

of this band in the  $N_2$  complexes and its absence in the CO complex is puzzling. We would speculate that in the nitrogen complexes this band originates from a transition of the type  $2p\pi_u \rightarrow 2p\pi_g^*$  on the  $N_2$  molecule itself. Although these are strongly allowed transitions, they are observed at very high energy in the spectrum of the uncomplexed  $N_2$  molecule.<sup>19</sup> However it seems conceivable that, owing to the expected bond lengthening upon coordination, correlated with the observed large reduction in the ligand stretching frequency, the  $\pi, \pi^*$  separation in the molecule could be reduced to near a value of  $50,000 \text{ cm}^{-1}$ , as observed for these bands

(19) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1950, p 449.

in the  $N_2$  complexes. The absence of a similar band in the CO complex in the accessible uv region would imply a larger excitation energy for this type of transition on the CO ligand than the  $N_2$  ligand. Orgel, some time ago, in his consideration of the expected differences in the bonding of  $N_2$  and CO to metals alluded to the fact of a larger  $\pi, \pi^*$  orbital separation in CO than  $N_2$ , based on the spectroscopy of the free molecules.<sup>20</sup>

**Acknowledgments.**—We wish to express appreciation to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

(20) L. E. Orgel, "An Introduction of Transition-Metal Chemistry," 1st ed, Methuen and Co., Ltd., London, 1960, pp 137–138.

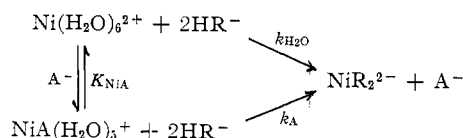
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## Kinetics of the Reaction of Some Monoacidopentaquonickel(II) Complexes with 4-(2-Pyridylazo)resorcinol

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Kinetics and mechanism of the reaction of monoacetato-, monoazido-, monofluoro-, and monohydroxonickel(II) complexes with 4-(2-pyridylazo)resorcinol have been studied spectrophotometrically at  $\mu = 0.10$  and at  $25.0^\circ$ . The reaction scheme can be described as



where  $\text{A}^-$  is a monodentate ligand such as hydroxide, azide, acetate, and fluoride and  $\text{HR}^-$  refers to monoionic species of 4-(2-pyridylazo)resorcinol. The stability constants,  $K_{\text{NiA}}$ , of the monoacidnickel(II) complexes and rate constants,  $k_{\text{H}_2\text{O}}$  and  $k_{\text{A}}$ , are kinetically determined:  $K_{\text{NiOH}} = 10^{4.3 \pm 0.1}$ ,  $K_{\text{NiN}_3} = 10^{0.66 \pm 0.10}$ ,  $K_{\text{NiO}_2\text{CCH}_3} = 10^{0.74 \pm 0.15}$ ,  $K_{\text{NiF}} = 10^{1.1 \pm 0.1}$ ,  $k_{\text{H}_2\text{O}} = (1.7 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ ,  $k_{\text{OH}} = (1.0 \pm 0.15) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ ,  $k_{\text{N}_3} = (1.1 \pm 0.15) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ ,  $k_{\text{CH}_3\text{CO}_2} = (4.5 \pm 0.4) \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ ,  $k_{\text{F}} = (1.1 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ . The difference of reactivity of these nickel(II) complexes is discussed in terms of electron donation of coordinated ligands on the basis of a model in which loss of the first water molecule coordinated to nickel(II) is the rate-determining step. The effect of electron donation of ligands on the rate of loss of water molecule is thus quantitatively accounted for.

### Introduction

The kinetics of complex formation of nickel(II) with various ligands have been extensively studied.<sup>1–3</sup> These studies have shown that the rate of complex formation is primarily determined by the rate of loss of a water molecule coordinated to nickel(II). In studies on the kinetics of the ligand substitution reaction<sup>4</sup> of the cobalt(II)- and nickel(II)-(ethylene glycol)bis(2-aminoethyl ether)-N,N,N',N'-tetraacetate complexes with 4-(2-pyridylazo)resorcinol (PAR), we found that the rate of incorporation of the second PAR

is much faster than the rate of addition of the first PAR to the metal ion. Similar results are noticed also in some other reactions.<sup>5–8</sup> Margerum and Rosen<sup>9</sup> have pointed that the electron-donor ability of coordinated groups is important in the rate of replacement of the remaining coordinated water molecules. Moorhead and Sutin<sup>10</sup> have shown that in the formation of the monoaxalate complex of iron(III) the rate of reaction of  $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$  with oxalate ion is about 20 times faster than that of reaction of  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  with oxalate

(1) M. Eigen and R. W. Wilkins in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.

(2) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

(3) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967.

(4) S. Funahashi and M. Tanaka, *Bull. Chem. Soc. Japan*, in press.

(5) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962); *J. Phys. Chem.*, **67**, 528 (1963).

(6) C. B. Honaker and H. Freiser, *ibid.*, **66**, 127 (1962).

(7) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 622 (1966).

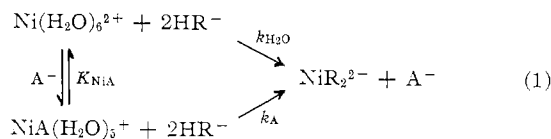
(8) R. G. Pearson and P. Ellgen, *ibid.*, **6**, 1379 (1967).

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

(10) E. G. Moorhead and N. Sutin, *Inorg. Chem.*, **5**, 1866 (1966).

ion. Insofar as the release of water molecule from the central metal is rate-determining, it is quite understandable, as pointed out previously,<sup>11</sup> that the coordination of the second ligand is faster than that of the first because of the electron donation from the first ligand to the metal.

The purpose of the present work is to study the kinetics of the formation of nickel(II)-PAR complex from some monovalent monoacidopentaquonickel(II) complexes and to elucidate the labilizing effect of a coordinated ligand in the substitution reaction of these nickel(II) complexes. The reaction scheme can be described as



where  $\text{A}^-$  is a monodentate and monovalent ligand such as hydroxide, azide, acetate, and fluoride ion,  $\text{HR}^-$  is the monoionic species of PAR (tridentate),  $K_{\text{NiA}}$  is the stability constant of the monoacidonickel(II) complex, and  $k_{\text{A}}$  is the second-order rate constant.

