most convenient way to show this relationship is to plot the equation $\log L_2 = \log L_n - (q - n) \log (H_2O)$. Such plots of our data for maleic acid give positive slopes of 0.5 to 0.8 indicating that n is larger than q but not by more than 1. Whether it is reasonable to expect the hydrogen bonded form to carry more water of hydration than the non-bonded form is moot, but the difference is small and probably permissible. At any rate the effect of urea solutions on hydrogen bonds of this character might be accounted for simply on the basis of differential hydration and the reduction of water concentration. This matter should be tested by measuring hydrogen bonding constants in other mixed solvents of similar water activities.

The Effect of Urea on Hydrogen Bonds.—The effects of urea on hydrogen bonds are given by the changes in the free energies of the bonds resulting from the presence of urea. For maleic acid at the three temperatures the differences between 0 and 7 *M* urea, 130 cal. for carboxyl–carboxylate interactions is in the direction of weakening. For the malonic acids these differences average 90 cal., for carboxyl–carboxyl interactions in the direction of weakening and 240 cal. for carboxyl–carboxylate interactions in the direction of strengthening. The differences are all rather small and not much greater or less than the estimated error (100–200 cal.) from the uncertainties in the *pK* values. We therefore conclude that urea in aqueous solution has little or no effect on such hydrogen bonds beyond that associated with differences related to the lower water concentrations at high urea concentration.

Our first calculations of hydrogen bonding constants were made following the equation of Westheimer and Benfey[10] and showed an *increase* of the bonding constants as urea concentration increased, and it was on this basis that our preliminary reports were made. The more sophisticated treatment outlined and applied above shows that the hydrogen bonding constants decrease with urea concentration but not sufficiently to alter our conclusion that urea does not have a significant effect on intramolecular carboxyl–carboxyl or carboxyl–carboxylate bonds.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI, COLUMBIA, MISSOURI]

The Rates of Formation and Dissociation of 2,2′-Ethylenediamino-bis-(2-methyl-3-butanone)-dioxime Nickel(II) Ions[1]

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The rate of formation $[Ni(EnAO\text{–}H]^+$ follows the law: rate of formation $= k_1[Ni^{+2}][EnAOH^+] + k_2[Ni^{+2}][EnAO]$ with $k_1 = 2.3 \times 10^2$ and $k_2 = 1.5 \times 10^6$ l. moles^{-1} min.$^{-1}$ at 24.3° and $\mu = 1.00$ with LiCl. The acid dissociation of $[Ni(EnAO\text{–}H]^+$ proceeds according to the rate equation: Rate $= k[Ni(EnAO)\text{–}H]^+ + k_1[Ni(EnAO)^{+2}] + k_2[NiEnAO^{+2}][H^+]$: at 24.3° and $\mu = 1.00$, $k = 4.58 \times 10^{-3}$ min.$^{-1}$, $k_1 = 2.65 \times 10^{-2}$ min.$^{-1}$ and $k_2 = 5.8 \times 10^{-2}$ at unit concentration of HCl. Substitution on the amine nitrogen and the loss of one of the chelate rings increases the rate of dissociation in acid. The equilibrium constant for the formation of $[Ni(EnAO)]^{+2}$ from the rate constants is smaller by a factor of $10^{2.5}$ than that obtained by equilibrium measurements. This may be due to the slow Ni(II) catalyzed geometrical rearrangement of the oxime groups or to the stepwise detachment of the ligand in the dissociation.

Introduction

The addition of 2,2′-ethylenediamino-bis-(2-methyl-3-butanone) dioxime (EnAO)[2] to Ni^{+2} in essentially neutral aqueous solution has been shown to lead to the formation of a yellow, planar complex having the structure shown in Fig. 1a. In rapid equilibrium with it is the blue, paramagnetic and presumably octahedral complex (Fig. 1b) which has the hydrogen bond broken by the addition of a hydrogen ion; the other two octahedral positions are probably filled with solvent molecules (not shown).

The kinetics of the formation and decomposition of this type of complex is especially interesting in the light of the work of Wilkins, *et al.*,[3a] on the rate of ligand exchange and the rate of dissociation of C-substituted ethylenediamine nickel(II) complexes in which the rates of dissociation were acid dependent and slower with increased alkyl size. $[Ni(EnAO)]^{+2}$ lends itself to a kinetic study because (a) both the forward and reverse rates are measurably slow, (b) the ligand is a tetradentate which removes the difficulties of varying ligand/metal ratio during the measurements and (c) most of the thermodynamic data necessary for evaluation of the rate expression have previously been measured.[1] Of special interest is the hydrogen ion dependence of the rate of formation and hydrolysis for the light it may shed on the mechanism of this and other complex ion reactions.

In this paper are reported the results of a study of the rate of formation and the rate of acid hydrolysis of $[Ni(EnAO)\text{-}H]^+$ at an ionic strength of 1.00 (LiCl) and 24.3°.

Experimental

$[Ni(EnAO)\text{-}H]ClO_4$ and EnAO were prepared by methods previously described.[1]

Anal. of $[Ni(EnAO)\text{-}H]ClO_4$. Calcd. for $NiC_{12}H_{25}N_4O_6Cl$: Ni, 14.14; N, 13.49; Cl, 8.54. Found: Ni, 14.23; N, 13.28; Cl, 8.57.

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[1] For previous papers on this topic see R. K. Murmann, *J. Am. Chem. Soc.*, **80**, 4147 (1958); **79**, 521 (1957).

