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Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

# Kinetics and Mechanism of the Metal-Exchange Reaction of the Bis(8-mercaptoquinolato)nickel(II) Chelate with Copper(II) Ion by an Exchange-Extraction Method

KENSAKU HARAGUCHI[1] and HENRY FREISER*

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The kinetics and mechanism of back-extraction of the bis(8-mercaptoquinolato)nickel(II) chelate ($NiL_2$) with copper(II) ion from a chloroform phase to an aqueous phase has been studied in the pH range of 3.7–5.8 at the ionic strength 0.1 ($NaClO_4$) and 25 °C. The reaction order with respect to $NiL_2$ was first order while that for copper ion varied from first to zero with increasing copper ion concentration. The observed rate constant was pH independent. The experimental results indicate that the exchange reaction proceeds in the aqueous phase through two intermediates, the partially unbonded nickel–8-mercaptoquinoline chelate and the dinuclear mixed-metal complex. At low copper ion concentration, the rate-determining step is the dissociation of nickel from the dinuclear intermediate, whereas at high copper ion concentration, the formation step of the partially unbonded intermediate becomes the rate-determining step.

## Introduction

It has been demonstrated that the solvent extraction technique is an elegant technique for the detailed examination of the kinetics and mechanism of inherently rapid metal complexation reactions[2–8] and ligand substitution reactions of water-insoluble neutral chelates.[9–11] The technique can be extended to determine the kinetics and mechanism of metal ion exchange reactions by measuring the rate of exchange extraction, generally expressed as eq 1, where the subscripts o and a represent organic and aqueous phase, respectively.

$$m\mathrm{M_IL}_n(\mathrm{o}) + n\mathrm{M_{II}}^{m+}(\mathrm{a}) \rightarrow n\mathrm{M_{II}L}_m(\mathrm{o}) + m\mathrm{M_I}^{n+}(\mathrm{a}) \qquad (1)$$

Although the exchange-extraction technique is frequently used in analytical procedures to improve the selectivity to metal ions,[12–15] little attention has, as yet, been given to the detailed reaction mechanism. Only semiquantitative kinetic descriptions of exchange extraction for some dithizonates,[16] cupferronates, and dithiocarbamates[17] have been reported so far.

The present paper describes the detailed kinetic study of the back-extraction of the bis(8-mercaptoquinolato)nickel(II) chelate ($NiL_2$) with copper(II) ion from chloroform to an aqueous phase (eq 2).

$$\mathrm{NiL_2(o)} + \mathrm{Cu^{2+}(a)} \rightarrow \mathrm{CuL_2(o)} + \mathrm{Ni^{2+}(a)} \qquad (2)$$

## Experimental Section

**Reagents.** 8-Mercaptoquinoline (HL) was obtained from Sigma Chemical Co. (St. Louis, MO) as the hydrochloride. A $1.00 \times 10^{-2}$ M stock solution was prepd. by dissolving this reagent in 3 N hydrochloric acid. A chloroform solution of HL was prepd. by extracting the reagent from an acetate buffer solution at pH 5.0. A chloroform solution of $NiL_2$ was prepared by extracting nickel(II) ion with a chloroform solution of HL at pH 6.5 with use of an excess of nickel(II) to avoid having any free HL in the resultant organic phase. An extraction time of 15 h was sufficient to obtain the equilibrium. The concentration of $NiL_2$ was standardized spectrophotometrically by measuring the absorbance at 538 nm.

Solutions that are $10^{-2}$ M in $Ni(ClO_4)_2$ and $Cu(ClO_4)_2$ in $10^{-2}$ M $HClO_4$ were prepared from metal salt hydrates (G. Frederick Smith Chemical Co., Columbus, OH). All chemicals used were reagent grade. All aqueous solutions were prepared with distilled–deionized water. The ionic strength was maintained at 0.1 in all measurements with $NaClO_4$.