### Experimental Section

**Reagents. Nickel(II) Perchlorate.**—The reagent grade nickel(II) chloride was recrystallized twice from distilled water. The recrystallized nickel chloride was then dissolved in perchloric acid and chloride was expelled by evaporation, excess perchloric acid being removed by an infrared lamp. The absence of chloride ion was checked by silver nitrate. Nickel concentration was determined by a standard EDTA solution using TAC<sup>12</sup> as an indicator. The nickel concentration was also checked gravimetrically with dimethylglyoxime (precipitation from homogeneous solution using biacetyl and hydroxylamine<sup>13</sup>).

**PAR.**—The acid form of PAR was obtained from Dojin-cho Chemical Co., Kumamoto, Japan, and purified by recrystallization from aqueous ethanol. PAR dried in an air bath at about 90° was dissolved in 2 equiv of sodium hydroxide prepared as described previously.<sup>11</sup>

**Sodium Azide.**—Reagent grade sodium azide was recrystallized twice from aqueous ethanol and from distilled water.

**Sodium Acetate.**—Reagent grade sodium acetate was recrystallized three times from distilled water.

**Sodium Fluoride.**—Reagent grade sodium fluoride was recrystallized once from distilled water.

Methods of preparation of the other reagents (sodium perchlorate, sodium hydroxide, boric acid, and borax) have been described previously.<sup>11</sup>

**Apparatus.**—The following instruments were used: a Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer with a thermostated 5.3-cm cell; a photoelectric spectrophotometer, Type 6 (Hirama Rikakenkyujo, Kawasaki, Japan), with a thermostated 2.0-cm cell; a Hitachi Model QPD-53 recorder; an X-Y recorder, Type VR-631 (Matsushita Communication Industrial Co., Yokohama, Japan); a Jasco Model ORD/UV-5 optical rotatory dispersion recorder; a Radiometer PHM-4d (Copenhagen) with a Type G202 B glass electrode and a Type K401 calomel electrode; a thermoelectric circulator, Coolnics Circulator Type CTE-1B (Komatsu Solidate Co., Komatsu, Japan).

**Equilibria.**—The nickel(II)-PAR complex forms the 1:2 complex<sup>14,15</sup>  $\text{NiR}_2^{2-}$ , under the present experimental conditions.

Over a pH range from 7.5 to 10, the absorbance of the nickel(II)-PAR complex is constant. The molar absorption coefficient is  $7.69 \times 10^4$  at 496 nm, the wavelength of maximum absorption.

In the pH range studied, 7.5–9.5, the dominant species of PAR is the monoionic species ( $\text{HR}^-$ ) as evident from the stability constants of PAR ( $\log K_{\text{H}_3\text{R}^{\text{H}}} = 2.69$ ,  $\log K_{\text{H}_2\text{R}^{\text{H}}} = 5.50$ ,  $\log K_{\text{HR}^{\text{H}}} = 12.31^{16}$ ). The monoionic species of PAR has the maximum absorption at 410 nm and the absorbance of PAR is independent of pH in this pH range. The molar absorption coefficient is  $1.57 \times 10^8$  at 496 nm.

Beer's law is obeyed for the nickel(II)-PAR complex and PAR. Under the present experimental conditions, reaction 1 is much favored to the right so that the reaction of the nickel complexes with PAR goes to completion and the reverse reaction can be neglected in the kinetic study.

**Kinetic Measurements.**—The nickel complex solution was prepared by mixing nickel perchlorate solution with ligand solution. Borate buffer solution (the concentration of borate is  $8.0 \times 10^{-3} M$ ) was added to adjust the pH of the solution. The ionic strength of the solution was maintained constant ( $\mu = 0.10$ ) by sodium perchlorate. A silica beaker with light path length of 5.3 cm or a quartz cell with light path length of 2.0 cm containing the nickel complex solution was placed in a thermostated compartment of a spectrophotometer capable of temperature control at  $25.0 \pm 0.2^\circ$ . The PAR solution was brought to temperature equilibrium in a bath kept at  $25.0 \pm 0.1^\circ$ . The reaction was started by mixing the nickel complex solution and the PAR solution. The transmittance at 496 nm of the reaction solution was recorded as a function of the reaction time by a recorder.

All pH values were measured with a Radiometer PHM-4d which was carefully calibrated with standard buffer solution (potassium dihydrogen phosphate, 0.025 M; disodium hydrogen phosphate, 0.025 M) prepared as described by Bates.<sup>17</sup> All experiments were carried out in a room thermostated at  $25 \pm 1^\circ$ .

### Results

**The Reaction of Nickel(II) Ion with PAR.**—The kinetic studies performed with a 20–200-fold excess of the entering group, PAR, showed that the reaction was first order in PAR (Table I) and the formation reaction of nickel(II)-PAR complex was found to be second order in nickel(II) ion and PAR. Therefore the kinetic equation for this reaction is described as

$$\frac{d[\text{NiR}_2^{2-}]}{dt} = k_0[\text{Ni}'][\text{R}'] \quad (2)$$

where  $[\text{Ni}']$  denotes the total concentration of nickel(II) not combined with PAR,  $[\text{R}']$  denotes the total concentration of unmetallized PAR, and  $k_0$  is the conditional rate constant.<sup>11</sup> In the reaction system, we have the relationships

$$E_0 = \epsilon_{\text{R}}C_{\text{R}}$$

$$E_t = \epsilon_{\text{R}}[\text{R}'] + \epsilon_{\text{NiR}_2}[\text{NiR}_2^{2-}]$$

$$E_\infty = \epsilon_{\text{R}}(C_{\text{R}} - 2C_{\text{Ni}}) + \epsilon_{\text{NiR}_2}C_{\text{Ni}}$$

where  $E_0$ ,  $E_t$ , and  $E_\infty$  are the absorbances of the reaction system at reaction time 0,  $t$ , and  $\infty$ , respectively;  $C_{\text{Ni}}$  and  $C_{\text{R}}$  represent the total concentrations of nickel and PAR, respectively;  $C_{\text{Ni}} = [\text{Ni}'] + [\text{NiR}_2^{2-}]$  and  $C_{\text{R}} = [\text{R}'] + 2[\text{NiR}_2^{2-}]$ . From these relationships,

(11) M. Tanaka, S. Funahashi, and K. Shirai, *Inorg. Chem.*, **7**, 573 (1968).

(12) G. Nakagawa and H. Wada, *Nippon Kagaku Zasshi*, **85**, 202 (1964).

(13) E. D. Salesin and L. Gordon, *Talanta*, **5**, 81 (1960).