[2] The following abbreviations will be used in this paper: (EnAO) = 2,2′-ethylenediamino-bis-(2-methyl-3-butanone)-dioxime, $[Ni(EnAO)]^{+2}$ = 2,2′-ethylenediamino-*bis*-(2-methyl-3-butanone) dioxime nickel(II) ion (Fig. 1b), $[Ni(EnAO)\text{-}H]^+$ is meant to express the product of the ionization of an hydrogen ion from $[Ni(EnAO)]^{+2}$ in the formation of a hydrogen bond. (MeEnAO) = 2,2′-propylenediamino-bis-(2-methyl-3-butanone)-dioxime. All other abbreviations are given in earlier papers.

[3] (a) R. G. Wilkins, *J. Chem. Soc.*, 4521 (1957). (b) F. P. Dwyer and A. Bryson. *J. Proc. Roy. Soc. N. S. W.*, **74**, 471 (1940).

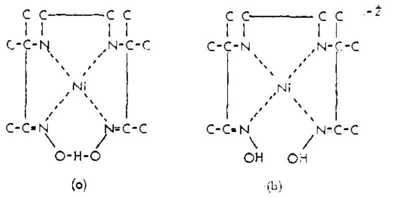

Fig. 1.

Anal. of EnAO. Calcd. for $C_{12}H_{26}N_4O_2$: C, 55.77; H, 10.15; N, 21.68. Found: C, 55.52; H, 10.16; N, 21.48.

All other ligands and compounds were prepared according to the general method previously outlined.[1]

Common reagents were of A.R. grade purified by crystallization in most cases; C,H,N analyses were conducted by Galbraith Laboratories; and metals, halogens, etc., by standard procedures.

Visible spectra were obtained on a Beckman model DU Spectrophotometer equipped with "cell-spacers" through which water (at a constant temperature) was pumped. The temperature of the cell compartment was found to differ from the bath by less than 0.1° and was constant to ± 0.05°.

Rates of formation were determined by measuring the change in molar absorbance of 1.00 cm. quartz cells at 388 mμ. A known volume ($\approx$3 ml.) of buffered amine solution at known ionic strength was brought to 24.3° and a small volume ($\approx$0.05 ml.) of a concentrated $Ni(ClO_4)_2$ solution quickly added with a manually operated microburet without removing the cell or contents from the thermostated spectrophotometer. Adsorption measurements were taken immediately after stirring. Fresh EnAO buffer solutions were made daily although less than 1% hydrolysis of the ligand occurs at 24° in 3 days below a [H$^+$] of 1×10^{-3}. In neither kinetic nor equilibrium measurements was evidence found for a metal ion catalyzed Beckmann oxime rearrangement of the type reported by Dwyer and Bryson.[3b] Presumably the conditions were not strenuous enough to produce such a ligand modification.

Rates of hydrolysis were measured in the same fashion by adding a concentrated solution of [Ni(EnAO)-H]ClO_4 ($\approx$0.1 *M*) with a manual microburet to a known volume of $HClO_4$-phthalate buffer solution, ($\approx$3 ml.) at constant temperature.

All measurements were carried out in duplicate and the rate constants agreed within 3%. In all rate measurements small corrections were made for the adsorption of Ni^{+2} in the 388 mμ range.

A Beckman model G *p*H Meter was used with lithium glass electrodes. Sodium ion corrections were small and the electrodes were given ample time for equilibration at a temperature controlled to ± 0.05°.

Results

a. Rate of Formation.—The formation of [Ni(EnAO)-H]$^+$ was followed at 388 mμ, the wave length of maximum absorption of this species, and Beer's Law was found to hold in the region 10^{-5} to 10^{-2} *M*. Interference by the ligand, or [Ni-EnAO]$^{+2}$ at this wave length is negligible, but small corrections were necessary for the absorption of Ni^{+2}. Preliminary measurements indicated that the rate was dependent on the concentration of Ni^{+2}, and the total amount of EnAO in all of its forms, and was highly sensitive to *p*H.

In order to determine the order with respect to reactants, a relatively high *p*H (buffered with KHP-thalate to a *p*H of 4.97) and a high amine to metal ion ratio (2.25) was used to lessen the effect of the backward reaction. These conditions were selected from titration curves previously reported.[1] Under these conditions a graph of $1/a - b \ln b(a - x)/a(b - x)$ *versus* time gave a straight line over that portion of the reaction which could be reliably measured (85%). This indication that the reaction was first order in [Ni^{+2}] and in total ligand was substantiated by measurement of the initial reaction rates at different initial concentration of reactants. These results demonstrated at *p*H 4.68 and 4.95 that the rate could be expressed by the following expression: rate = k [Ni^{+2}][EnAO]$_T$. This expression was valid within 3% in the concentration range of 5–50 $\times 10^{-3}$ *M* in each reactant.

The nature of the reacting ligand may be discerned by the use of the hydrogen ion dependence of the reaction rate, a sample of which is given in Fig. 2. It is necessary to know the concentration of EnAO, EnAOH$^+$ and EnAOH$_2^{+2}$ as a function of acidity in order to evaluate the *p*H dependence. For this purpose the acid-dissociation constants of the amine were determined by *p*H titration as previously described.[1] Calculation of the dissociation constants followed the usual pattern and care was taken to correct for the overlap of the equilibria. Table I gives these values.

