Ni(EDDA)(phen) and $Ni(HEDDA)(phen)^+$, as shown in eqns. (2) and (3), were obtained by mixing known amounts of $Ni(phen)(H_2O)_2(NO_3)_2$ and H_2EDDA and titrating the mixture using carbonate free NaOH. An attempt was made to measure a stable protonated complex, $Ni(HEEDA)^+$, by the same method. All titrations were done at an ionic strength of 0.1 M and at 25.0 ± 0.1 °C.

$$Ni(phen)^{2+} + EDDA^{2-} \rightarrow Ni(EDDA)(phen) \quad (2)$$

$$Ni(EDDA)(phen) + H^+ \rightarrow Ni(HEDDA)(phen)^+ \quad (3)$$

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TABLE I. Stability Constants for Ni(L)(phen) and NiL Species where L is trien or EDDA. All values at 25 °C, $\mu = 0.1$ *M*.

Reaction	K
$Ni^{2+} + EDDA^{2-} \rightarrow NiEDDA$	4.47×10^{13} [a]
$Ni(phen)^{2+} + EDDA^{2-} \rightarrow Ni(EDDA)(phen)$	$(5.66 \pm 0.53) \times 10^{11}$ [b]
$Ni(EDDA)(phen) + H^+ \rightarrow Ni(HEDDA)(phen)^+$	$(5.04 \pm 2.18) \times 10^{2}$ [b]
$Ni^{2+} + trien \rightarrow Nitrien^{2+}$	6.31×10^{13} [c]
$Ni(phen)^{2+} + trien \rightarrow Ni(trien)(phen)$	3.98×10^{13} [d]

[a] Reference 6.. [b] This study. [c] Reference 7. [d] Reference 2.

TABLE II. First-Order Rate Constants for the Reaction of NiEDDA and Phen. All values at 25 °C, $\mu = 0.1$ *M*.

pH	$phen_{total} \times 10^3$, *M* [a]	$k^\circ \times 10^4$, sec^{-1}
6.55	0.990	0.908
6.55	2.49	2.04
6.51	2.89	2.22
6.53	3.99	3.26
6.21	7.14	5.41
5.72	7.14	5.23
5.40	7.14	5.12
5.39	7.14	5.20
5.39	7.14	5.14
5.20	7.14	5.09
5.06	7.14	4.96
4.92	7.14	4.67
4.79	7.14	4.90
4.72	7.14	4.63
4.63	7.14	4.68
4.54	7.14	4.88

[a] Values represent total phen after correction for phen which reacted immediately upon mixing to make Ni(EDDA)(phen).

Results and Discussion

Stability Constants

The titration of $Ni(NO_3)_2$ and H_2EDDA yielded only a value for the formation of Ni(EDDA). The results were analyzed using the method of Schwarzenbach [4] as described by Jonassen and Westerman [5]. Attempts to include a term for $NiHEDDA^+$ using the known value of NiEDDA led to a worse fit of the data. The lack of this term is consistent with previous work [6] in which no protonated terms were reported. The titration of $Ni(phen)^{2+}$ and H_2-EDDA, also analyzed as described above, yielded values for both eqns. (2) and (3). The values are shown in Table I. The presence of phen coordinated to nickel lowers the stability constant for the addition of EDDA by about 80. This is surprising in view of the stability constant for the formation of $Ni(trien)(phen)^{2+}$ compared to that of $Ni(trien)^{2+}$, given in Table I, which show that the addition of trien to $Ni(phen)^{2+}$ is not affected by the presence of phen. The value for the protonation of Ni(EDDA)(phen) is extremely small and results in the formation of appreciable amounts of $Ni(HEDDA)phen)^+$ only at low pH values.