(14) A. Corsini, I. M. Yih, Q. Fernando, and H. Freiser, *Anal. Chem.*, **34**, 1090 (1962).

(15) M. Tanaka, S. Funahashi, and K. Shirai, *Anal. Chim. Acta*, **39**, 437 (1967).

(16) W. J. Geary, G. Nickless, and F. H. Pollard, *ibid.*, **27**, 71 (1962).

(17) R. G. Bates, "Determination of pH, Theory and Practice," John Wiley & Sons, Inc., New York, N. Y., 1964.

TABLE I

CONDITIONAL FIRST-ORDER RATE CONSTANT  $k_{0(R)}$  AND  
CONDITIONAL SECOND-ORDER RATE CONSTANT  $k_0$  OF THE  
REACTION OF NICKEL(II) ION WITH PAR AT 25.0° AND  
 $\mu = 0.10$  (NaClO<sub>4</sub>)

$C_{Ni}, M$	$C_R, M$	pH	$k_{0(R)}, \text{sec}^{-1}$
$5.1 \times 10^{-7}$	$1.00 \times 10^{-5}$	8.54	$2.1 \times 10^{-2}$
	$2.00 \times 10^{-5}$	8.54	$4.6 \times 10^{-2}$
	$2.50 \times 10^{-5}$	8.54	$6.0 \times 10^{-2}$
	$5.00 \times 10^{-5}$	8.55	$1.1 \times 10^{-1}$
	$1.00 \times 10^{-4}$	8.56	$2.4 \times 10^{-1}$
$C_{Ni}, M$	$C_R, M$	pH	$k_0, M^{-1} \text{sec}^{-1}$
$1.27 \times 10^{-6}$	$2.50 \times 10^{-5}$	9.01	$3.16 \times 10^3$
		9.32	$3.96 \times 10^3$
		9.42	$4.64 \times 10^3$
		9.50	$4.50 \times 10^3$
		9.50	$4.56 \times 10^3$
$1.53 \times 10^{-6}$	$1.00 \times 10^{-5}$	8.51	$2.23 \times 10^3$
		8.52	$2.29 \times 10^3$
$2.03 \times 10^{-6}$	$2.00 \times 10^{-5}$	7.66	$1.74 \times 10^3$
		7.89	$1.74 \times 10^3$
$2.54 \times 10^{-6}$	$2.50 \times 10^{-5}$	9.02	$3.00 \times 10^3$
		9.32	$3.94 \times 10^3$
$5.09 \times 10^{-6}$	$5.00 \times 10^{-5}$	7.84	$1.85 \times 10^3$
		7.96	$1.82 \times 10^3$
		8.07	$1.84 \times 10^3$
		8.08	$1.91 \times 10^3$
		8.08	$1.84 \times 10^3$
		8.13	$1.95 \times 10^3$
		8.20	$1.87 \times 10^3$
8.40	$2.08 \times 10^3$		
8.50	$2.25 \times 10^3$		
8.66	$2.43 \times 10^3$		
8.81	$2.71 \times 10^3$		
8.88	$2.92 \times 10^3$		
9.04	$3.35 \times 10^3$		

we have the concentrations of nickel(II)-PAR and PAR. Integration of eq 2 yields

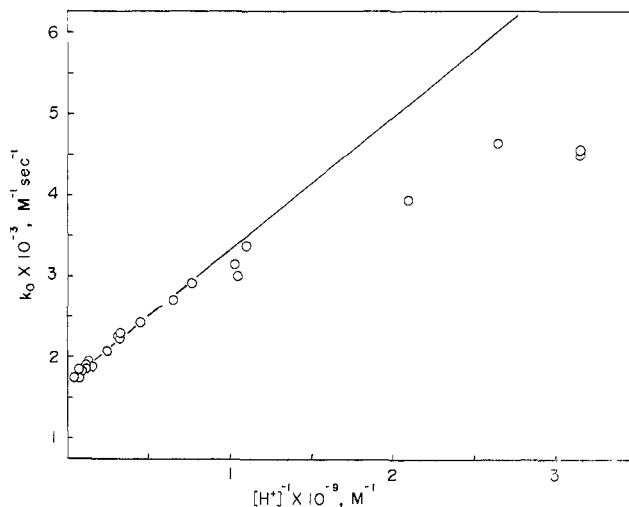
$$\log \frac{C_R - 2[\text{NiR}_2^{2-}]}{C_{Ni} - [\text{NiR}_2^{2-}]} = \frac{C_R - 2C_{Ni}}{2.303} k_0 t + \log \frac{C_R}{C_{Ni}} \quad (3)$$

The plot of

$$\log \frac{C_R - 2[\text{NiR}_2^{2-}]}{C_{Ni} - [\text{NiR}_2^{2-}]} \text{ vs. } t$$

according to eq 3 gave a good straight line up to at least 85% of the reaction. This linearity confirms that the formation reaction of nickel(II)-PAR complex is second order in nickel(II) ion and PAR. Conditional second-order rate constants,  $k_0$ , were calculated from the slope of the straight line obtained. Some conditional second-order rate constants,  $k_0$ , of the reaction of nickel(II) ion with PAR at various pH's are given in Table I. The result shows that the rate constant increases with increasing pH. As the nickel(II) ion is subject to hydrolysis to produce the hydroxonickel(II) ion and PAR ( $\text{HR}^-$ ) dissociates to form diionic species  $\text{R}^{2-}$ , we have two possible mechanisms to interpret these kinetic data.

If the increase of the rate constant is attributed to the diionic species  $\text{R}^{2-}$  which seems to react with

Figure 1.—Plot of  $k_0$  vs.  $[\text{H}^+]^{-1}$ .

nickel(II) ion much faster than  $\text{HR}^-$ , the rate law would be expressed as

$$\begin{aligned} \frac{d[\text{NiR}_2^{2-}]}{dt} &= k_1[\text{Ni}(\text{H}_2\text{O})_6^{2+}][\text{HR}^-] + k_2[\text{Ni}(\text{H}_2\text{O})_6^{2+}][\text{R}^{2-}] \\ &= \left( k_1 + \frac{k_2}{K_{\text{HR}^{\text{H}}[\text{H}^+]}} \right) (C_{Ni} - [\text{NiR}_2^{2-}])[\text{HR}^-] \end{aligned}$$

because the stability constant of PAR is  $\log K_{\text{HR}^{\text{H}}} = 12.31^{16}$  as described in the Experimental Section and PAR exists quantitatively as the monoionic species  $\text{HR}^-$  in the pH range 7.5–9.5. In this case the conditional rate constant

$$k_0 = k_1 + \frac{k_2}{K_{\text{HR}^{\text{H}}[\text{H}^+]}}$$

must be linearly related with the reciprocal of the hydrogen ion concentration. In effect the plot of  $k_0$  vs.  $[\text{H}^+]^{-1}$  did not fall on a straight line but yielded a curve (Figure 1). Therefore the reaction mechanism involving  $\text{R}^{2-}$  can be excluded.