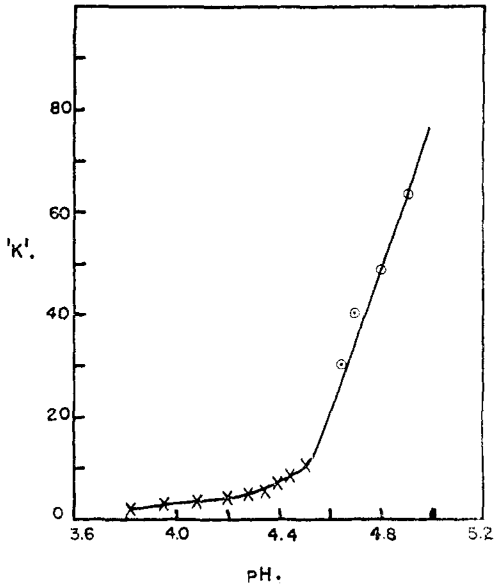

Fig. 2.—Rate of formation of [Ni(EnAO)—H]$^+$ 24.3°, 0.1 *M* phthalate buffer: ⊙, μ = 0.1; ×, μ = 1.0.

TABLE I

ACID DISSOCIATION CONSTANTS

EnAOH$_2^{+2}$ and [Ni(EnAO)]$^{+2}$ μ = 1.0 LiCl

ΔH_1 = 7.5 kcal./mole, ΔH_2 = 7.9 kcal./mole

	2.7°	9.3°	23.4°
$pK_{eq.}'$ amine	6.44	6.31	6.05
$pK_{eq.}$ amine	8.87	8.73	8.45
pK complex	3.12[a]	3.20	2.64

[a] μ = 0.10.

The assumption that only one form of the ligand was responsible for the formation, that is rate = k'[Ni^{+2}][ligand] where [ligand] is either [EnAO], [EnAOH$^+$] or [EnAOH$_2^{+2}$] was found to satisfy the experimental data only approximately. Using the expression $k' = k \frac{[\text{EnAO}]_T}{[\text{Ligand}]}$ the value of k' was not constant, decreasing with increasing *p*H for EnAO and increasing with EnAOH$^+$. There was no reasonable correlation between the EnAOH$_2^{+2}$

and the rate of formation. This behavior suggested a dual mechanism involving both EnAO and EnAOH$^+$. Thus the rate would correspond to this equation, rate = $[Ni^{+2}]$ (k_1[EnAO] + k_2[EnAOH$^+$]). In the *p*H range 4.0–5.0 this equation was obeyed, but at lower *p*H's k_2 was not constant. The apparent disagreement can be resolved, however, when one considers the equilibrium which is rapidly established between the products [Ni(EnAO)-H]$^+$ and [Ni(EnAO)]$^{+2}$. This equilibrium is highly *p*H dependent, and since only the concentration of the former is measured spectrophotometrically at 388 mμ, the measured concentration of product is lower than the actual. The magnitude of this effect increases with increasing acidity. To correct for this, the equilibrium constant for the reaction $[Ni(EnAO)\text{-}H]^+ + [H^+] \rightleftarrows [Ni(EnAO)]^{+2}$ was determined and was given in Table I. The specific rate constants of reaction, 'K,' were corrected for this equilibrium and are labeled 'K_c.' Table II gives the results of these calculations. The rate of formation of [Ni(EnAO)-H]$^+$ can be described using the equations given below which follow from the previous discussion.

$$\begin{tikzcd}
EnAOH_2{}^{+2} \arrow[r, shift left, "K_{eq.}'"] & EnAOH^+ + H^+ \arrow[l, shift left] \arrow[r, shift left, "K_{eq.}'"] \arrow[d, phantom, "+"] & EnAO + H^+ \arrow[l, shift left] \arrow[d, phantom, "+"] \\
& Ni^{+2} \arrow[d, "k_1"] & Ni^{+2} \arrow[d, "k_2"] \\
& \text{Product} & \text{Product}
\end{tikzcd}$$

Product = $[Ni(EnAO)]^{+2} + [Ni(EnAO)\text{-}H]^+$

$$\frac{d[\text{Prod.}]}{dt} = k_1\,[Ni^{+2}][EnAOH^+] + k_2[Ni^{+2}][EnAO] \quad (1)$$

$$\frac{d[\text{Prod.}]}{dt} = [Ni^{+2}][EnAO]_T \times \left[\frac{K_{eq.}'\,K_{eq.}}{H^2 + [H]K_{eq.}' + K_{eq.}'\,K_{eq.}} + \frac{k_1[H] + K_{eq.}\,k_2}{K_{eq.}}\right] \quad (2)$$

$$\frac{d[\text{Prod.}]}{dt} = 'K_c'\,[Ni^{+2}][EnAO]_T \quad (3)$$

From equations 2 and 3 it can be shown that

$$'K_c' = \frac{K_{eq.}'\,k_1[H] + K_{eq.}'\,K_{eq.}\,k_2}{[H]^2 + [H]K_{eq.}' + K_{eq.}'\,K_{eq.}} \quad (4)$$

$$\text{or } [H]^2\,'K_c' + [H]K_{eq.}'\,'K_c' + 'K_c'\,K_{eq.}'\,K_{eq.} = K_{eq.}'\,k_1[H] + K_{eq.}'\,K_{eq.}\,k_2 \quad (5)$$