**Apparatus.** The extraction kinetic apparatus has been described previously.[8,18] The stirrer was made of Teflon to avoid metal contamination. The concentration of nickel in the aqueous phase was determined with a Varian AA-6 atomic absorption spectrophotometer at 232 nm with an air–acetylene flame. UV and visible absorptions were measured with a Perkin-Elmer 552 spectrophotometer using 10-mm quartz cells. All pH measurements were made with an Orion 701 pH meter calibrated with pH 4.00 and 7.00 standard buffer solutions. The temperature was controlled to 25 ± 0.1 °C with use of a thermoelectric water bath.

**Kinetic Procedure.** The kinetic runs were carried out under pseudo-first-order conditions, copper ion in the aqueous phase being in large excess over $NiL_2$ in the organic phase. After thermal equilibration in a water bath, 100-mL portion of aqueous copper solution and an equal volume of chloroform solution $2.00 \times 10^{-5}$ M in $NiL_2$ were transferred carefully into the reaction flask. The reaction was begun by starting the high-speed stirring motor. Experiments were carried out in the "plateau" region, where an increase of stirring speed gave no effect on the rate of back-extraction. At selected time intervals, samples were taken into test tubes by means of positive nitrogen pressure and then immediately centrifuged to separate the phases. The concentration of nickel back-extracted into the aqueous phase was determined by means of atomic absorption spectrophotometry.

The pseudo-first-order rate constants, $k_{\mathrm{obsd}}$, were determined from

$$\ln \frac{[\mathrm{NiL_2}]_{\mathrm{o},t=0}}{[\mathrm{NiL_2}]_{\mathrm{o},t}} = k_{\mathrm{obsd}}t \qquad (3)$$

where $t$ is the reaction time and $[\mathrm{NiL_2}]_{\mathrm{o},t=0}$ and $[\mathrm{NiL_2}]_{\mathrm{o},t}$ are the

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(1) On study leave from the Government Industrial Development Laboratory, Hokkaido, Sapporo, Japan.
(2) (a) C. B. Honaker and H. Freiser, *J. Phys. Chem.*, **66**, 127 (1962). (b) B. E. McClellan and H. Freiser, *Anal. Chem.* **36**, 2262 (1964).
(3) J. S. Oh and H. Freiser, *Anal. Chem.*, **39**, 295 (1967).
(4) P. R. Subbaraman, Sr. M. Cordes, and H. Freiser, *Anal. Chem.*, **41**, 1878 (1969).
(5) G. Colovos, A. Yokoyama, and H. Freiser, *Anal. Chem.*, **47**, 2441 (1975).
(6) K. Yamada, K. Nakagawa, K. Haraguchi, and S. Ito, *Nippon Kagaku Kaishi*, 294 (1975).
(7) K. Yamada, K. Nakagawa, K. Haraguchi, and S. Ito, *Nippon Kagaku Kaishi*, 1431 (1975).
(8) K. Haraguchi and H. Freiser, *Inorg. Chem.*, in press.
(9) K. Haraguchi and S. Ito, *Nippon Kagaku Kaishi*, 2082 (1972).
(10) K. Haraguchi, K. Yamada, and S. Ito, *J. Inorg. Nucl. Chem.*, **36**, 1611 (1974).
(11) K. Haraguchi, K. Nakagawa, and S. Ito, *J. Inorg. Nucl. Chem.*, **41**, 379 (1979).
(12) H. Bode and K. J. Tusche, *Fresenius' Z. Anal. Chem.*, **157**, 414 (1957).
(13) H. Bode and F. Newman, *Fresenius' Z. Anal. Chem.*, **172**, 1 (1960).
(14) Z. Marczenko, M. Krasiejko, and L. Choluj, *Chem. Anal. (Warsaw)*, **8**, 375 (1963).
(15) K. Ohashi, M. Ozaki, and H. Freiser, *Bunseki Kagaku*, **30**, 139 (1981).
(16) K. Ohashi and H. Freiser, *Anal. Chem.*, **52**, 2214 (1980).
(17) B. Ya. Spivakov and Yu. A. Zolotov, *Zh. Anal. Khim.*, **24**, 1773 (1969).
(18) S. P. Carter and H. Freiser, *Anal. Chem.*, **51**, 1100 (1979).