If the increase of rate constant with increasing pH is attributed to the monohydroxonickel(II) complex, the kinetic equation is expressed by

$$\frac{d[\text{NiR}_2^{2-}]}{dt} = k_{\text{H}_2\text{O}}[\text{Ni}(\text{H}_2\text{O})_6^{2+}][\text{HR}^-] + k_{\text{OH}}[\text{NiOH}(\text{H}_2\text{O})_5^+][\text{HR}^-] \quad (4)$$

From the equilibrium relationships and mass balance, we have

$$\begin{aligned} \frac{[\text{NiOH}(\text{H}_2\text{O})_5^+]}{[\text{Ni}(\text{H}_2\text{O})_6^{2+}][\text{OH}^-]} &= K_{\text{NiOH}} \\ C_{Ni} - [\text{NiR}_2^{2-}] &= [\text{Ni}(\text{H}_2\text{O})_6^{2+}] + [\text{NiOH}(\text{H}_2\text{O})_5^+] \\ &= [\text{Ni}(\text{H}_2\text{O})_6^{2+}](1 + K_{\text{NiOH}}[\text{OH}^-]) \end{aligned} \quad (5)$$

Combining eq 4 and 5, we obtain

$$\begin{aligned} \frac{d[\text{NiR}_2^{2-}]}{dt} &= (k_{\text{H}_2\text{O}} + k_{\text{OH}}K_{\text{NiOH}}[\text{OH}^-])[\text{Ni}(\text{H}_2\text{O})_6^{2+}][\text{HR}^-] \\ &= (k_{\text{H}_2\text{O}} + k_{\text{OH}}K_{\text{NiOH}}[\text{OH}^-]) \frac{C_{Ni} - [\text{NiR}_2^{2-}]}{1 + K_{\text{NiOH}}[\text{OH}^-]}[\text{HR}^-] \\ &= k_{0(\text{OH})}(C_{Ni} - [\text{NiR}_2^{2-}])[\text{HR}^-] \end{aligned} \quad (6)$$

where

$$k_{0(\text{OH})} = \frac{k_{\text{H}_2\text{O}} + k_{\text{OH}}K_{\text{NiOH}}[\text{OH}^-]}{1 + K_{\text{NiOH}}[\text{OH}^-]}$$

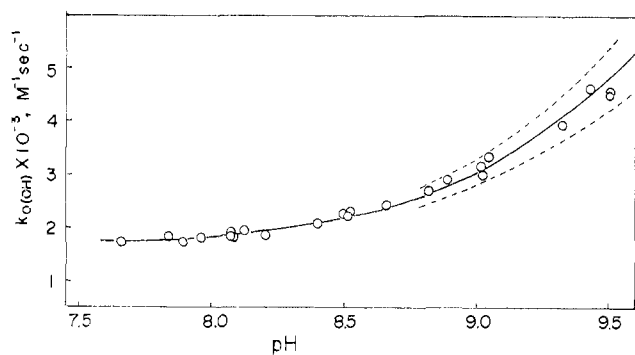


Figure 2.—Plot of  $k_{0(\text{OH})}$  vs. pH. The line is the theoretical curve calculated with the values obtained by the curve fitting. The points are experimental. Two dotted lines show the range of deviation of  $k_{\text{OH}}$  ( $k_{\text{OH}} = (1.0 \pm 0.15) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ ).

is a conditional second-order rate constant composed of rate constant, stability constant, and concentration of reaction species, etc., and  $[\text{OH}^-]$  represents the activity of hydroxide ion calculated by the relation  $[\text{H}^+][\text{OH}^-] = K_w = 10^{-14.00}$  at  $25^\circ$ .

The conditional rate constant  $k_{0(\text{OH})}$  can be rewritten as

$$k_{0(\text{OH})} = k_{\text{OH}} + \frac{k_{\text{H}_2\text{O}} - k_{\text{OH}}}{1 + K_{\text{NiOH}}[\text{OH}^-]} \quad (7)$$

The result may be compared with a normalized function

$$y = \frac{\beta}{1+x} = f(\log x) \quad (8)$$

The experimental plot of  $k_{0(\text{OH})}$  vs.  $\log [\text{OH}^-]$  fits well with one of a family of the normalized curves. Thus the increase of the rate with increasing pH is attributable to the monohydroxonickel(II). Fitting the plot with curves of  $y$  vs.  $\log x$  at various values of  $\beta$ , we obtain  $\log K_{\text{NiOH}}$  from the reading of the abscissa,  $k_{\text{OH}}$  from the ordinate, and  $k_{\text{H}_2\text{O}} - k_{\text{OH}}$  from the value of  $\beta$  of a curve of the best fit. The stability constant  $K_{\text{NiOH}}$  and rate constants  $k_{\text{H}_2\text{O}}$  and  $k_{\text{OH}}$  are  $10^{4.3 \pm 0.1}$ ,  $(1.7 \pm 0.1) \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ , and  $(1.0 \pm 0.15) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ , respectively (Figure 2).

Though many authors have studied the hydrolysis of the nickel(II) ion, their data vary widely and are not fully convincing.<sup>18</sup> According to a study by Biedermann and Ohtaki,<sup>19</sup> the dominant hydrolyzed species of the nickel(II) ion is monohydroxonickel(II) under the present experimental condition. Recently, Perrin<sup>20</sup> has determined the stability constant of monohydroxonickel(II) complex by potentiometric titration:  $\log K_{\text{NiOH}} = 4.12$  at  $\mu = 0.043$  and  $25^\circ$ . Thus the value determined in the present study seems reasonable.

