Steric Effects in Chelation Kinetics. The Formation and Dissociation of Nickel(II) Complexes with Branched Poly(amino alcohols) Related to Ethylenediaminetetraacetic Acid[1]
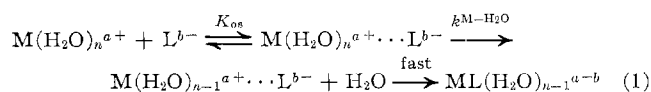
By D. B. RORABACHER, T. S. TURAN, J. A. DEFEVER, and W. G. NICKELS

The formation and dissociation kinetics of the 1:1 nickel complexes of N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine (TKED) and N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine (THPED) were investigated in aqueous solution at 25° over the pH range from 5.0 to 7.8 using spectrophotometric and pH-stat techniques. Formation and dissociation rate constants for both proton-independent and -dependent terms were evaluated for each compound. A comparison of these systems with previous results for nickel ion reacting with ammonia and the polyamines indicates that the formation rates are anomalously slow. Two alternate mechanisms are proposed to account for the kinetic behavior, both of which involve steric hindrance. Consideration of one of these mechanisms, involving the formation of a metastable intermediate where nickel is bonded to an alcoholic oxygen donor atom, permits the calculation of a minimum value of the rate constant for the rupture of a nickel–alcoholic oxygen bond in the aqueous environment. Based on the similarity in ligand structure, the results are correlated to the kinetic behavior of EDTA.

Introduction

In recent years a large number of kinetic studies have been carried out on the reactions of aquometal ions with both unidentate and multidentate ligands. Nearly all such studies support the general dissociative mechanism formulated by Eigen[2] as represented by the scheme

$$M(H_2O)_n{}^{a+} + L^{b-} \underset{}{\overset{K_{os}}{\rightleftharpoons}} M(H_2O)_n{}^{a+}\cdots L^{b-} \xrightarrow{k^{M-H_2O}}$$

$$M(H_2O)_{n-1}{}^{a+}\cdots L^{b-} + H_2O \xrightarrow{fast} ML(H_2O)_{n-1}{}^{a-b} \quad (1)$$

In this mechanism $M(H_2O)_n{}^{a+}$ represents an aquometal ion; L^{b-}, a ligand; K_{os}, the diffusion-controlled equilibrium constant for the formation of an outer-sphere complex, $M(H_2O)_n{}^{a+}\cdots L^{b-}$ (a species in which the reactants are nearest neighbors); and k^{M-H_2O}, the rate constant for metal–water bond rupture.

Steps following the first loss of a coordinated water molecule from the metal ion in the outer-sphere complex are usually rapid so that the first such metal–water bond rupture represents the rate-determining step, even for reactions of multidentate ligands which involve subsequent bonding steps. Therefore, the formation rate constant, $k_M{}^L$, for the observed second-order rate equation

$$-\frac{d[M(H_2O)_n{}^{a+}]}{dt} = k_M{}^L[M(H_2O)_n{}^{a+}][L^{b-}] \quad (2)$$

can be expressed as

$$k_M{}^L = K_{os}k^{M-H_2O} \quad (3)$$

Since K_{os} can be calculated with fair accuracy from diffusion equations[3,4] and k^{M-H_2O} values have been determined independently for many metal ions from sound absorption, temperature-jump, and nuclear mag-

netic resonance measurements, values for $k_M{}^L$ can, in many instances, be approximated from *a priori* calculations using eq 3. In this manner comparison can be made between theoretical and experimental rate constant values as a test for the applicability of the dissociative mechanism.[4] The constancy of formation rate constants for reactions involving a series of ligands of the same charge reacting with a specific aquometal ion also serves to support this mechanism.[2,5]

Although exceptions to the kinetic rates predicted by eq 3 are rare, a few anomalous systems have been noted. In earlier work it was found that the rate constants for the formation of nickel–polyamine complexes[6] markedly exceed the theoretical values. An internal conjugate base (ICB) mechanism, dependent on the highly basic nature of the donor atoms, has been proposed to account for the increase in these formation rate constants.[4] This mechanism represents a modification of the dissociative mechanism in which the value of K_{os} (and perhaps the value of k^{M-H_2O}) is enhanced for the polyamine reactions.

In the current investigation further anomalous kinetic behavior is reported involving the reactions of aquonickel ion with two closely related branched poly(amino alcohols): N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine (TKED)—the alcoholic analog of ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA)—and N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine (THPED). In marked contrast to the

$$\underset{R}{\overset{R}{>}}NCH_2CH_2N\underset{R}{\overset{R}{<}}$$
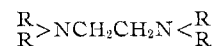
$$TKED, R = CH_2CH_2OH$$
$$THPED, R = CH_2CH(OH)CH_3$$

abnormally large rate constants noted in the preceding paragraph for the straight-chain polyamines, the

(1) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967; see Abstract No. O-104.

(2) M. Eigen in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 373.

(3) M. Eigen, W. Kruse, G. Maass, and L. deMaeyer, *Progr. Reaction Kinetics*, **2**, 287 (1964).