Kinetics of the Phenanthroline Exchange with Ni(EDDA)

The mixing of Ni(EDDA) and phen gives rise to the immediate formation of a ternary complex, Ni(EDDA)(phen). The formation of this species is complete within 0.1 sec. A discussion of its formation will be reported elsewhere [8]. The ternary complex reacts slowly with phen to yield $Ni(phen)_3^{2+}$ and EDDA as shown in eqn. 4:

$$Ni(EDDA)(phen) + 2phen \rightarrow Ni(phen)_3^{2+} + EDDA \quad (4)$$

All runs were carried out with at least a 20 fold excess of phen over Ni(EDDA)(phen) and at constant hydrogen ion concentration. The data, listed in Table II, gave excellent first-order plots and thus followed equation 5. An increase of the total phen concentration at constant pH yielded a corresponding increase

$$\frac{-d[Ni(EDDA)(phen)]}{dt} = k^\circ [Ni(EDDA)(phen)] \quad (5)$$

in k° (see runs at pH 6.5, Table II), thus establishing first-order behavior in phen. As the data in Table II show, the reaction is pH dependent. A plot of the second-order rate constant *vs.* pH, shown in Fig. 1, demonstrates this.

There was no evidence of any biphasic behavior in the first-order plots over three half lives. This means that there was only one reactant and rules out the possibility of $Ni(HEDDA)(phen)^+$ as a reactant species. In view of this, the proton dependence must be due to protonation of the partially unwrapped EDDA prior to complete dissociation. Thus k° of equation 5 can be written as shown in eqn. (6). A plot of $k^\circ/[phen]$ *vs.* $[H^+]$, shown in Fig. 2, was

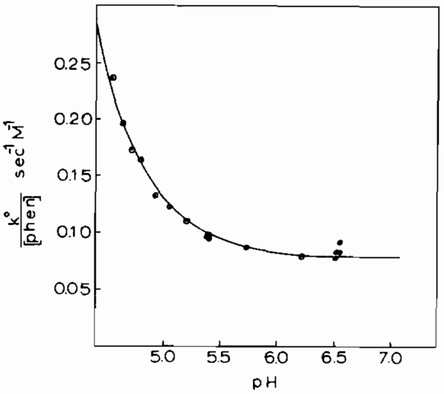

Fig. 1. Variation of second-order rate constant with pH at 25 °C and $\mu = 0.1$ *M*. Solid line calculated using equation 6 and resolved rate constants.

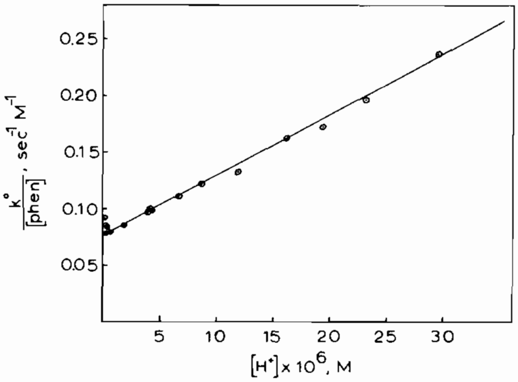

Fig. 2. Resolution of second-order rate constant into proton dependent and independent terms of equation 6.

$$\frac{k^\circ}{[\text{phen}]} = k_P^{NiLP} + k_{H,P}^{NiLP}[H^+] \qquad (6)$$

linear over the entire pH range studied. The least squares values from the plot of Fig. 2 are $k_P^{NiPL} = (7.84 \pm 0.18) \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$ and $k_{H,P}^{NiLP} = (5.17 \pm 0.16) \times 10^3\ M^{-2}\ \text{sec}^{-1}$.

Phenanthroline imposes the requirement that at least two dentate sites of EDDA dissociate from nickel before it can coordinate. Thus the first-order dependence seen in phen means that the rate determining step must lie after a glycine segment of EDDA has dissociated and after the addition of phen to a partially unwrapped intermediate species. The first-order proton dependence seen shows that below pH 6, hydrogen protonates the partially unwrapped EDDA, preventing it from re-coordinating to nickel. Protonation would occur at the free nitrogen. The reaction order dependence does not allow a determination of the exact location of the rate determining step which must be either nickel–nitrogen or nickel–acetate bond rupture of the glycine segment of EDDA still coordinated to nickel. The mechanism is shown in Fig. 3.