One may suspect whether or not the equilibrium between aquo- and monohydroxonickel(II) is maintained during a kinetic run. We found no difference in rate for reactions started about 2, 10, and 100 min after

(18) I. G. Sillén and A. E. Martell, "Stability Constants of Metal Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

(19) G. Biedermann and H. Ohtaki, private communication, 1964:  $\text{NiOH}^+$ ,  $\log \beta_{1,1} = -10.5$ ;  $\text{Ni}_2\text{OH}^{2+}$ ,  $\log \beta_{1,2} = -10.5$ ;  $\text{Ni}_3(\text{OH})_4^{3+}$ ,  $\log \beta_{1,4} = -28.55$  at  $25^\circ$  in an aqueous solution containing 3 M NaCl as an ionic medium, where  $\beta_{p,q} = [\text{Ni}_q(\text{OH})_p]^{(2q-p)} / [\text{H}^+]^p / [\text{Ni}^{2+}]^q$ .

(20) D. D. Perrin, *J. Chem. Soc.*, 3644 (1964).

the adjustment of pH of the nickel solution. This fact confirms that the hydrolysis reaction of the nickel(II) ion is sufficiently rapid<sup>21</sup> and that the hydrolysis equilibrium of the nickel(II) ion precedes the rate-determining step. Kinetically the concentration (0.08–0.0001 M) of the borate buffer gives no effect.

**The Reactions of Monoacetato-, Monoazido- and Monofluoronickel(II) Complexes with PAR.**—For a complex formation of the nickel(II) ion with azide, acetate, and fluoride ions one can reasonably expect a rate similar to that of the nickel(II) ion with PAR. The concentration of these monodentate ligands (about  $5 \times 10^{-2} \text{ M}$ ) being some 1000 times higher than that of entering ligand, PAR ( $10^{-5} \text{ M}$ ), these acidonickel(II) complexes are certainly in equilibrium with the aquonickel(II) ion during the reaction. In the present experimental conditions the predominant complex species are  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  and  $\text{NiA}(\text{H}_2\text{O})_5^+$  as expected from the reported values<sup>22</sup> of stability constants of these complexes. This is confirmed by the present study. Thus the reaction can be considered to proceed as eq 1.

The rate law is similar to that of the reaction of the hydroxonickel(II) complex with PAR

$$\begin{aligned} \frac{d[\text{NiR}_2^{2-}]}{dt} &= k_{\text{H}_2\text{O}}[\text{Ni}(\text{H}_2\text{O})_6^{2+}][\text{HR}^-] + k_{\text{A}}[\text{NiA}(\text{H}_2\text{O})_5^+][\text{HR}^-] \\ &= \frac{k_{\text{H}_2\text{O}} + k_{\text{A}}K_{\text{NiA}}[\text{A}^-]}{1 + K_{\text{NiA}}[\text{A}^-]}(C_{\text{Ni}} - [\text{NiR}_2^{2-}])([\text{HR}^-]) \\ &= k_{0(\text{A})}(C_{\text{Ni}} - [\text{NiR}_2^{2-}])([\text{HR}^-]) \end{aligned} \quad (9)$$

The conditional second-order rate constants  $k_{0(\text{A})}$  are shown in Table II. The contribution of the hydroxonickel(II) complex being taken into account, the

TABLE II  
CONDITIONAL SECOND-ORDER RATE CONSTANT  $k_{0(\text{A})}$  AT  
 $C_{\text{Ni}} = 2.03 \times 10^{-6} \text{ M}$ ,  $C_{\text{R}} = 2.00 \times 10^{-5} \text{ M}$ ,  $\mu = 0.10$  (NaClO<sub>4</sub>),  
AND  $25.0^\circ$

$C_{\text{H}_3\text{CO}_2^-}$ , M	pH	$10^{-3}k_{0(\text{CH}_3\text{CO}_2^-)}$ , $\text{M}^{-1} \text{ sec}^{-1}$	$C_{\text{N}_3^-}$ , M	pH	$10^{-3}k_{0(\text{N}_3^-)}$ , $\text{M}^{-1} \text{ sec}^{-1}$
0	7.89	1.73	0.03	7.79	2.93
0.01	7.81	1.90	0.04	7.79	3.15
0.02	7.83	1.92 <sup>a</sup>	0.05	7.79	3.28
	7.89	2.00		7.62	3.36
0.03	7.79	2.12	0.06	7.78	3.68
0.04	7.86	2.24	0.08	7.76	4.46
0.05	7.78	2.32 <sup>a</sup>	0.10	7.72	4.95
	7.85	2.38			
0.06	7.85	2.47	$C_{\text{F}^-}$ , M		$10^{-3}k_{0(\text{F}^-)}$ , $\text{M}^{-1} \text{ sec}^{-1}$
0.07	7.83	2.53	0	7.66	1.74
0.08	7.75	2.62	0.01	7.81	1.78
	7.82	2.64	0.02	7.79	1.63
0.09	7.81	2.79		7.59	1.61
0.10	7.80	2.87	0.04	7.75	1.60
			0.05	7.47	1.50
$C_{\text{N}_3^-}$ , M	pH	$10^{-3}k_{0(\text{N}_3^-)}$ , $\text{M}^{-1} \text{ sec}^{-1}$			
0.01	7.82	2.14	0.07	7.66	1.49
0.02	7.82	2.55	0.10	7.57	1.48

<sup>a</sup>  $C_{\text{R}} = 4.00 \times 10^{-5} \text{ M}$ .

(21) T. J. Swift and T. A. Stephenson, *Inorg. Chem.*, **5**, 1100 (1966).

(22) A. Ringbom, "Complexation Analytical Chemistry," Interscience Publishers, New York, N. Y., 1963.

TABLE III  
 STABILITY AND RATE CONSTANTS AT  $\mu = 0.10$  AND  $25.0^\circ$ 

	$\text{Ni}(\text{H}_2\text{O})_6^{2+} + \text{A}^- \xrightleftharpoons{K_{\text{NiA}}} \text{NiA}(\text{H}_2\text{O})_5^+$			
Log $K_{\text{NiOH}}$	Log $K_{\text{NiN}_3}$	Log $K_{\text{NiO}_2\text{CCH}_3}$	Log $K_{\text{NiF}}$	
$4.3 \pm 0.1$	$0.66 \pm 0.10$	$0.74 \pm 0.15$	$1.1 \pm 0.1$	
	$\text{NiA}(\text{H}_2\text{O})_5^+ + 2\text{HR}^- \xrightarrow{k_A} \text{NiR}_2^{2-} + \text{A}^-$			
$k_{\text{OH}}^a$	$k_{\text{N}_3}$	$k_{\text{CH}_3\text{CO}_2}$	$k_{\text{F}}$	$k_{\text{H}_2\text{O}}$
$(1.0 \pm 0.15) \times 10^4$	$(1.1 \pm 0.15) \times 10^4$	$(4.5 \pm 0.4) \times 10^3$	$(1.1 \pm 0.2) \times 10^3$	$(1.7 \pm 0.1) \times 10^3$
$E_{\text{OH}}^b$	$E_{\text{N}_3}$	$E_{\text{CH}_3\text{CO}_2}$	$E_{\text{F}}$	$E_{\text{H}_2\text{O}}$
1.65	1.58	0.95	-0.27	0.00

<sup>a</sup> In  $M^{-1} \text{sec}^{-1}$ . <sup>b</sup>  $E_A$  is a measure of electron donation of ligand A. See J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954); **78**, 1819 (1956).