(4) D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

(5) M. Eigen and R. G. Wilkins in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55 ff.

(6) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).

branched poly(amino alcohols) included in this study exhibit reaction rates which are significantly *slower* than the theoretical values predicted by eq 3. This behavior is particularly notable since the latter ligands contain the ethylenediamine moiety and might, therefore, be expected to exhibit enhanced formation rate constants as a result of the ICB mechanism.

The kinetic sluggishness of the poly(amino alcohols) is attributed to steric hindrance and is discussed in terms of two alternate mechanisms, one of which involves a shift in the rate-determining step to the point of second bond formation. The role of the alcoholic oxygen donor atoms in the reaction mechanism is discussed and a lower limit is calculated for the rate constant of nickel–alcoholic oxygen bond rupture. The correlations to EDTA and the implications for related multidentate ligands are also noted.

Experimental Section

THPED ("QUADROL") was a gift of the Wyandotte Chemicals Corp., Wyandotte, Mich., and was obtained as a viscous colorless liquid with a purity level of better than 99.7% as determined by potentiometric titration with standard $HClO_4$ solution. TKED was donated by I.C.I. Organics, Inc., Providence, R. I., and was light yellow. Two separate samples of considerably different age yielded, by titration, apparent purity levels of 98 and 103%, the latter sample apparently containing a significant amount of lower molecular weight amines.

Reagents.—After vacuum distillation, preparative gas chromatography, and other purification methods proved unsuitable, TKED was purified by crystallizing the perchlorate salt using the following procedure. Liquid TKED (1 ml) was dissolved in 25 ml of methanol; 0.5–1.0 ml of 73.6% $HClO_4$ (G. F. Smith Chemical Co.) was added and the mixture was shaken well. Anhydrous ether was added until precipitation began and continued to be added slowly until precipitation was complete. The mixture was cooled in Dry Ice for a few minutes and vigorous scratching was performed immediately until white crystals began to form (if an oil is formed initially, scratching will convert this material to the crystalline form provided the initial TKED concentration is not too high). The precipitate was filtered, washed with ether, and dried at 80°. The yield obtained was about 70%. Recrystallization twice from methanol yielded a pure white, crystalline solid. *Anal.* Calcd for $C_{10}H_{24}N_2O_4 \cdot 2HClO_4$: C, 27.47; H, 5.99; N, 6.41. Found: C, 27.84; H, 5.82; N, 6.28.

Thin layer chromatography revealed that an unidentified impurity, present in significant amounts in the initial TKED samples, was removed by successive recrystallizations of the perchlorate salt (tlc solvents used include 4:1:1 $CH_3OH–H_2O–CCl_4$ for liquid TKED samples and 4:1 phenol–NH_4OH for perchlorate salt samples). Potentiometric titrations yielded values increasing from 96 to 98% purity as drying time was increased. Slight acid contamination was also indicated by these titrations.

Although no detectable impurities were present in the original THPED sample, the perchlorate salt of this ligand was also prepared for kinetic experiments using the procedure described above. *Anal.* Calcd for $C_{14}H_{32}N_2O_4 \cdot 2HClO_4$: C, 34.09; H, 6.95; N, 5.68. Found: C, 33.89; H, 7.02; N, 5.38.

All other chemicals were reagent grade and were used without further purification. All solutions were prepared with conductivity water. Poly(amino alcohol) solutions were standardized primarily by potentiometric acid–base titrations although spectrophotometric mole ratio plots with primary standard copper were utilized for some of the spectrophotometric experiments. $Ni(ClO_4)_2$ (prepared from reagent grade $NiCO_3$ and $HClO_4$) and $NiCl_2$ solutions were standardized by EDTA titration.

Kinetic Measurements.—The kinetics of the nickel complex formation reactions with TKED and THPED were studied spectrophotometrically at 250 and 255 mμ, respectively, using a Beckman DU-2 equipped with a thermostated 10-cm cell compartment maintained at 25.0 ± 0.1°. The molar absorptivity values determined for the purified substances were: at 250 mμ, ϵ_{TKED} 21, ϵ_{HTKED^+} 4.4, $\epsilon_{Ni^{2+}}$ 0.18, $\epsilon_{NiTKED^{2+}}$ 263; at 255 mμ, ϵ_{THPED} 23, ϵ_{HTHPED^+} 1.6, $\epsilon_{Ni^{2+}}$ 0.17, $\epsilon_{NiTHPED^{2+}}$ 215.

For the spectrophotometric experiments the pH was controlled with a borate–mannitol buffer[8] which was also incorporated into the reference solution. Constant ionic strength was maintained at 0.1 M using KCl, NaCl, or $NaClO_4$ with the type of salt used having no detectable kinetic effect.