Equation 5 will give a straight line when the left terms are graphed against [H$^+$]. From the slope and intercept k_1 and k_2 can be evaluated. Figure 3 shows such a graph. This reaction can be measured over only a short *p*H range due to incompleteness of reaction in more acidic solutions and to the extreme rapidity at higher *p*H's, but within the *p*H range available, agreement with the form of the rate expression, the equilibrium constants of the ligand and of the complex is satisfactory. The values for the rate constants in 0.1 *M* potassium acid phthalate buffer according to equation 1 are given in Table III.

b. **Rates of Decomposition, Weak Acids.**—At *p*H's lower than 3, [Ni(EnAO)-H]$^+$ decomposes to Ni^{+2} and EnAOH$_2$$^{+2}$ at a measurable rate. This decomposition is easily followed spectrophotometrically at the absorption maximum of that species, 388 mμ. In the more acid buffer regions (*p*H 2.0–2.3) a graph log [Ni(EnAO)-H]$^+$ *vs.* time was a straight line. Two factors complicate the kinetic evaluation. (a) The reaction does not go to completion in the regions of low acidity where the magnitude of the rate makes it most amenable to study; (b) An equilibrium exists between [Ni(EnAO)-H]$^+$ and [Ni(EnAO)]$^{+2}$ in this *p*H range. (Only the former complex absorbs appreciably at 388 mμ.) The first of these factors was overcome

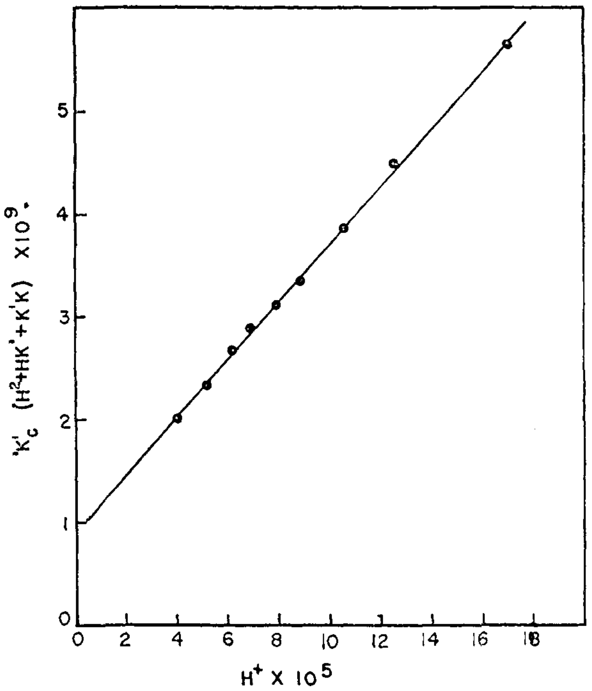

Fig. 3.—Rate of formation of [Ni(EnAO)—H]$^+$ 9.3°, 0.1 *M* phthalate buffer μ = 1.0 (LiCl).

TABLE II

RATE OF FORMATION OF [Ni(EnAO)-H]$^+$

9.3°, μ = 1.0 with LiCl, [Ni^{+2}] = 1.25 × 10^{-3} *M*, [EnAO]$_T$ = 3.75 × 10^{-3} *M*, *p*$K_{eq.}'$ amine = 6.31, *p*$K_{eq.}$ amine = 8.73, *p*K complex = 3.20.

*p*H	'K'	'K_c'	'K_c'(H^2 + HK$_{eq.}$' + K$_{eq.}$'K$_{eq.}$) × 10^9
3.73	0.136	0.196	5.65
3.90	.217	.285	4.51
3.98	.286	.354	3.86
4.05	.351	.421	3.35
4.10	.430	.492	3.12
4.16	.532	.605	2.92
4.21	.620	.700	2.68
4.28	.749	.833	2.32
4.38	1.065	1.151	2.01

TABLE III

RATE CONSTANTS OF FORMATION[a]

9.3° μ = 1.0 LiCl; k_1 = 60; k_2 = 9.9 × 10^5 l., mole^{-1}, min.$^{-1}$
24.3° μ = 1.0 LiCl; k_1 = 230; k_2 = 1.51 × 10^6 l., mole^{-1}, min.$^{-1}$
24.3° μ = 0.5 NaCl; k_1 = 739; k_2 = 5.08 × 10^5 l., mole^{-1} min.$^{-1}$

RATE CONSTANTS OF DISSOCIATION[b]

9.3° μ = 1.0 LiCl; k_1 = 9.4 × 10^{-3} k = 1.2 × 10^{-3} min.$^{-1}$
24.3° μ = 1.0 LiCl; k_1 = 2.7 × 10^{-2}; k = 4.6 × 10^{-3} min.$^{-1}$

[a] *p*H range 3.5–5.0, potassium phthalate buffer 0.10 *M*.
[b] *p*H range 2.16–3.10, potassium H phthalate buffer 0.10 *M*.

by using the initial rates of reaction (the first 10% or less), while the second factor was taken into account using the known equilibrium constant. Preliminary experiments indicated that the decomposition was first order in complex and was strongly affected by acid strength. The dependence can be understood if one assumes a first order decomposition of each of the species present in large amounts. Such a scheme is given below, including the anticipated hydrogen ion dependence.