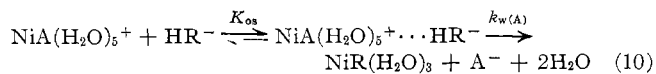
conditional second-order rate constant  $k_{0(\text{A},\text{OH})}$  can be written as

$$k_{0(\text{A},\text{OH})} = \frac{k_{\text{H}_2\text{O}} + k_{\text{OH}}K_{\text{NiOH}}[\text{OH}^-] + k_A K_{\text{NiA}}[\text{A}^-]}{1 + K_{\text{NiOH}}[\text{OH}^-] + K_{\text{NiA}}[\text{A}^-]}$$

Under the experimental conditions given in Table II, the term  $K_{\text{NiOH}}[\text{OH}^-]$  can be neglected and the term  $k_{\text{OH}}K_{\text{NiOH}}[\text{OH}^-]$  amounts to: 12% of  $k_{\text{H}_2\text{O}}$  at pH 8.0, 7.4% at pH 7.8, 4.7% at pH 7.6, and 2.9% at pH 7.4. However the formation of hydroxonickel(II) gives rise to no effect in the determination of  $k_A$  and  $K_{\text{NiA}}$  provided that pH is kept constant. In effect, variation of the conditional rate constants due to the variation of pH is within  $\pm 3\%$  in a series of runs for a given ligand A (Table II). Then the stability constants  $K_{\text{NiA}}$  and rate constants  $k_A$  are determined by the curve-fitting method and the results are tabulated in Table III. The uncertainty of constants in Table III indicates the maximum deviation.  $K_{\text{NiOH}}$  is the mixed constant. The other stability constants are the concentration constants.

### Discussion

The kinetic behavior of the reaction in the present study is compared with the behavior predicted by current general mechanisms for metal-ligand complex formation as formulated by Eigen:<sup>1,2,23,24</sup> the monoacidonickel(II) ion  $\text{NiA}(\text{H}_2\text{O})_5^+$  and the entering ligand  $\text{HR}^-$  are in rapid equilibrium with an outer-sphere complex in which the entering group occupies a position in the second coordination sphere and the rate-determining step is the loss of a coordinated water molecule



where  $K_{\text{os}}$  is the equilibrium constant for outer-sphere association,  $\text{NiA}(\text{H}_2\text{O})_5^+ \cdots \text{HR}^-$  is the outer-sphere complex, and  $k_{\text{w}(\text{A})}$  is the rate constant for metal-water bond rupture.

The formation of the nickel(II)-PAR complex proceeds by a second-order reaction. If these reactions follow the general mechanism given in eq 10, the experimentally obtained rate constants,  $k_A$ , can be

equated with corresponding rate constants for metal-water bond rupture,  $k_{\text{w}(\text{A})}$ , by eq 11. Mechanism 10

$$k_A = K_{\text{os}}k_{\text{w}(\text{A})} \quad (11)$$

can be tested by this relationship if the value of  $K_{\text{os}}$  is available. Unfortunately, experimental  $K_{\text{os}}$  values are not available for the systems studied. Consequently, it is necessary to rely on estimates calculated from a theoretical equation. The value of the outer-sphere association constant can be calculated using an equation for ion-pair formation<sup>23,25</sup>

$$K_{\text{os}} = \frac{4\pi N a^3}{3000} e^{-U(a)/kT} \quad (12)$$

where

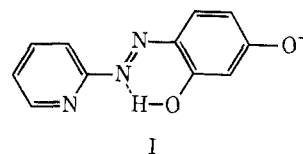
$$U(a) = \frac{z_1 z_2 e^2}{aD} - \frac{z_1 z_2 e^2 \kappa}{D(1 + \kappa a)}$$

and

$$\kappa^2 = \frac{8\pi N e^2 \mu}{1000 D k T}$$

In these equations  $N$  is Avogadro's number,  $a$  is the distance of closest approach of the two ions (in centimeters),  $k$  is Boltzmann's constant (in ergs),  $T$  is the absolute temperature,  $e$  is the charge of an electron (in electrostatic units),  $D$  is the bulk dielectric constant,  $\mu$  is the ionic strength, and  $z_1$  and  $z_2$  are the charges on ions 1 and 2, respectively.

As  $K_{\text{os}} \simeq 1$  is expected for +2 and -1 ions from eq 12 in the reaction of  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  with  $\text{HR}^-$ , the rate constant  $k_{\text{w}}$  for nickel-water bond rupture will be of the order of  $10^3 \text{sec}^{-1}$ . On the other hand, Swift and Connick have determined the rate constant of water exchange for nickel(II) ion from nmr line-broadening measurements of  $\text{O}^{17}$ -labeled water exchanging in the inner coordination sphere of nickel(II) ion. The rate constant is  $2.7 \times 10^4 \text{sec}^{-1}$  at  $25^\circ$ .<sup>26</sup> This discrepancy may suggest that an intramolecular hydrogen bond in PAR ( $\text{HR}^-$ ) as shown in I slows the rate



(23) M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960).

(24) M. Eigen and K. Tamm, *ibid.*, **66**, 93 (1962).

(25) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

(26) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962)

of complexation. However this point of view seems unlikely, previous experimental facts being taken into account.