The reaction kinetics with THPED were also measured using a Radiometer TTT1 automatic titrigraph as a pH-stat where the protons released in the reaction

$$Ni^{2+} + H_xL^{x+} \longrightarrow NiL^{2+} + xH^+ \qquad (4)$$
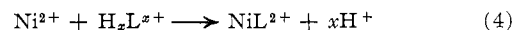
were automatically titrated with standard NaOH solution. For each pH studied, the value of x was calculated from the relationship

$$x = \bar{n}_H = \frac{[HL^+] + 2[H_2L^{2+}]}{[L] + [HL^+] + [H_2L^{2+}]}$$
$$= \frac{K_{H_1}[H^+](1 + 2K_{H_2}[H^+])}{1 + K_{H_1}[H^+](1 + K_{H_2}[H^+])} \qquad (5)$$

where L, HL^+, and H_2L^{2+} represent the unprotonated, monoprotonated, and diprotonated forms of the ligand, respectively, and K_{H_1} and K_{H_2} are the respective first and second protonation constants. When using the pH-stat method, reaction solutions were continuously swept with nitrogen to prevent interference from CO_2 absorption. Temperature and ionic strength conditions were identical with those used for the spectrophotometric measurements.

Results

Since all previous studies on TKED and THPED have apparently involved the use of unpurified ligands, the reaction rates of nickel ion with these ligands were measured using both liquid ligand samples as received without further purification and the recrystallized perchlorate salts. As shown by a comparison of the results, the impurities present in the original samples have no significant kinetic effect.

Under the conditions used, the complex formation reactions did not proceed to 100% completion but, at constant pH, were found to obey the reversible mixed second- and first-order rate equation

$$-\frac{d[Ni^{2+}]}{dt} = k_f[Ni^{2+}][\Sigma L] - k_d[NiL^{2+}] \qquad (6)$$

where k_f and k_d represent the observed formation and dissociation rate constants, respectively, for the prevailing conditions and $[\Sigma L]$ represents the total concentration of all species of uncomplexed ligand. The rate constants were evaluated by plotting the integrated form of the reversible rate equation[7]

$$\ln\left(\frac{2x - R - Q}{2x - R + Q}\right) = \ln\left(\frac{R + Q}{R - Q}\right) + k_f Q t \qquad (7)$$

where $R = (ab/x_e) + x_e$, $Q = (R^2 - 4ab)^{1/2}$, a, b = $[Ni^{2+}]$, $[\Sigma L]$ at time zero, $x = [NiL^{2+}]$ at any time t, and $x_e = [NiL^{2+}]$ at infinite time.

Computer iteration was utilized to determine the best x_e value consistent with the experimental data.[7] In this way it was possible to obtain an independent

(7) W. J. MacKellar and D. B. Rorabacher, to be submitted for publication.

check of the x_e values calculated from the protonation and stability constants and lend further confirmation to the latter constants (as listed in Table III).

Despite the complex nature of eq 7, this treatment yielded kinetic plots which were linear for greater than 95% of the approach toward equilibrium as shown in Figure 1 for typical THPED kinetic runs using the pH-stat. By means of such plots, the values of k_f and k_d were calculated from the relationships

$$k_f = \text{slope}/Q \tag{7a}$$

$$k_d = \frac{k_f}{\left(\dfrac{x_e}{(a - x_e)(b - x_e)}\right)} \tag{7b}$$

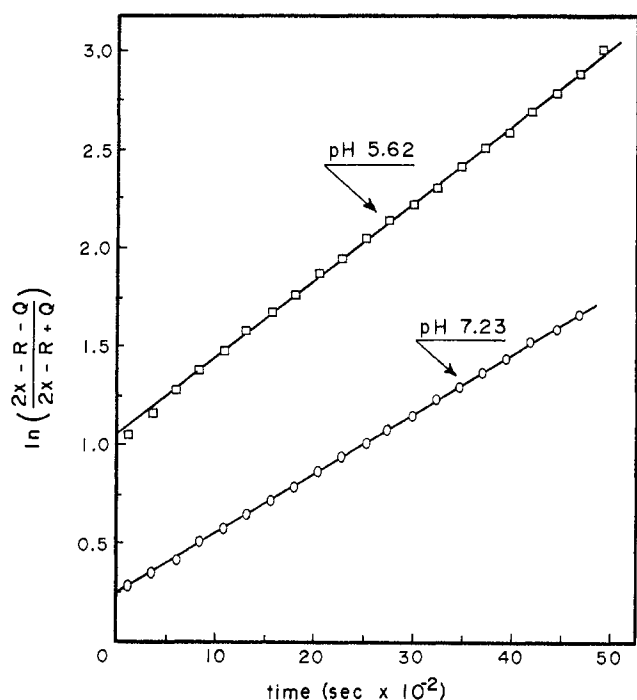The values of k_f and k_d for all runs are tabulated in Tables I and II.

Figure 1.—Typical plots of the integrated form of the mixed second- and first-order reversible rate equation (eq 7) illustrating the excellent linearity obtained by this treatment over the pH range studied. The plots shown are for the aquonickel ion reacting with THPED using the pH-stat method.

For each of the reactions studied the formation rate constants increase with increasing pH. This behavior is consistent with the behavior noted earlier for the polyamines[6] where electrostatic factors favor reaction of Ni^{2+} with the less protonated species. Similarly, the decrease of k_d values with increasing pH indicates the active role of the proton in assisting the dissociation of the complex.