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Table I. Summary of the Exchange-Extraction Kinetics of the Bis(8-mercaptoquinolato)nickel(II) Chelate[a] ($NiL_2$) with Copper(II) Ion at Ionic Strength 0.1 ($NaClO_4$) and 25 °C

| $10^4 \times [Cu^{2+}]$, M | pH | $10^3 k_{obsd}$, $s^{-1}$ | $10^4 \times [Cu^{2+}]$, M | pH | $10^3 k_{obsd}$, $s^{-1}$ |
|---|---|---|---|---|---|
| 2.50 | 4.46 | 2.12 | 5.00 | 5.08 | 3.38 |
| 3.75 | 4.45 | 2.69 | 5.00 | 5.80 | 3.79 |
| 5.00[b] | 3.68 | 3.61 | 7.50 | 4.43 | 4.11 |
| 5.00 | 3.92 | 3.72 | 10.00 | 4.36 | 4.86 |
| 5.00 | 4.27 | 3.52 | 15.00 | 4.16 | 5.78 |
| 5.00 | 4.43 | 3.58 | 20.00 | 3.63 | 6.42 |
| 5.00 | 4.68 | 3.29 | 25.00 | 4.03 | 6.67 |
| 5.00 | 4.99 | 3.60 | 30.00 | 4.20 | 6.75 |
| 5.00 | 5.03 | 3.55 | | | |

[a] $[NiL_2]$ in the organic phase is $2.00 \times 10^{-5}$ M. [b] The mean value of $k_{obsd}$ at $[Cu^{2+}] = 5.00 \times 10^{-4}$ M is $(3.56 \pm 0.29) \times 10^{-3}$ $s^{-1}$.

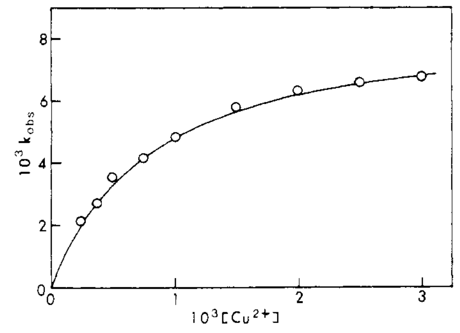

**Figure 1.** Effect of copper ion concentration upon $k_{obsd}$ (ionic strength 0.1 ($NaClO_4$); 25 °C). The solid curve is calculated with the rate constants $k_{12}$ and $k^{NiL_2}{}_{Cu}$ obtained.

concentrations of $NiL_2$ in the organic phase at reaction times zero and *t*, respectively. Since the ratio $[NiL_2]_{0,t=0}/[NiL_2]_{0,t}$ is equal to the ratio $[NiL_2]_{t=0}/[NiL_2]_t$, where $[NiL_2]_{t=0}$ and $[NiL_2]_t$ represent the concentrations of $NiL_2$ in the aqueous phase at reaction times 0 and *t*, respectively, the distribution constant of $NiL_2$, $K_{DC}$, is irrelevant to the concentration of $NiL_2$. Therefore, the observed rate constant, $k_{obsd}$, can be attributed as a pseudo-first-order rate constant of the reaction in the aqueous phase.

## Results and Discussion

Plots of ln $([NiL_2]_{0,t=0}/[NiL_2]_{0,t})$ against the reaction time, *t*, were linear at least up to 2 half-lives through the origin, demonstrating that the reaction was first order with respect to $NiL_2$. From the slopes of these lines the $k_{obsd}$ values were obtained, summarized in Table I. No pH dependence of $k_{obsd}$ was observed in a pH range between 3.7 and 5.8 as shown in Table I, which suggests that there is no acid-catalyzed contribution to the reaction, under the conditions studied.

As shown in Figure 1, plots of $k_{obsd}$ vs. copper ion concentration deviated from linearity, the copper dependence decreasing with increasing concentration, from first- to zero-order dependence.