$$\begin{tikzcd}
|\mathrm{Ni(EnAO)}|^{+2} \arrow[r, shift left, "k_{\mathrm{eq.}}"] \arrow[d, "k_1"] & |\mathrm{Ni(EnAO)\text{-}H}|^{+} + \mathrm{H}^{+} \arrow[l, shift left] \arrow[d, "k"] \\
\text{Product} & \text{Product}
\end{tikzcd}$$

It follows that

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{k_1[\mathrm{H}] + kK_{\mathrm{eq.}}}{[\mathrm{H}] + K_{\mathrm{eq.}}}[\mathrm{A}]$$

and slope =

$$\frac{\ln \dfrac{A_0}{A}}{t} = \frac{k_1[\mathrm{H}] + kK_{\mathrm{eq.}}}{[\mathrm{H}] + K_{\mathrm{eq.}}} = \text{'}K\text{'}$$

where $[\mathrm{A}] = [\mathrm{Ni(EnAO)}^{+2}] + [\mathrm{Ni(EnAO)\text{-}H}^{+}]$.

If the system behaves according to this expression, a graph of $\text{'}K\text{'}[\mathrm{H}] + \text{'}K\text{'}K_{\mathrm{eq.}}\text{'}$ against $[\mathrm{H}^+]$ should give a straight line whose slope is k_1 and intercept $kK_{\mathrm{eq.}}\text{'}$. Figure 4 shows that this relationship is followed and from it k and k_1 were evaluated. The results are listed in Table III.

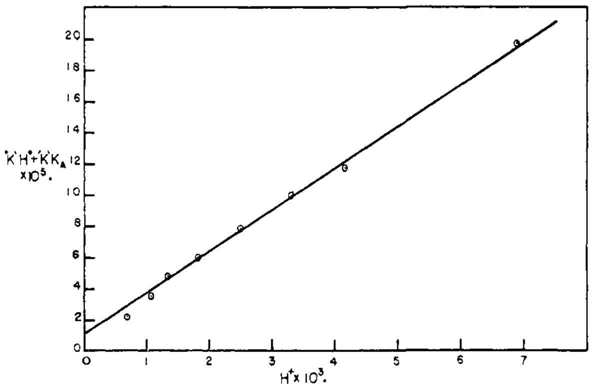

Fig. 4.—Rate of dissociation of $[\mathrm{Ni(EnAO)—H}]^+$ 24.3°, $\mu = 0.5$.

Above a $[\mathrm{H}^+]$ of 0.1 *M*, nearly all of the undissociated complex is in the form $[\mathrm{Ni(EnAO)}]^{+2}$. Although the molar absorptivity of this blue complex is small, its spectra differs markedly from Ni^{+2} (Table IV). The rates of decomposition were studied at the wave length of maximum molar absorbance difference. The rate of reaction followed the law: rate = $k_2\ [\mathrm{Ni(EnAO)}^{+2}][\mathrm{H}^+]$. Table V (a) shows the pseudo first order rate constant (k at constant H^+) as a function of acid concentration. The essentially constant value for $\dfrac{k}{[\mathrm{acid}]} = k_2$ points out the first order hydrogen ion dependence. The small deviations from a constant value probably are due to the inherent error in measuring these rapid reactions and to changes in activity coefficients in replacing HCl with LiCl.

TABLE IV

ABSORPTION SPECTRA OF $[\mathrm{Ni(EnAO)}]^{+2}$ TYPE SPECIES

Complex	Molar absorbance	Wave length, mμ
$[\mathrm{Ni\text{-}(EnAO)\text{-}H}]^+$	330	388
$[\mathrm{Ni(EnAO)}]^{+2}$	8	560
	16	925
$[\mathrm{Ni(AO)_2\text{-}H}]^+$	133	419
$[\mathrm{Ni(AO)_2}]^{+2}$	4	630
	11	975
$[\mathrm{Ni}(n\text{-PrAO})\text{-H}]^{+a}$	153	426
$[\mathrm{Ni}(n\text{-PrAO})]^{+2a}$	25	630
	210	980

[a] $[\mathrm{Ni}(n\text{-AmAO})_2\text{-H}]^+$ has essentially the same spectral behavior.

Table V (b) gives the temperature dependence of the rate which requires an activation energy of 14.7 kcal./mole.

0° μ = 1.0 (LiCl)	k_2 l. mole^{-1}, min.$^{-1}$
$[\mathrm{Ni(EnAO)}]^{+2}$	0.0064
$[\mathrm{Ni(MeEnAO)}]^{+2}$	.0090 (μ = 0.4)
$[\mathrm{Ni(AO)_2}]^{+2}$	.106
$[\mathrm{Ni}(n\text{-PrAO})_2]^{+2}$	.28
$[\mathrm{Ni}(n\text{-AmAO})_2]^{+2}$	.25

TABLE V

RATES OF DISSOCIATION OF $[\mathrm{Ni(EnAO)}]^{+2}$

μ = 2.0 (LiCl), Temp. = 15.0°

a. [Acid], *M*	$k \times 10^2$ (min.$^{-1}$)	$\dfrac{k}{[\mathrm{acid}]} \times 10^2 = k_2$
1.00	2.64	2.64
0.83	2.24	2.70
.66	1.80	2.73
.47	1.25	2.66
.30	0.752	2.51

b. [HCl] = 0.30 *M* Temp., °C.	$k \times 10^2$ (min.$^{-1}$)	$\dfrac{k}{[\mathrm{acid}]} \times 10^2 = k_2$
25.0	1.95	6.50
15.0	0.716	2.39
6.0	.364	1.21
0.0	.192	0.64