In order to evaluate the individual contributions of the various protonated forms of the ligand to the overall observed formation rate, the protonation constants of the purified ligands were determined *via* potentiometric titration under conditions of temperature and ionic strength identical with those utilized for the kinetic measurements. To obtain the stability constant for the Ni–THPED complex, the titration pro-

TABLE I

EXPERIMENTAL RATE CONSTANTS FOR THE REACTION OF Ni^{2+} WITH TKED AT 25° AND $\mu = 0.1$

pH	$10^4[Ni^{2+}]$, M	$10^4[TKED]$, M	k_f, $M^{-1} sec^{-1}$	$10^4 k_d$, sec^{-1}
		Ligand Sample No. 1		
5.22	1.50	1.50	6.62	43.3
5.37	1.50	1.50	8.21	31.7
5.57	1.50	1.50	6.90	25.0
5.75	1.50	1.50	6.94, 6.22	15.1, 14.4
5.85	1.50	1.50	6.08	13.4
5.95	1.50	1.50	8.85	9.88
6.02	1.50	1.50	7.33	8.24
6.05	1.50	1.50	9.24, 9.69	7.25, 10.1
6.12	1.50	1.50	8.62	7.58
6.27	1.50	1.50	10.1	6.01
6.50	1.50	1.50	10.6	5.20
6.70	1.50	1.50	10.4	4.69
6.88	1.50	1.50	11.6	3.01
6.91	2.01	0.930	11.2	2.83
6.91	5.02	0.930	16.3	1.63
6.93	1.00	0.930	16.2	1.95
6.97	2.50	2.50	14.2, 15.2	2.25, 2.46
6.97	1.00	1.00	19.2	1.91
7.07	2.50	2.50	19.0	3.59
7.10	1.50	1.50	13.9	3.01
7.10	1.00	1.00	17.5, 17.7	3.48, 3.60
7.52	1.50	1.50	32.6	1.74
7.86	1.50	1.50	51.3	1.88
		Ligand Sample No. 2		
6.20	1.59	1.61	9.78	4.35
6.36	1.59	1.61	10.2	3.08
6.56	1.59	1.61	14.8	2.34
6.59	1.59	1.61	14.0	1.75
6.92	1.59	1.61	18.4	1.68
7.75	1.59	1.61	49.5	0.877
		Perchlorate Salt		
5.81	1.59	1.48	6.06	11.06
6.00	1.59	1.57	7.97	6.18
6.10	1.59	1.48	6.43	6.97
6.25	1.59	1.48	6.67, 7.92	5.45, 4.40
6.50	1.59	1.48	12.65	2.26
6.67	1.59	1.57	10.24	3.22
7.08	1.59	1.48	20.45	1.50
7.19	1.59	1.57	18.57	1.67

cedure was repeated in the presence of a 10-fold excess of nickel ion using a modification of the method of Bjerrum.[8] For the Ni–TKED complex, the stability constant was calculated from spectrophotometric measurements. The resultant values for both the protonation and stability constants are listed in Table III where they are compared with literature values[9–12] previously determined at different ionic strength using unpurified ligands. The stability constants obtained from the ratio of the resolved kinetic rate constants are also given for comparison.

The kinetic data are found to conform to a reaction scheme in which it is assumed that only the unprotonated and monoprotonated ligand species react at a

(8) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(9) K. H. Pearson and K. H. Gayer, *Inorg. Chem.*, **3**, 476 (1964).

(10) J. L. Hall, W. E. Dean, and E. A. Pacofsky, *J. Am. Chem. Soc.*, **82**, 3303 (1960).

(11) J. L. Hall, F. R. Jones, C. E. Delchamps, and C. W. McWilliams, *ibid.*, **79**, 3361 (1957).

(12) D. A. Keyworth, *Talanta*, **2**, 383 (1959).

TABLE II

EXPERIMENTAL RATE CONSTANTS FOR THE REACTION
OF Ni^{2+} WITH THPED AT 25° AND $\mu = 0.1$

pH	$10^4[\text{Ni}^{2+}]$, M	$10^4[\text{THPED}]$, M	k_f, $M^{-1} \sec^{-1}$	$10^5 k_d$, $\sec^{-1}$
		Ligand Sample No. 3		
4.90	10.6	1.00	2.00	
5.14	2.50	2.50	2.18	
5.30	2.50	2.50	2.68	
5.39	5.30	1.00	2.28	
5.43	21.0	1.00	2.55	
5.51	2.50	2.50	3.43	
5.63	5.30	1.00	3.18	
5.70	10.6	1.00	2.81	
5.73	2.50	2.50	3.22	
5.82	2.50	2.50	3.35	
5.92	2.50	2.50	3.45	
6.08	5.30	1.00	3.81	
6.10	2.50	2.50	3.47	
6.16	10.6	1.00	3.08	
6.49	2.50	2.50	4.25	
6.53	10.6	1.00	3.16	
6.75	5.30	1.00	4.43	
6.81	10.6	1.00	4.02	
6.84	2.50	2.50	5.13	
6.92	2.50	2.50	5.67	
7.36	2.50	2.50	7.13	
7.54	2.50	2.50	9.35	
7.84	5.30	1.00	9.33	
7.88	2.50	2.50	12.10	
		Perchlorate Salt		
5.45	1.54	1.53	2.21	(10.9)
5.62	1.54	1.53	2.56	(9.39)
5.82	1.54	1.53	2.78	(6.63)
5.90	1.23	2.65	2.82	
6.01	2.06	1.06	2.89	
6.16	2.57	0.530	3.02	
6.39	1.03	1.02	3.03	
6.58	1.23	2.64	3.89	
6.59	1.54	1.53	3.67	(3.65)
6.67	2.57	0.530	3.67	
6.79	2.05	1.06	4.28	
7.09	1.54	1.53	7.58	(2.41)
7.20	2.57	0.525	6.33	
7.21	1.23	2.64	6.83	
7.23	1.54	1.53	7.96	(1.64)
7.63	2.05	1.06	11.23	