The rate constants for reactions<sup>27</sup> of bipy and bipyH<sup>+</sup> with nickel(II) ion are  $2.0 \times 10^3$  and  $26 M^{-1} \text{sec}^{-1}$  at 25°, respectively. The corresponding rate constants for ida<sup>2-</sup> (iminodiacetate) and idaH<sup>-28</sup> and for nta<sup>3-</sup> (nitrilotriacetate) and ntaH<sup>2-29</sup> are  $4.5 \times 10^4$  and  $7.7 \times 10^{-2} M^{-1} \text{sec}^{-1}$  at 25° ( $\mu = 1.25$ ) and  $4.8 \times 10^5$  and  $7.5 M^{-1} \text{sec}^{-1}$ , respectively. Thus these protonated ligands involving an intramolecular protonated structure show a rate constant 10<sup>2</sup>–10<sup>5</sup> times lower than the corresponding unprotonated ligands. Cassatt and Wilkins<sup>27</sup> have clarified the effect of charge and its distribution in the ligand and donor atom protonation on the complex formation of the aquonickel(II) ion with 22 different ligands. They have pointed that "a negatively charged group removed from the eventual coordination site is relatively unimportant." For example, the values of rate constants for diglycinate, triglycinate, and tetraglycinate are close to one another and to that of neutral ligand (Table IV). The value of  $k_{\text{H}_2\text{O}}$  for PAR obtained in the present study is also close to that of the similar neutral ligand (bipy, terpy, phen, etc). The negative charge removed from coordination sites in PAR thus seems unimportant in the complex formation.

TABLE IV  
FORMATION RATE CONSTANTS OF NICKEL(II) COMPLEXES

Ligand	$10^{-3}k$ , $M^{-1}$ $\text{sec}^{-1}$	$E_a$ , kcal/mol	Conditions	Ref
NH <sub>3</sub>	4		25°, $\mu = 0.1$ (NH <sub>4</sub> NO <sub>3</sub> )	a
Pyridine	4	12	25°	b
Imidazole	5		25°, $\mu = 0.15$	c
PAD <sup>g</sup>	4.0		15°, pH 6, $\mu = 0.1$ (KNO <sub>3</sub> )	d
bipy <sup>h</sup>	1.5	13.8	25°	b
	2.0		25°	e
phen <sup>i</sup>	3.9	13.7	25°	b
5-NO <sub>2</sub> phen <sup>j</sup>	1.9		25°	b
5-CH <sub>3</sub> phen	3.1		25°	b
5-Cl(phen)	0.28		25°	b
2-Cl(phen)	1.0		25°	b
terpy <sup>k</sup>	1.4	14.7	25°	f
NH <sub>2</sub> CH <sub>2</sub> CONH <sub>2</sub>	2.2		25°	e
NH <sub>2</sub> CH <sub>2</sub> CONHCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> (diglycine)	3.6		25°	e
NH <sub>2</sub> CH <sub>2</sub> (CONHCH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> <sup>-</sup> (triglycine)	3.7		25°	e
NH <sub>2</sub> CH <sub>2</sub> (CONHCH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> <sup>-</sup> (tetraglycine)	4.2		25°	e
PAR <sup>l</sup>	3.2		25°, pH 6.7, $\mu = 0.001$	f
	1.7	14.4 ± 0.5	25°, $\mu = 0.10$ (NaClO <sub>4</sub> )	This work

<sup>a</sup> D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966). <sup>b</sup> R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *ibid.*, **4**, 929 (1965). <sup>c</sup> G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962). <sup>d</sup> Reference 30. <sup>e</sup> Reference 27. <sup>f</sup> R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 621 (1966). <sup>g</sup> Pyridine-2-azo-*p*-dimethylaniline. <sup>h</sup> 2,2'-Bipyridine. <sup>i</sup> 1,10-phenanthroline. <sup>j</sup> 5-Nitro-1,10-phenanthroline. <sup>k</sup> 2,6-Bis(2'-pyridyl)pyridine(2,2',2''-terpyridine). <sup>l</sup> Monoanionic ligand.

In calculating the outer-sphere association constant for the case in which one of the reactive species is uncharged, eq 12 reduces to  $K_{\text{os}} = \frac{4}{3}a^3N \times 10^{-3}$ . Assuming a most probable value of 5 Å for  $a$  in the case of the reaction of the nickel(II) ion with PAR,  $K_{\text{os}}$  is approximately equal to 0.3. This value is in line with estimates made by previous workers who have utilized values of 0.3 and 0.1 for reactions involving the neutral ligands imidazole<sup>5</sup> and pyridine-2-azo-*p*-dimethylaniline,<sup>30</sup> respectively. Therefore the rate constant for nickel-water bond rupture is calculated to be  $6 \times 10^3 \text{sec}^{-1}$  which is in reasonable agreement with some previous kinetic results,<sup>31</sup> the difference in conditions being taken into consideration.

The effect of a ligand coordinated with the nickel(II) ion on the ease of replacement of remaining water molecules is then considered. It appears reasonable to assume that the values of outer-sphere association constants,  $K_{\text{os}}$ , for the nickel(II)-PAR complex formation reactions are similar because  $K_{\text{os}}$  is mainly determined by electrostatic factors and especially in the present case PAR behaves like an uncharged ligand as described above and that the rates of dissociation of water molecule from nickel(II) are not affected much by the formation of outer-sphere complexes. Therefore, in the reaction of the nickel(II)-PAR complex formation which proceeds by mechanism 10, the effect of a coordinated ligand, A, on the rate can be relatively estimated by comparison of the experimentally obtained rate constants  $k_A$ .

The rate of dissociation of water molecules from nickel complexes is considerably dependent on the nature of the ligand A coordinated to nickel. The order of increasing  $10Dq$  which is the difference between  $t_{2g}$  and  $e_g$  for an octahedral complex is usually found to be  $\text{N}_3^- < \text{F}^- < \text{OH}^- < \text{H}_2\text{O} < \text{CH}_3\text{CO}_2^-$ . If the dissociation of the acido ligand in monoacidopentaquo-nickel complexes is rate-determining, it is expected that the reactivity of these complexes decreases with increasing stability of the complexes: The order of reactivity should be  $\text{NiN}_3^+ > \text{NiO}_2\text{CCH}_3^+ > \text{NiF}^+ > \text{NiOH}^+$ . In effect the order of reactivity obtained in the present experiment is  $\text{F}^- < \text{H}_2\text{O} < \text{CH}_3\text{CO}_2^- < \text{OH}^- < \text{N}_3^-$  and does not agree with that described above. The effect of ligands already present in a complex on the ease of replacement of the remaining water molecules appears to be related to the electron donation from the ligands. As a measure of electron donation of ligands  $E_A$  values<sup>32</sup> are given in Table III.  $E_A$  is a redox factor defined by  $E_A = E^\circ + 2.60$ , where  $E^\circ$  is the standard oxidation potential for the process  $2A^- \rightleftharpoons A_2 + 2e$ .  $E_{\text{H}_2\text{O}}$  for water is zero by the definition. The plot of  $\log k_A$  vs.  $E_A$  is given in Figure 3. The plot yields a straight line.