The dissociation of complexes containing bidentate ligands is much more complicated in weak acid media, probably due to the presence of appreciable quantities of complexes containing only one ligand. In strong acid however, the rate expression for these complexes is identical with that for $|\mathrm{Ni(EnAO)}|^{+2}$ as is the hydrogen ion dependence. It is apparent that the high acid stability is closely related to the thermodynamic stability[1] especially for bidentate ligands. But, on this basis the EnAO complex is more stable kinetically than expected which reflects the increased rigidity of the molecule containing a tetradentate ligand. The rate of dissociation is strongly affected by both the ionic strength and the total ionic atmosphere. The rate increases with increasing ionic strength and Cl^-, Br^- lead to faster reactions than $\mathrm{ClO_4}^-$

A comparison of $[\mathrm{Ni(EnAO)}]^{+2}$ and $[\mathrm{Ni(MeEnAO)}]^{+2}$ shows nearly identical behavior in strong acid solution. This is in contrast to the extreme kinetic stability of $[\mathrm{Ni(MeEnAO)\text{-}H}]^+$ in more neutral solutions.[4] This gain in stability can be attributed to the greater acidity of the C-substituted complex due to the increased strength

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[4] R. K. Murmann, to be published.

of the hydrogen bond as indicated by the acid dissociation constants of the complexes. $[Ni(EnAO)]^{+2}$, $pK_{eq.} = 2.64$, $[Ni(MeEnAO)]^{+2}$, $pK_{eq.} = 1.67$, $(24°, \mu = 1.0)$.

Discussion

It is apparent from Table III that the free ligand is a great deal faster reacting than the half-protonated amine while, apparently, $EnAOH_2^{+2}$ reacts so slowly (if at all) that its contribution to the total rate of complex formation is not noticeable. The rather large k_2/k_1 ratio (7×10^3) in the formation rate constants suggests that the activated state involves the amine nitrogen to metal bonds. Since the inductive effect on the basicity of the amine by the oxime group is small (see acid–base dissociation constants[1]), little charge appears to be transferred through the carbon chain, suggesting that the addition of a H^+ to the amine would not extensively modify the electronic distribution of the oxime nitrogen. If the first rate controlling step involved the formation of an oxime to metal bond followed by rapid ring closure, the rates of reaction with EnAO and $EnAOH^+$ should differ only slightly. Two of the simpler pictures which are in agreement with the facts are: (a) initial rate controlling amine–nitrogen bonding to the metal ion followed by rapid H^+ expulsion and ring closures; (b) the formation of a single chelate ring with an oxime and amine nitrogen as the rate controlling step followed by rapid additional chelate ring formations. Since the strong acid dissociation studies indicate the possible stability of a species containing one amine–oxime chelate ring and having an extra hydrogen ion presumably attached to the other amine nitrogen, the latter argument is favored.

This approach is also indicated by qualitative work on the sterically hindered (N-alkyl)-amineoximes. The rate of formation of the *n*-propyl or *n*-amyl derivatives of AO is quite slow with respect to AO. Since the rate controlling step in these reactions is probably connected with the addition of the second ligand (this is the point at which the magnetic moment and configuration change), the steric factor becomes important if that bond formation involves the alkyl substituted amine. By analogy these measurements indicate that the slow step in the formation of $[Ni(EnAO)\text{-}H]^+$ is the formation of the first chelate ring using an oxime and an amine nitrogen. Following this the additional two rings close around the metal ion rapidly.

The rate of dissociation in acids of $[Ni(EnAO)]^{+2}$ is considerably slower than that observed for AO or other bidentate α-amineoxime complexes of nickel(II) reflecting both its thermodynamic stability and the increased rigidity of the bound ligand. The increased kinetic stability for $[Ni(EnAO)\text{-}H]^+$ over $[Ni(EnAO)]^{+2}$ is expected on the basis of the necessity of breaking the hydrogen bond either previous to or simultaneously with the metal-ligand bond rupture with a resultant increase in activation energy.

Preliminary results of isotopic exchange studies give a corrected value of 4.3×10^{-3} at 25° $\mu = 0.80$, $pH = 7.0$ for the isotopic exchange of the ligand. This is in excellent agreement with *k*-(dissociation) for $[Ni(EnAO)\text{-}H]^+$, which is the species present at $pH = 7.0$, considering the change in ionic strength.

In the high acid region the first order hydrogen ion dependence is interesting because it indicates a protonated form of $[Ni(EnAO)]^{+2}$. Since the ligand has no aromatic character and thus probably could not protonate on the periphery of the ring, in the same manner as postulated for dipyridyl and 1,10-phenanthroline complexes,[5] it seems more plausible that the protonated activated state has a H^+ attached to one of the ligand nitrogens. Since it is not expected that proton interaction will occur with a nitrogen already coördinated to the metal ion, a structure involving a partially coordinated ligand appears probable. Although either oxime or amine nitrogen may be protonated, the much greater basicity of the latter makes it probable as the proton acceptor. Since the spectra of $[Ni(EnAO)]^{+2}$ would not be expected to differ radically from the structure involving attachment through only two nitrogens with a third protonated and since the intermediate would be expected to be present in very small amounts, the change of absorbance with time would follow that observed.