TABLE III

PROTONATION CONSTANTS AND NICKEL COMPLEX
STABILITY CONSTANTS FOR TKED AND THPED AT 25°

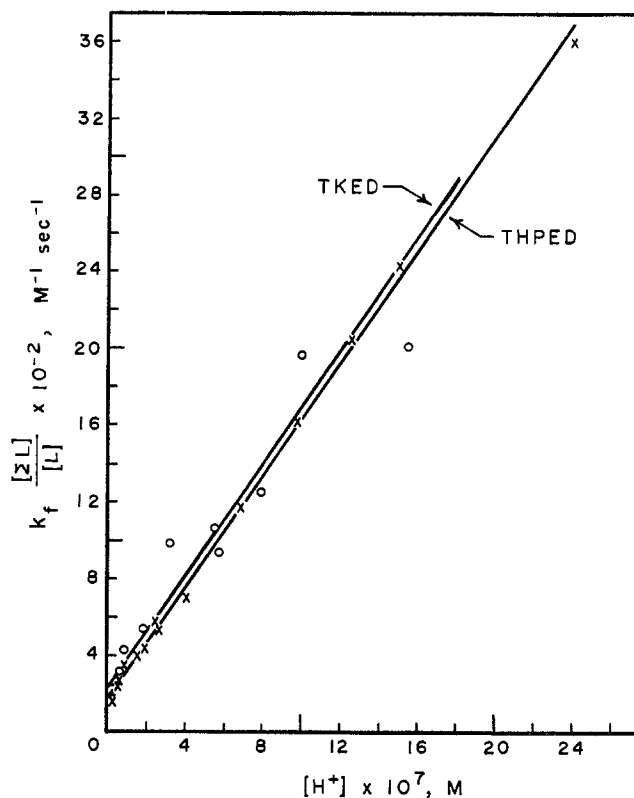| Ionic strength, M	Log K_{H1}	Log K_{H2}	Log K_{NiL}	Ref
		TKED		
0.1 NaClO$_4$	8.38[a]	4.37[a]	6.5 (spectro) 6.5 (kinetic)	This work
0.5 NaClO$_4$	8.45	4.45	6.50	9
0.5 KNO$_3$	...	...	6.27	10
		THPED		
0.1 NaClO$_4$	8.75	4.24	7.45 (titrim) 7.0 (kinetic)	This work
0.5 KNO$_3$	8.84	4.33	7.65	11
0.05 KNO$_3$	...	...	6.85	12

[a] Data courtesy of W. J. MacKellar.

Figure 2.—Resolution of the formation rate constants for the aquonickel ion reacting with the unprotonated and monoprotonated ligand species. Plot of eq 9: O, TKED data; ×, THPED data.

significant rate. Since proton transfer is very rapid compared to the other reaction steps,[3] this scheme yields the expanded differential rate expression

$$-\frac{d[\text{Ni}^{2+}]}{dt} = k_{\text{Ni}}{}^{L}[\text{Ni}^{2+}][\text{L}] + k_{\text{Ni}}{}^{HL}[\text{Ni}^{2+}][\text{HL}^+] -$$
$$k^{\text{NiL}}[\text{NiL}^{2+}] - k_{\text{H}}{}^{\text{NiL}}[\text{H}^+][\text{NiL}^{2+}] \quad (8)$$

Combining eq 6 and 8, it is possible to resolve the individual rate constants by plotting the expressions

$$k_f \frac{[\Sigma \text{L}]}{[\text{L}]} = k_{\text{Ni}}{}^{L} + k_{\text{Ni}}{}^{HL} K_{H1}[\text{H}^+] \quad (9)$$

$$k_d = k^{\text{NiL}} + k_{\text{H}}{}^{\text{NiL}}[\text{H}^+] \quad (10)$$

Plots of eq 9 and 10 are shown in Figures 2 and 3 for the data obtained with the perchlorate salts and the resolved rate constants for each of the systems studied are listed in Table IV. TKED data obtained by another worker using the pH-stat method are also listed for comparison. The data for TKED ligand sample no. 1 are considered to contain a slight imprecision in the

selection of the equilibrium position and are not included in determining the median values for the resolved rate constants. For the THPED data the larger stability constant for the nickel complex results in equilibria which greatly favor complex formation. As a result, the dissociation rate constants obtained from the use of eq 7b are much less precise.

