BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 833—835 (1969)

Kinetics of Multidentate Ligand Substitution Reactions. V. Effects of Ammonia and Thiocyanate Ion on the Substitution Reaction of Eriochrom Black T with Nickel(II)-Ethylenediaminetetraacetate Chelate

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(Received July 24, 1968)

In an earlier paper,[1] the substitution reaction of Eriochrom Black T (BT) with nickel(II)-ethylenediaminetetraacetate (Ni(II)-EDTA) chelate was studied spectrophotometrically. The study showed that reaction proceeds through two simultaneous reaction paths involving doubly- and completely-deprotonated BT anions. The present paper deals with the effects of ammonia, thiocyanate and bromide ions on the reaction of BT with Ni(II)-EDTA chelate. Even in the presence of ammonia or thiocyanate, Ni(II)-EDTA chelate showed the same kinetic behavior as in the absence of ammonia or thiocyanate, but the rate of reaction was reduced appreciably. This was ascribed to the fact that the concentration of normal Ni(II)-EDTA chelate, which is reactive in the present situation, is reduced by the formation of a mixed ligand chelate involving ammonia or thiocyanate.

Experimental

Reagents. The preparations of nickel(II) perchlorate and ethylenediaminetetraacetate solutions were described previously.[1] Ammonia and potassium thiocyanate were of analytical reagent grade and used without further purification. A spectrophotometric test showed that the addition of ammonia or thiocyanate did not affect the absorption curve of BT solution (pH=10.0) containing 10.0 mM ethylenediaminetetraacetate. The concentration of ammonia was determined by titrating against standard hydrochloric acid using Methyl Orange as indicator. The concentration of thiocyanate was standardized against a standard silver nitrate solution.[2]

Apparatus and Experimental Procedure. All apparatus and experimental procedures were as described previously.[3] Reactions were followed spectrophotometrically by observing the absorbance at 630 mμ. The ionic strength of sample solutions was adjusted to 0.30 by adding an appropriate amount of sodium perchlorate (ammonia system) or potassium nitrate (thiocyanate or bromide system). A pseudo first-order rate constant, k^+, was obtained from the plot of log-$(A_{\mathrm{HD}}/(A-A_{\mathrm{NiD}}))$ against time, t, where A_{HD}, A and A_{NiD} have the same meanings as previously.[1]

Results and Discussion

Effects of ammonia and thiocyanate on the substitution reaction of BT with Ni(II)-EDTA chelate were examined at 25°C for solutions containing an excess of ethylenediaminetetraacetate in the pH range 8.50 to 10.50. Therefore, no buffer reagent was used in this study. Even in the presence of ammonia or thiocyanate, nickel(II)-EDTA chelate shows quite the same kinetic behavior as in their absence.[1] However, as illustrated in Fig. 1, ammonia or thiocyanate appreciably reduces the rate of the substitution reaction. The reduction in the pseudo first-order rate constant, k^+,[1] increases

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[1] M. Kodama, C. Sasaki and M. Murata, This Bulletin, **41**, 1333 (1968).

[2] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York (1951), p. 647.

[3] K. Kodama, This Bulletin, **40**, 2575 (1967).

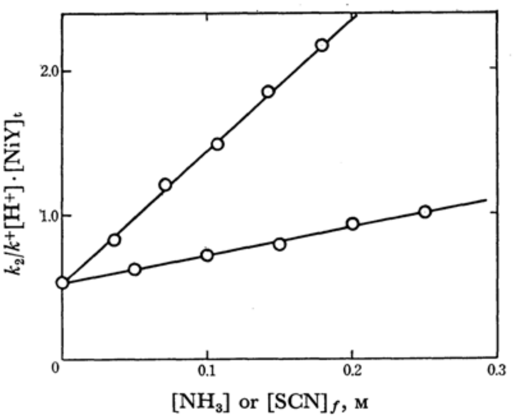

Fig. 1. The relation between $1/k^+$ and the concentration of ammonia or thiocyanate ion.
$\mu=0.30$, 25°C, $\lambda=630$ mμ
Concentration of nickel(II)-EDTA = 10.45 mM
Concentration of uncomplexed EDTA = 10.0 mM

with increasing concentration of ammonia or thiocyanate. All the above facts suggest that the present reaction has the same mechanism as in the absence of ammonia or thiocyanate, but that the concentration of reactive Ni(II)-EDTA chelate in the reaction is reduced by the addition of ammonia or thiocyanate. This can be explained simply by considering the formation of a mixed ligand chelate involving ammonia or thiocyanate which is much less reactive than a normal chelate, NiY^{2-}. If the present reaction proceeded only through NiY^{2-}, the apparent rate constant, k^+, should be given by

$$k^+=\frac{k_2^+\cdot k_2}{[H^+]}\cdot\frac{[NiY]_t}{1+K^{NCS}\cdot[NCS]_f}$$

$$\text{or}\quad \frac{k_2^+\cdot k_2}{[H^+]}\cdot\frac{[NiY]_t}{1+K^{NH_3}\cdot[NH_3]_f} \qquad (1)$$

where $k_2{}^+$ and k_2 have the same meanings as in a previous paper,[1)] and other notations are defined: $[NiY]_t$, the total concentration of Ni(II)-EDTA chelate; $[NCS]_f$, the concentration of uncomplexed thiocyanate, $[NH_3]_f$,[*1] the concentration of uncomplexed ammonia; $K^{NCS}=[NiY(NCS)^{3-}]/[NiY^{2-}]\cdot[NCS^-]$; $K^{NH_3}=[Ni(NH_3)Y^{2-}]/[NiY^{2-}]\cdot[NH_3]$.