The formation constant of $[Ni(EnAO)]^{+2}$ is known from equilibrium measurements, ($\log K_{eq.} = 10.1$ at 24.2°). It is interesting to compare the same constant derived from kinetic results. The

$$\frac{k_2\text{ (formation)}}{k_1\text{ (dissociation)}} = K_{eq.};\ \log \frac{1.5 \times 10^6}{2.7 \times 10^{-2}} = \log K_{eq.} = 7.7$$

difference between these two values is far outside experimental error and may be due either to rate of formation slower, or a rate of dissociation faster, than expected on the basis of the equilibrium situation.

The non-equivalence of $K_{eq.}$ from rate and equilibrium data may be the result of the geometrical structure of the free ligand in solution being incorrect for complex formation. The slow geometrical rearrangement of oximes of aldehydes and ketones is known[6] and since the formation of the yellow planar complex requires that the ligand assume the *syn*-methyl form for both oxime groups, the rate of change of the other forms into this (unless very rapid) would be involved in the kinetics of the complex formation.

The isomerization of oximes is not well understood,[7,8] but it is generally accepted that saturated aliphatic aldoximes and ketoximes occur predominately in one form.[9] The particular isomer which predominates at equilibrium often depends on the relative interaction of the two surrounding groups with the oxime–OH group. Hydrogen bonding between the oxime-hydrogen and the amino-nitrogen is expected to strongly favor the *anti*-methyl form (a) of EnAO as opposed to the complex forming *syn* form (b) especially in the solid state.

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[8] G. Wittig, "Stereochemie," Akademische Verlagsgesellschaft M. B. H., Leipzig, 1930.

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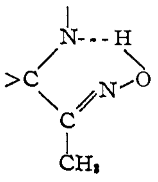
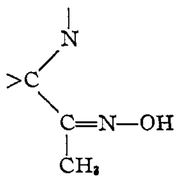
In aqueous solution isomerization may take place catalyzed by acids, bases and metallic ions, but the rate and the equilibrium constant for isomerization cannot be reliably estimated. However, because of the strong hydrogen bonding tendencies of water, the *syn*-methyl form (b) is expected to predominate in this solvent at equilibrium.


(a)


(b)

A plausible explanation of the difference in the equilibrium constants from the two sources centers around the geometrical rearrangement of the oxime by catalysis through chelation with nickel ion. Making the following assumptions concerning the system, each of which is reasonable in the light of other measurements, gives a satisfactory explanation. A. The free ligand in the solid state is in the wrong geometrical form for oxime chelation,[10] B. The rate of geometrical isomerization in nearly neutral solution is very slow (relative to the rate of formation of the Ni(II) complex). C. The partially chelated ligand isomerizes at a measurable rate. D. In nearly neutral water solutions the equilibrium constant, EnAO/EnAO* is large. In support of these assumptions recent experiments[11] have shown metal ions to be catalysts for *syn-anti*-conversions. Both forms of benzoyl-2-pyridine oxime are known and the interconversion in water or organic solvents at room temperature is immeasurably slow. In the presence of Fe(II) or Ni(II) the rate increases and the complex-forming *syn*-phenyl ligand is favored.

If EnAO exists in the solid state in a different geometrical form than that present in the complex, it might be possible to demonstrate the nonequivalence of the two materials by their infrared absorption providing the ligand can be obtained from the complex with retention of configuration. A comparison by infrared absorption of $EnAOH_2PtCl_6$ samples from solid EnAO and from the decomposition of $[Ni(EnAO)\text{-}H]^+$ in 1 *M* acid showed them to be identical. EnAO samples from solid EnAO and that obtained from $[Ni(EnAO)\text{-}H]^+$ by reaction with EDTA at a *p*H of 9–10 were also identical. But, a sample of $EnAOH_2PtCl_6$ prepared using EDTA at a *p*H of 6.0–6.5 gave absorption peaks at 6.10 and 12.23 microns which were not present in the same material prepared in strong acid. These absorption could not be attributed to EDTA salt impurities and corresponded with the observed differences between *syn* and *anti*-benzoyl-2-pyridine oxime. The spectral differences are not large, but this may be due to partial isomerization of EnAO during the rather long time (15–20 minutes at 35°) required for the reaction with EDTA.

Using this approach the formation of $[Ni(EnAO)]^{+2}$ could follow this path

$$EnAO^* + Ni^{+2}_{aq} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \boxed{Ni(EnAO^*)} \xrightarrow{k_r} \boxed{Ni(EnAO)} \xrightarrow{\text{fast}} [NiEnAO]^{+2}$$

The encircled species are considered to be present in low concentration with the ligand partially bound through either two amine nitrogens or through one amine and one oxime group. The form of the rate equation would be that which is experimentally found and k_2(observed) can be shown to equal $\frac{k_f k_r}{k_b + k_r}$ where k_r is the rate constant for oxime rearrangement when associated with Ni^{+2}. The observed rate constant of formation is composed of several terms and the rate constant of formation (k_f) cannot be obtained from it without a knowledge of k_b and k_r.

After the equilibration period used in the earlier equilibrium constant measurements, the predominant free ligand form in solution would be the *syn*-methyl because of the catalytic effect of the nickel(II) on the reaction $EnAO^* \rightarrow EnAO$. Thus the equilibrium measurements are not complicated by geometrical isomerism in the ligand.

With this approach, the reason for the discrepancy in the equilibrium constant can be seen to be the non-equilibrium state of the starting ligand with respect to its geometrical forms in the rates of formation studies. This necessitates the inclusion of an isomerization rate term of unknown magnitude in the rate expression.