Discussion

Comparison with Related Systems.—Since both TKED and THPED are neutral species, a direct comparison can be made between the formation rate constants obtained in this study and previously determined values for other neutral ligands on the assumption that the K_{os} values will be approximately of the
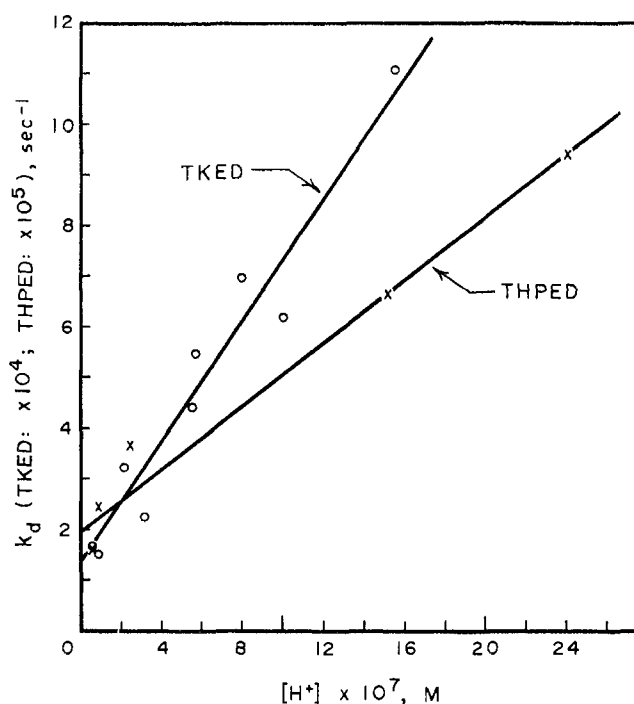
Figure 3.—Resolution of the dissociation rate constants involving proton-independent and proton-dependent terms. Plot of eq 10: O, TKED data; ×, THPED data.

TABLE IV

RESOLVED RATE CONSTANTS FROM EQ 8 AT 25° AND $\mu = 0.1$

Data set	$10^{-2}k_{Ni}^{L}$, M^{-1} sec^{-1}	k_{Ni}^{HL}, M^{-1} sec^{-1}	$10^{5}k^{NiL}$, sec^{-1}	$10^{-2}k_{H}^{NiL}$, M^{-1} sec^{-1}
		TKED		
Ligand sample no. 1 (spectro)	(2.6)	(8.0)	(18)	(7.4)
Ligand sample no. 2 (spectro)	2.8	8.6	8.5	5.2
Purified HClO$_4$ salt (spectro)	2.1	6.1	13.2	6.0
Purified HClO$_4$ salt (pH-stat)	2.4[a]	9.2[a]	7.5[a]	7.2[a]
Median values	2.4	8.6	8.5	6.0
		THPED		
Ligand sample no. 3 (spectro)	1.5	3.1	. . .	. . .
Purified HClO$_4$ salt (pH-stat)	1.8	2.6	(1.9)	(0.27)
Median values	1.7	2.8	(1.9)	(0.27)

[a] W. J. MacKellar, unpublished results.

same magnitude. Such a comparison with representative systems is given in Table V.

From a comparison of the k_{Ni}^{L} values it is apparent that the unprotonated species of TKED and THPED react with aquonickel ion 1000 times more slowly than does ethylenediamine. This difference is particularly significant since both TKED and THPED contain the ethylenediamine moiety. However, as noted in the Introduction, the formation rate constant shown for unprotonated ethylenediamine reacting with aquonickel ion is anomalously large relative to the theoretical value. This fact has been attributed to an internal conjugate base (ICB) mechanism in which hydrogen-bond formation in the outer-sphere complex be-

TABLE V

COMPARISON OF RATE CONSTANTS FOR NICKEL COMPLEXES IN AQUEOUS SOLUTION AT 25° AND $\mu = 0.1$

Ligand	Log k_{Ni}^{L}, M^{-1} sec^{-1}	Log k_{Ni}^{HL}, M^{-1} sec^{-1}	Log k^{NiL}, sec^{-1}	Log k_{H}^{NiL}, M^{-1} sec^{-1}	k_{Ni}^{L} remarks
NH$_3$[a]	3.6	. . .	0.6	. . .	Normal
en[b]	5.3[c]	2.8	-2.7	(5.2)	Fast
TKED	2.4	0.9	-4.1	2.8	Slow
THPED	2.2	0.4	(-4.7)	(1.4)	Slow

[a] Reference 4. [b] A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 3700 (1959); cf. ref 5. [c] In ref 4 the 0° value for log k_{Ni}^{L} = 4.6 for ethylenediamine was inadvertently listed instead of the 25° value which is correctly given here.

tween a highly basic donor atom and a proton of one of the coordinated water molecules increases the value of K_{os} and/or k^{M-H_2O}.[4] If TKED and THPED are presumed to react by the same mechanism without further modification, the formation rate constants for aquonickel ion reacting with these two ligands would also be expected to be abnormally large, although the decreased basicity of the nitrogen donor atoms (Table III) would lead one to expect a smaller accelerative effect.