The reaction sequence (eq 4–6) in the aqueous phase can account for the observed results.

$$\underset{\text{I}}{NiL_2} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{\text{II}}{NiL{\cdot}L} \qquad (4)$$

$$NiL{\cdot}L + Cu^{2+} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{\text{III}}{(NiL{\cdot}L{\cdot}Cu)^{2+}} \qquad (5)$$

$$(NiL{\cdot}L{\cdot}Cu)^{2+} \xrightarrow{k_{34}} \underset{\text{IV}}{CuL_2} + Ni^{2+} \qquad (6)$$

In this mechanism, the reaction proceeds via the formation of two intermediates, II and III; intermediate II is a partially unbonded form of $NiL_2$, and III is a dinuclear intermediate.

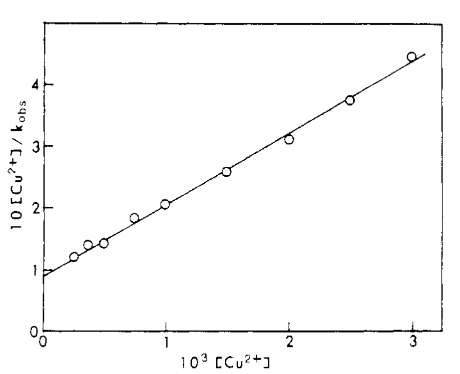

**Figure 2.** Resolution of $k_{obsd}$ into terms of $k_{12}$ and $k^{NiL_2}{}_{Cu}$. The solid line is obtained by a least-squares treatment of the data.

Using steady-state approximations for the intermediate species II and III, we can obtain the expression for the observed pseudo-first-order rate constant as shown by eq 7.

$$k_{obsd} = \frac{k_{12}k_{23}k_{34}[Cu^{2+}]}{k_{21}(k_{32} + k_{34}) + k_{23}(k_{32} + k_{34} - k_{32}[Cu^{2+}])[Cu^{2+}]} \qquad (7)$$

The expression given by eq 7 can be simplified to eq 8 if

$$k_{obsd} = \frac{k_{12}k_{23}k_{34}[Cu^{2+}]}{k_{21}k_{32} + k_{23}k_{32}[Cu^{2+}]} \qquad (8)$$

it is noted that under the conditions of the experiment $[Cu^{2+}] << 1$ and if it is assumed that $k_{32} >> k_{34}$. This assumption is reasonable because the step III → II ($k_{32}$) involves the reaction of the more labile copper ion rather than that of the nickel ion, which is involved in the step III → IV ($k_{34}$). Rearranging eq 8 gives

$$\frac{[Cu^{2+}]}{k_{obsd}} = \frac{k_{21}k_{32}}{k_{12}k_{23}k_{34}} + \frac{[Cu^{2+}]}{k_{12}} \qquad (9)$$

Thus if the mechanism postulated above is correct, the plot of $[Cu^{2+}]/k_{osbd}$ against the copper concentration should give a straight line whose slope is equal to $1/k_{12}$ and whose intercept gives $1/k^{NiL_2}{}_{Cu}$. As shown in Figure 2, the result gave a linear relation, which supports the above assumption. The values $k_{12} = (8.7 \pm 0.4) \times 10^{-3}$ $s^{-1}$ and $k^{NiL_2}{}_{Cu} = (1.1 \pm 0.2) \times 10^1$ $M^{-1}$ $s^{-1}$ were obtained.

Although, unfortunately, no kinetic data of comparable extraction systems are available, the variation of the reaction order with entering metal concentration is not unique. Similar types of kinetic behavior had been reported for metal-exchange reactions of some polyaminopolycarboxylate chelates.[19-21] It is of interest that similar kinetic behavior was observed in spite of the great difference in the characteristic reactivity of the bidentate sulfur-containing ligand HL from that of the multidentate flexible polyaminopolycarboxylates. Unlike the case for the polyaminopolycarboxylate systems, however, $k_{12}$ in the present system was pH independent between pH 3.7 and 5.8. Higher acidity might be expected to accelerate the dissociation of $NiL_2$. In fact, our preliminary observation showed that the equilibrium is attained in about 1 h for the back-extraction of $NiL_2$ with 1 M hydrochloric acid. This observation suggests that the contribution of hydrogen ion to $k_{12}$ is quite small.