From the known equilibrium constant of $[Ni(EnAO)]^{+2}$ and the dissociation rate constant k_1, the rate constant k_f is 3.35×10^8 l. moles^{-1} min^{-1}. Using this value and the formation rate constant k_2(observed) a value of 4.5×10^{-8} is obtained for $\frac{k_r}{k_b + k_r}$ so that only 0.5% of the reactions of coördinated $\boxed{Ni(EnAO^*)}$ are isomerization, the rest (99.5%) are dissociation back to starting materials.

An alternative explanation of the difference between the equilibrium constants from kinetic and equilibrium constants considers the rate constant of formation to be correctly assigned and the rate constants of dissociation to be too fast. This may come about through an incorrect assignment of the rate constants of dissociation. The measured dissociation rate constants could be for the conversion to a complex having the ligand bound through only two or three positions and having an absorption spectra similar to simple paramagnetic nickel(II) complexes. The dissociation of this species, leading to the aquated metal ion and the free ligand, may be somewhat slower as indicated by Wilkins, *et al.*,[12] and would not be observed by our spectral techniques.

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(10) EnAO* will signify the ligand in one of the wrong geometrical forms for chelation with the oxime nitrogen. This may involve either one or both oxime groups.

(11) E. G. Vassian and R. K. Murmann, to be published.

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It is clear that the configuration and modes of attachment in the activated states in the formation and dissociation of this complex are not known. A knowledge of the factors influencing *syn-anti* isomerization in aliphatic ketoximes along with thermodynamic and kinetic studies on planar complexes containing bidentate ligands would help evaluate the activated states involved.

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The Kinetics of Halogen Hydrolysis

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By means of the temperature jump relaxation technique, the kinetics of hydrolysis of the halogens Cl_2, Br_2 and I_2 have been studied. The over-all process is fastest for Br_2 and slowest for Cl_2. Numerical values for the rate constants of the over-all reaction mechanism $X_2 + H_2O \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftharpoons}} X^- + H^+ + XOH$ could be determined. The measured values for the over-all hydrolysis rate constant $\overrightarrow{k}$ are: $\overrightarrow{k}_{Cl_2} = 11.0$ sec.$^{-1}$, $\overrightarrow{k}_{Br_2} = 110$ sec.$^{-1}$, $\overrightarrow{k}_{I_2} = 3.0$ sec.$^{-1}$. A general mechanism, in which hydrolysis occurs *via* the intermediate X_2OH^-, is proposed. From studies of *p*H and concentration dependence individual rate constants could be determined or estimated. General trends exhibited by the measured or estimated values are discussed.

Introduction

When the halogens Cl_2, Br_2 and I_2 are dissolved in pure water, the ensuing solution becomes acidic with production of the corresponding hypohalogen acid. The hydrolysis equilibrium, which can be formally written as

$$X_2 + H_2O \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftharpoons}} H^+ + X^- + XOH \qquad (I)$$

(where X = Cl, Br or I and $\overrightarrow{k}$ (sec.$^{-1}$) or $\overleftarrow{k}$ (M^{-2} sec.$^{-1}$), respectively, are over-all rate constants) has been the subject of intensive research for a long period of time. The solutions are generally unstable with respect to the formation of more highly oxidized species, but this process is relatively slow. It has therefore been possible to achieve an almost complete thermodynamic description of all the primary equilibria pertinent to these systems. A comparably complete kinetic description has been lacking because most of the reactions involved in the hydrolysis occur in times around or shorter than 10^{-3} sec. (An exception is exhibited by the over-all hydrolysis of chlorine which has been studied with flow techniques.) By the application of relaxation techniques, it has now become possible to observe directly the rates of hydrolysis of all three halogens and to analyze the above formal mechanism in terms of individual elementary steps.

It will prove useful for the evaluation of the results to summarize first the thermodynamic data and to review the most important attempts at kinetic measurements.

The equilibrium constant for reaction (I) in the case of chlorine had been well characterized by Jakowkin[1] as long ago as 1899. We have used the more inclusive values of Connick and Chia,[2] adjusted to 20° and ionic strength $\mu = 0.1$ M, however. The same authors also measured the heat of reaction (I). The stability constant of trichloride ion has been measured spectrophotometrically by Zimmermann and Strong.[3] Latimer[4] reviews the data for the protonic dissociation constant of ClOH. The over-all rate of hydrolysis of chlorine was first measured by Shilov and Soloduschenkov[5] and later confirmed by Lifschitz and Perlmutter-Hayman,[6a] who have extended the measurements to acetate buffer solutions.[6b]

For bromine the equilibrium constant as well as heat of reaction (I) has been definitively measured by Liebhafsky,[7] whose value we have used, applied to the conditions of our experiments. Latimer[4] reviews the literature with respect to tribromide ion formation and protonic dissociation constant of BrOH. An attempt was made by Lifschitz and Perlmutter–Hayman[8] to measure the rate of bromine hydrolysis using a flow method. They found attainment of equilibrium to be essentially complete within their shortest measurable time, 3.8 milliseconds.

The iodine system has probably been the subject of the most extensive measurement of all three halogens. The equilibrium constant and heat of reaction for reaction (I) has been most recently redetermined by Allen and Keefer[9] (*cf.* for previous literature) whose value, adjusted to our conditions, we have used. Awtrey and Connick[10] and Allen and Keefer[9] review the spectrophotometric data

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