The $k_2[NiY]_t/[H^+]\cdot k^+$ value was plotted against $[NH_3]_f$ or $[NCS]_f$. Results are shown in Fig. 1. The slope *vs.* intercept ratios of the linear relation in Fig. 1 were 17.1 and 3.47 for the ammonia and thiocyanate systems, respectively.

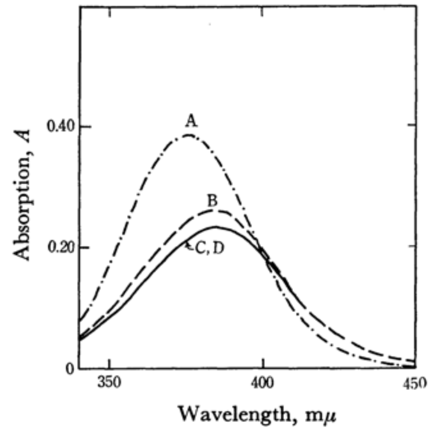

Fig. 2. Absorption curves of nickel(II)-EDTA chelate.
Concentration of nickel(II)-EDTA chelate = 10.0 mM
Concentration of uncomplexed EDTA = 20.0 mM
$\mu=0.50$, pH = 9.70
A: 0.25 M ammonia
B: 0.25 M potassium thiocyanate
C: 0.25 M potassium bromide
D: none

As shown in Fig. 2, the addition of ammonia or thiocyanate results in a change in the absorption curve of Ni(II)-EDTA chelate. This can be ascribed to the formation of a mixed ligand chelate involving ammonia or thiocyanate. From the increase in absorbance, K^{NCS} and K^{NH_3} were determined with the aid of the following relation derived thermodynamically,

$$\log\frac{A-A_{NiY}}{A_{NiYX}-A}=\log K^X+\log[X]_f \qquad (2)$$

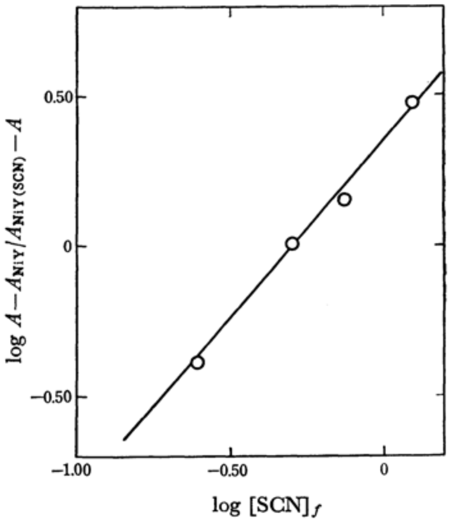

Fig. 3. Determination of K^{SCN}.
$\mu=2.0$, pH = 9.70, $\lambda=380$ mμ
Concentration of nickel(II)-EDTA = 20.0 mM
Concentration of uncomplexed EDTA = 20.0 mM
Concentration of thiocyanate ion ranged from 0.25 to 1.25 M

[*1] Precisely, $[NH_3]_f$ means the concentration of uncomplexed ammonia.

where K^X denotes K^{NH_3} or K^{NCS} and $[X]_f$, $[NH_3]_f$ or $[NCS]_f$ and where A_{NiY} is the absorbance of a solution containing only NiY^{2-}, A_{NiYX}, the absorbance of a solution in which all Ni(II)-EDTA chelate is present in the form of NiYX, and A the absorbance of a solution containing both Ni(II)-EDTA chelate and ammonia or thiocyanate.

A typical result obtained for the thiocyanate system was given in Fig. 3 (at 380 mμ). The K^{NCS} value was estimated as 3.02 (μ=0.30) from the linear relation. In a similar way, K^{NH_3} was determined as 12.6 (μ=2.0) at 370 mμ, in good agreement with a reported value.[4]

The agreement of the slope *vs.* intercept ratio in the kinetic study with the K^X value determined strongly supports the present authors' explanation that the present reaction proceeds only through NiY^{2-}, and that the mixed ligand chelate involving thiocyanate or ammonia is essentially non-reactive.

In the d^8 octahedral system, any reaction going by the coordination number seven (pentagonal bipyramid) would inevitably lead to a considerable loss in crystal field separation energy, and hence be slow.[5] Therefore, the explanation that ammonia or thiocyanate may form the seventh bond to the nickel(II) ion in the pentagonal bipyramid reaction intermediate, thus making the Ni(II)-EDTA chelate less reactive, is impossible as far as crystal field effects are concerned.

Generally, the rate of dissociation of water from nickel(II) ion is expected to be much faster than that of ammonia. Therefore, if the formation of a Ni(II)-OH_2 bond prior to the formation of the first Ni(II)-BT bond is essentially required in the present reaction, the ammonia coordinated to the nickel(II) ion might considerably reduce the rate of reaction of BT with Ni(II)-EDTA chelate. The same explanation may also be applied to the effect of thiocyanate on the reaction. To understand the precise role of the coordinated ammonia or thiocyanate in the present exchange reaction, further systematic and advanced investigations must be undertaken. The effect of bromide ion which does not form a mixed ligand chelate with NiY^{2-} was also studied, but no practical effect observed.

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4) D. W. Margerum and H. M. Rosen, *J. Am. Chem. Soc.*, **89**, 1088 (1967).

5) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York (1958), p. 108.