As noted in Table V, however, both TKED and THPED exhibit rate constants which are about 20 times *smaller* than the theoretical value for neutral ligands (as represented by the rate constant for ammonia[4]). An even larger decrease is observed for the formation rate constants of the monoprotonated species relative to the theoretical value for unipositive ligands (where the formation rate constant for monoprotonated ethylenediamine may be taken as an approximate standard[13]). Therefore, it is evident that tetraalkanol substitution on the nitrogen donor atoms of ethylenediamine involves the introduction of one or more factors which slows complex formation to a rate below that which is anticipated on the basis of the normal dissociative mechanism.

In accord with previous arguments, the following factors are proposed as possible modifying influences which are most consistent with the results obtained in related studies:[14] (a) the concept of rapid ligand insertion into the inner coordination sphere of the intermediate of lower coordination number is modified by the substitution of the alkyl alcohol groups, or (b) the first bond formation does not represent the rate-determining step. These factors, both of which can be related to steric hindrance, are discussed in terms of

(13) Applying the equation for outer-sphere complex formation

$$K_{os} = \frac{4}{3}\pi a^3 N_A \exp\left(\frac{-z_A z_B e_0^2}{\epsilon k T a'}\right) \times 10^{-3}$$

(see ref 4 for definition of symbols) to the reaction between Ni(H$_2$O)$_6^{2+}$ and Hen$^+$, where a (the center-to-center distance of closest approach between the aquonickel ion and the unprotonated nitrogen donor atom of en) is assumed to be 3.5 Å and a' (the center-to-center distance between the nickel ion and the protonated nitrogen) is assumed to be 7 Å, one obtains $K_{os} = 0.018$ at 25°. Using $k^{Ni-H_2O} = 3 \times 10^4$ sec^{-1}, eq 3 yields log $k_{Ni}^{Hen} = 2.7$, which is in excellent agreement with the calculated experimental value of 2.8 (J. C. Cassatt and R. G. Wilkins, *J. Am. Chem. Soc.*, 90, 6045 (1968)).

(14) The possibility of an associative mechanism is discounted on the basis of arguments presented in ref 4. In addition, the possibility that K_{os} and/or k^{Ni-H_2O} might be decreased in a manner analogous but opposite in effect to the ICB mechanism is discounted on the basis of the physical properties of the species involved.

the two available stepwise reaction paths for the poly-(amino alcohols) which are depicted schematically in Figure 4.[15]
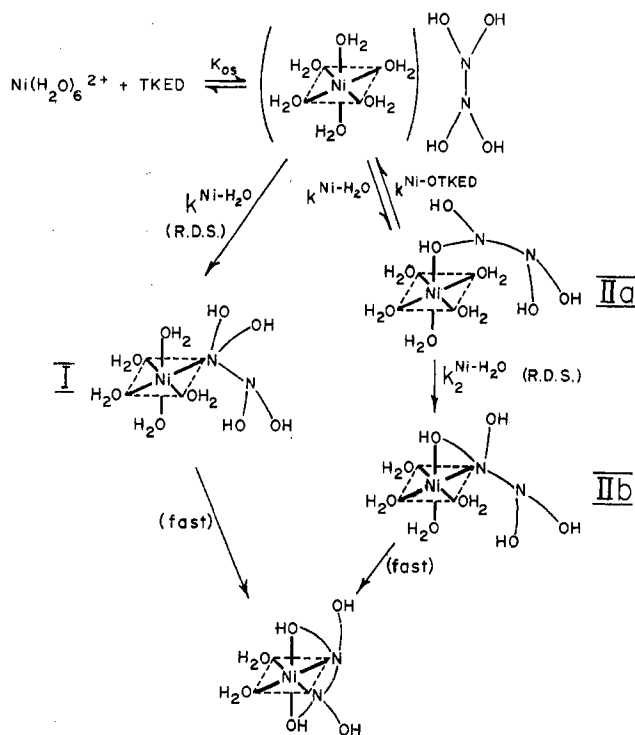

Figure 4.—Schematic representation of the two alternate reaction mechanisms proposed in the text. Mechanism I is represented by the reaction path involving intermediate I while intermediates IIa and IIb designate the reaction path for mechanism II.

Mechanism I. Initial Bonding to a Nitrogen Donor Atom.