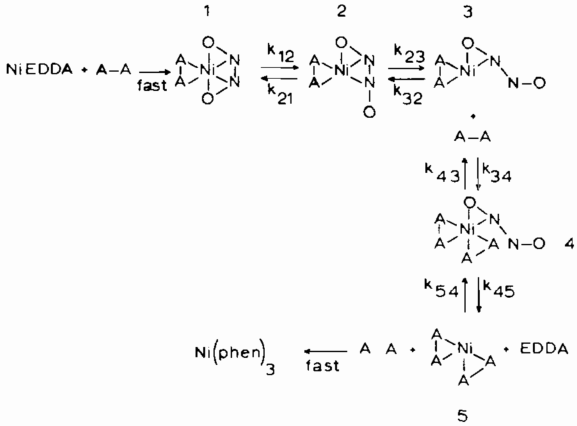

Fig. 3. Mechanism for exchange of phen and EDDA on nickel. Protons, carbon atoms and charges have been omitted for simplicity. A–A represents phen and O–N–N–O represents EDDA.

The effect phen has on the reaction can be seen by predicting the rate of dissociation from the relative stability of the intermediate preceeding the rate determining step, species IV of Fig. 3, and the value of k_{45} approximated by the rate of dissociation of glycine. This method has been used in both ligand and metal exchange reactions [3, 10–12] and is shown in eqn. (7). The relative stability constant, K_{rel}, is defined in terms of the stability of the ligands

$$k_P^{NiPL} = K_{rel} k^{Nigly} K_{el} \qquad (7)$$

and ligand segments coordinated to nickel compared to the stability of the initial complex as shown in equation 8. The value of k^{Nigly} is 0.024 sec^{-1} [13] and $K_{el} = 0.422$ and

$$K_{rel} = \frac{K_{Nigly} \times K_{Ni(phen)_2}}{K_{Ni(EDDA)(phen)}} = 134 \qquad (8)$$

represents a correction for the added electrostatic attraction of the free acetate arm for nickel which is not present in the model system [11]. The predicted value obtained from eqn. (7) is 1.35 M^{-1} sec^{-1} which is about 17 times greater than that seen experimentally for k_P^{NiPL} of 0.0784 M^{-1} sec^{-1}.

The presence of phen coordinated to nickel does not affect the rate of water loss of nickel [14] so that the slower than expected dissociation rate cannot be due to phen affecting bond rupture of the remaining glycine segment. Use of the dissociation of Niglycine$^+$ to predict the dissocation of intermediate IV is not perfect since the intermediate has a free glycine segment which can re-coordinate to the nickel. Further, intermediate IV is in equilibrium with intermediate III so that a certain fraction of the system has two open coordination sites which can accept the free glycine segment. To the extent that the above occurs, the experimental rate will be slower than that predicted from a model which has no unwrapped ligand segment for re-coordination.

The pathway involving protonation of the partially unwrapped EDDA appears normal. Protonation of the unwrapped ligand segment prevents its re-coordination to nickel and results in an accelerated rate. The ratio of $k_{H,P}^{NiPL}/k_{P}^{NiPL}$ in the present study is about 6.6×10^4 which compares with the analogous ratio of k_{H}^{NiT}/k^{NiT} in the $Ni(trien)^{2+}$ system of 8.5×10^4 [9].

The present system is in marked contrast to the ligand exchange of $Ni(trien)(phen)^{2+}$ and phen [2]. In that system, a ternary complex, $Ni(trien)(phen)^{2+}$ formed immediately upon mixing, analogous to the present system but then trien completely dissociated from nickel before a second phen was able to coordinate. Further, the rate of dissociation was 200 times faster than expected. This was attributed to an enhanced ICB effect as a result of the presence of phen.

The mechanism of formation and dissociation of aminocarboxylic ligands involves initial bond formation of the carboxylate group followed by ring closure involving nitrogen coordination [15]. Both steps contribute to the observed formation rate making it impossible to sort out any ICB contribution to the rate of formation. The same applies to the dissociation. Ring opening involving nickel–nitrogen bond rupture followed by nickel–acetate bond rupture must both contribute to the rate of dissociation. Thus the presence or absence of an ICB effect cannot be determined in the present study. In conclusion, since the experimental rate is within a factor of 17 of that expected and certainly not faster, it can be stated that phen does not appear to alter the rate of dissociation of EDDA from nickel or exert any special effect on its dissociation.

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