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(19) D. W. Margerum, D. L. Janes, and H. M. Rosen, *J. Am. Chem. Soc.*, **87**, 4463 (1965).

(20) R. K. Steinhaus and R. L. Swann, *Inorg. Chem.*, **12**, 1855 (1973).

(21) E. Menstasti and E. Pelizzetti, *Inorg. Chem.*, **17**, 3133 (1978).

It can be noted that the study presented here not only clarifies the mechanism of the back-extraction of $NiL_2$ with copper(II) ion but also validates the extraction technique for the kinetic examination of metal-exchange reactions of water-insoluble chelates.

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Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

# Electron Transfer. 59. Reactions of Pyrazine-Related Radicals and Dihydro Species with Metal-Center Oxidants[1]

A. N. SINGH, P. N. BALASUBRAMANIAN, and E. S. GOULD*

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The reductions of various substituted pyrazines and quinoxalines, using $V^{2+}$ or $Eu^{2+}$ in strongly acid media, yield long-lived colored aromatic radicals. With phenazines, reductants in deficiency give radicals whereas an excess of reductant brings about transfer of a second electron to form the corresponding dihydro aromatics. In the case of 1-deazariboflavin (IV), the radical is observed only as a transient species ($\lambda_{max}$ 665 nm), which is converted rapidly to the dihydro derivative. The specific rates for most of these conversions, when carried out with $V^{2+}$, are great enough to ensure that they occur mainly by outer-sphere paths. Reduction of the 1-deazaflavin to its radical appears to be catalyzed by the dihydro compound. The patterns of specific rates for oxidation of the pyrazinium and quinoxalinium radicals with halopentaamminecobalt(III) complexes indicate that these conversions also utilize an outer-sphere path, a conclusion confirmed in one instance by characterization of the oxidation product as the parent heterocycle with the ring system unhalogenated. Phenazinium radicals are found to react inconveniently slowly with substitution-inert cobalt(III) complexes but measurably rapidly with a number of substitution-labile metal-center oxidants. The observed acidity dependence for oxidation of the *N*-methylphenazinium radical by $Fe^{3+}$ is consistent with the intervention of an N-bound Fe(III)-radical precursor. As observed in flavin-related systems, the dihydro derivatives of the phenazines are more rapid reductants than the corresponding radicals. The acid dependencies for the reactions of these dihydro compounds (and of the dihydro derivatives of riboflavin and 1-deazariboflavin as well) with a series of $(NH_3)_5Co^{III}$ complexes point to partition of each of these reductants between an active basic form and an inactive acidic form with a $pK_A$ value in the range 0.4–1.0. In these reductions there is no acceleration attributable to carboxyl bridging nor any rate enhancements resulting from extension of conjugation in the ligand; we are thus dealing again with outer-sphere processes. log–log plots comparing the reactivities of any two of these dihydro reductants are linear with near-unit slope, in accordance with the model of Marcus. Analogous plots comparing specific rates for a dihydro derivative with those for reduction by $Ru(NH_3)_6^{2+}$ exhibit severe scatter, with Ru(II) reductions of $(NH_3)_5CoCl^{2+}$ and the complexes of $\alpha$-keto acids proceeding unexpectedly rapidly. Attempted Eu(II) reduction of 5-deazariboflavin (VII), in which the pyrazine-like system has been disrupted, yields colorless solutions containing only small steady-state concentrations of the corresponding radical. This deazaflavin, unlike its 1-deaza isomer, catalyzes the reductions, by $Eu^{2+}$, of $Co(NH_3)_5py^{3+}$ and $Co(en)_3^{3+}$.