When a ligand coordinated to the central metal ion donates electrons to the central metal to a greater extent, the bond of the central metal with the remain-

(27) J. C. Cassatt and R. G. Wilkins, *J. Am. Chem. Soc.*, **90**, 6045 (1968).

(28) T. J. Bydalek and A. H. Constant, *Inorg. Chem.*, **4**, 833 (1965).

(29) T. J. Bydalek and M. L. Blomster, *ibid.*, **3**, 667 (1964).

(30) R. G. Wilkins, *ibid.*, **3**, 520 (1964).

(31) Reference 3, p 156.

(32) J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954); **78**, 1819 (1956).

ing coordinated water molecules will weaken and more easily be broken. Thus the rate of loss of water molecule, *i.e.*, the rate of complex formation, will be faster. The effect of electron donation of ligands on the reactivity of the metal is quantitatively accounted for by the linear free energy relationship shown in Figure 3.

In a study on the rates of reaction of diethylenetriamine and of nitrilotriacetate ion with mono(5-X-1,10-phenanthroline)nickel(II) complexes, Steinhaus and Margerum<sup>33</sup> have indicated that the rates of formation of the mixed complexes increase with increasing electron-donating properties of the substituents (X). Moorhead and Sutin<sup>10</sup> have shown that the monohydroxoiron(III) complex loses water molecule from the inner sphere about 20 times faster than observed for the hexaquoiron(III) ion in the formation of the mono-oxalate complex of iron(III). The results of studies<sup>34,35</sup> on the formation of monoazidoiron(III) indicate that  $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$  undergoes reaction more rapidly than  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ . Plumb and Harris<sup>36</sup> have shown by measurements of the exchange of water between oxygen-18-labeled solvent and aquorhodium(III) ion that the rate for the dissociation of a water molecule from the monohydroxopentaaquorhodium(III) ion is about 150 times faster than that from the hexaquoiron(III) ion. Recently, Hunt, *et al.*,<sup>37</sup> have provided

(33) R. K. Steinhaus and D. W. Margerum, *J. Am. Chem. Soc.*, **88**, 441 (1966).

(34) D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

(35) D. W. Carlyle and J. H. Espenson, *ibid.*, **6**, 1370 (1967).

(36) W. Plumb and G. M. Harris, *ibid.*, **3**, 542 (1964).

(37) S. Marks, H. Dogen, and J. P. Hunt, "Proceedings of the 11th International Conference on Coordination Chemistry," Haifa and Jerusalem, Sept 1968, p 186.

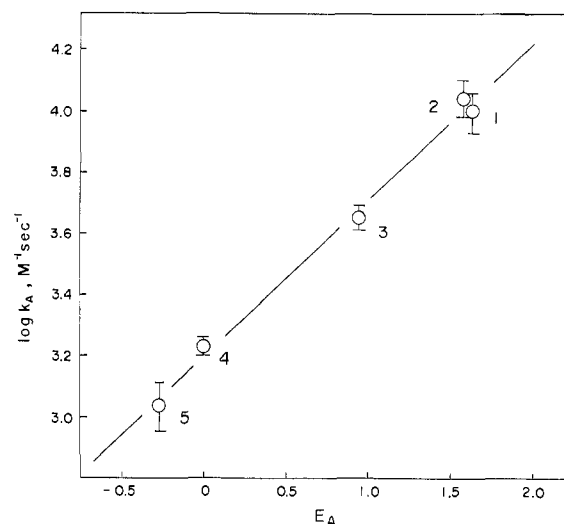


Figure 3.—Plot of  $\log k_A$  vs.  $E_A$ : 1,  $k_{\text{OH}}$ ; 2,  $k_{\text{N}_3}$ ; 3,  $k_{\text{CH}_3\text{CO}_2}$ ; 4,  $k_{\text{H}_2\text{O}}$ ; 5,  $k_{\text{F}}$ .

evidence that water exchange is labilized by the coordinated ammine ligand. The increase of these rates can be mainly attributed to the effect of loosening the water-metal bond owing to the electron donation of ligands coordinated to metal. Such an effect of coordinated ligands on the ease of replacement of the leaving ligands is also of particular importance in the stepwise coordination and dissociation of ligands.

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## The Preparation and Properties of Some Triphenylarsine- and Triphenylstibine-Stabilized Organoplatinum(II) Compounds

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The reaction of alkyl- and arylplatinum(II)-olefin complexes with triphenylarsine and triphenylstibine yields a series of compounds of the type  $\text{L}_2\text{PtR}_2$ , where L is  $(\text{C}_6\text{H}_5)_3\text{As}$  or  $(\text{C}_6\text{H}_5)_3\text{Sb}$  and R is a  $\sigma$ -bonded aryl or alkyl group. The properties of these compounds differ with the size of the stabilizing ligand and the position of substitution on the benzene ring. These properties are reported and discussed.

### Introduction

Aryl and alkyl derivatives of platinum(II) have been prepared using various tertiary phosphines and triethylarsine as strong-field-splitting ligands.<sup>2-5</sup> It has been reported<sup>3,6</sup> that the stability of tertiary-phosphine-

stabilized complexes of platinum(II), palladium(II), and nickel(II) containing alkyl-metal  $\sigma$  bonds decreases with an increase in the size of the alkyl chain. Also, the stability of complexes containing  $\sigma$ -bonded aryl groups varies with the position of substitution on the benzene ring; the *ortho*-substituted derivatives have greater thermal stability and are less reactive. This stability is attributed to the steric effects of the *ortho* groups which cause the aromatic rings to lie perpendicular to the square plane of the complex. In the platinum(II) compounds, this allows a maximum overlap

(1) To whom inquiries should be addressed.

(2) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

(3) J. Chatt and B. L. Shaw, *ibid.*, 4020 (1959).

(4) D. M. Adam, J. Chatt, and B. L. Shaw, *ibid.*, 2047 (1960).

(5) C. R. Kistner, J. H. Hutchinson, J. R. Doyle, and J. C. Storlie, *Inorg. Chem.*, **2**, 1255 (1963).

(6) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).