Electron-transfer processes involving pyrazine-related systems have received a spate of recent and detailed attention. A number of research groups have examined ligated pyrazines in their role as mediators of charge transfer between metal ion centers,[2] whereas the prominence of flavins (which are fused-ring derivatives of pyrazine) as oxidation coenzymes has prompted a multitude of studies of the function which they serve in controlling organic oxidations in vitro.[3] Ancillary areas of investigation are the electrochemistry of pyrazine species[4] and the transformations of metal-bound pyrazine radicals.[5] The recognized richness of the chemistry of pyrazines reflects, in large part, the presence of the two donor centers lying in conjugation in the ring, the ease with which many derivatives undergo separable and reversible 1-and 2-electron reduction, and the persistence of certain pyrazine-related radicals in solution near room temperature.

The present paper deals with the reduction of several substituted pyrazines in aqueous solution at high acidity to the related radicals or dihydro derivatives and with the reactions of these reduced species with a variety of metal-center oxidants.

## Experimental Section

**Materials.** Solutions of the perchlorates of Eu(II)[6a] and V(II)[6bc] were prepared as described. Master solutions of $UO_2(ClO_4)_2$, $Fe(ClO_4)_3$, and $Cu(ClO_4)_2$ were prepared from the hydrated perchlorates (Alfa) and were standardized spectrophotometrically as described.[7] Quinoxaline (Aldrich) was purified by fractional freezing. Samples of 1-deazariboflavin[8a] and 5-deazariboflavin[8b] were generously supplied

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(2) See, for example: (a) Malin, J. M.; Ryan, D. A.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1978**, *100*, 2097. (b) Haddad, M. S.; Hendrickson, D. N.; Cannady, J. P.; Drago, R. S.; Bieksza, D. S. *Ibid.* **1979**, *101*, 898. (c) Von Kameke, A.; Tom, G. M.; Taube, H. *Inorg. Chem.* **1978**, *17*, 1790. (d) Johnson, E. C.; Callahan, R. W.; Ickberg, R. P.; Hatfield, W. E.; Meyer, T. J. *Ibid.* **1979**, *18*, 618.

(3) For recent reviews, see: (a) Hemmerich, P. *Adv. Chem. Ser.* **1977**, *No. 162*, 312. (b) Walsh, C. *Ann. Rev. Biochem.* **1978**, *47*, 881. (c) Bruice, T. C. *Acc. Chem. Res.* **1980**, *13*, 256.

(4) (a) Klatt, L. N.; Rouseff, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 7295. (b) Swartz, J.; Anson, F. C. *Inorg. Chem.* **1981**, *20*, 2250.

(5) (a) Dunne, T. G.; Hurst, J. K. *Inorg. Chem.* **1980**, *19*, 1152. (b) Wu, M.-Y.; Paton, S. J.; Fanchiang, Y.-T.; Gelerinter, E.; Gould, E. S. *Ibid.* **1978**, *17*, 326.

(6) (a) Dockal, E. R.; Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 6673. (b) Guenther, P. R.; Linck, R. G. *Ibid.* **1971**, *93*, 2769. (c) Linck, R. G. *Inorg. Chem.* **1970**, *9*, 2529.

(7) "IUPAC Spectrometric Data"; Butterworths: London, 1963; pp 149 ($Cu^{II}$), 223 ($Fe^{III}$), 550 ($UO_2^{2+}$).

(8) (a) 1-Deazariboflavin, prepared by the procedure of Ashton and coworkers (Ashton, W. T.; Graham, D. W.; Brown, R. D.; Rogers, E. F. *Tetrahedron Lett.* **1977**, *30*, 2551) was donated by the Research Laboratories of Merck Sharp and Dohme. We are grateful to Dr. W. T. Ashton for arranging transfer of this sample. (b) 5-Deazariboflavin was obtained through the courtesy of Dr. C. C. Cheng of the Mid-America Cancer Center with the authorization of the Drug Synthesis and Chemistry Branch of the National Cancer Institute.

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