—Reaction path I involves first-bond formation to a nitrogen donor atom, thereby paralleling the mechanism for the reaction of aquonickel ion with ethylenediamine. On the basis of the dissociative mechanism, the nature of substitution on a neutral ligand should not affect the rate of complex formation (except as it may increase the center-to-center distance of closest approach) and the poly(amino alcohols) should react at least as fast as the rate predicted by eq 3. However, as originally applied to the dissociative mechanism, eq 3 does not consider the fact that the ligand must be properly oriented in the outer-sphere complex at the time of metal–solvent bond rupture in order to promote coordinate bond formation.[16]

Molecular models indicate that, in the case of TKED

(15) It is to be noted that, whereas the final product in Figure 4 is shown with two alcoholic oxygens bonded to the nickel ion, the actual time-averaged number of such bonds formed is not discernible by the techniques used. Previous workers have suggested that all four alcoholic oxygen donor atoms are bonded in the complex ion: ref 9. Based on the weakly bonding nature of these donor atoms, this seems unlikely although steric considerations and/or the hydrophobic nature of the ethylene chains in the ligand might tend to favor such bonding in a species in which the two nitrogen donor atoms are already bonded to the nickel ion. The slower dissociation rate constants for the TKED and THPED complexes relative to the en complex (Table V) can be interpreted to represent evidence of significant bonding of nickel to the alcohol groups in the complex ion.

(16) This phenomenon is suggested in ref 3 where the rate constants for proton combination with F^- and HS^- are in the ratio of 4:3, in line with the degree of accessibility to reactive sites on the anion. Corresponding decreases are noted for other asymmetric bases.

and THPED, a majority of possible ligand configurations result in steric blocking of the nitrogen donor atoms by the bulky alkanol groups so that metal–nitrogen coordinate bond formation cannot proceed. Although it appears possible to fold back the alkanol groups in such a way as to make bonding of the nitrogens to a solvated metal ion feasible, such a configuration involves considerable crowding on the back side of the ligand and should be less favorable energetically than other configurations. Furthermore, this situation appears more acute for THPED than for TKED.

It is postulated that the configurational changes required to fold back the alkanol groups in the poly-(amino alcohols), in order to expose the nitrogen donor atoms, cannot occur within the short lifetime normally assumed for the intermediate of lower coordination number, represented in eq 1 as $M(H_2O)_{n-1}{}^{a+} \cdot L^{b-}$ (not shown in Figure 4). The reaction rate *via* mechanism I then reflects the percentage of ligand molecules in the outer-sphere complex which are in a configuration suitable for bonding at the time metal–solvent bond rupture occurs. For all other configurations, only simple solvent exchange results, thereby producing no observable reaction.

Minimum Values for Steric Factors.—In relating the experimentally observed rate constants to a steric factor as described above, it is useful to express the magnitude of the steric effect in terms of some reference value. A convenient relationship to apply is the logarithmic ratio defined for the organic substituent effect, E_s,[17] where k_0 is a reference rate constant for a

$$E_s = \log (k/k_0) \tag{11}$$

system without appreciable steric hindrance. Taking for k_0 the theoretical rate constant values for nickel reactions as calculated from eq 3, one obtains the E_s values listed in Table VI.

TABLE VI
APPARENT STERIC FACTORS FOR AQUONICKEL ION
REACTING WITH THE POLYAMINO ALCOHOLS AT 25°

Ligand species	Log $k_{Ni}{}^L$				Apparent ICB effect
	Theoret	Exptl	E_s	ΔE_s	
TKED	3.6[a]	2.4	−1.2		
				0.6	Fourfold
HTKED+	2.7[b]	0.9	−1.8		
THPED	3.6[a]	2.2	−1.4		
				0.9	Eightfold
HTHPED+	2.7[b]	0.4	−2.3		

[a] Reference 4. [b] Reference 13.

Since the monoprotonated ligands cannot involve an ICB mechanism, the E_s values calculated for HTKED+ and HTHPED+ are presumed to represent the extent of steric hindrance involved in these ligands if mechanism I is the actual reaction path. Further, since this mechanism will be preferred only if this path represents the most favorable route kinetically, these values are presumed to be minimal E_s values. There-

(17) (a) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 3120 (1952); (b) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956.

fore, steric factors must decrease the reactivity of HTKED$^+$ and HTHPED$^+$ at least 60 and 200 times, respectively, relative to the theoretical rate constant predicted by the dissociative mechanism.

Although the steric considerations are not directly comparable, values reported for organic substitution reactions[17b] indicate that these E_s values are of a reasonable order of magnitude as is the threefold difference observed between the tetraethanol- and tetrakis-2-propanol-substituted ligands. It is concluded, therefore, that mechanism I cannot be ruled out on the basis of the apparent magnitude of the steric factor as calculated from the experimental rate constants.

Evidence of an Internal Conjugate Base Effect.— The smaller E_s values calculated for the unprotonated species can be attributed to the superimposition of the ICB mechanism upon the steric effect. As represented logarithmically by the ΔE_s values in Table VI, there is an apparent acceleration of 4 times for TKED (log K_{H1} = 8.38) and 8 times for THPED (log K_{H1} = 8.75). As correlated to the relative basicities of the ligand donor atoms, this interpretation is consistent with the accelerating ICB effects previously reported:[4] 6 times for 2,2′-ethylenediaminobis(2-methyl-3-butanone) dioxime (log K_{H1} = 8.5), 20 times for monoprotonated triethylenetetramine (log K_{H2} = 9.2), and 50 times for ethylenediamine (log K_{H1} = 10.0). It is implied, therefore, that a nitrogen donor atom which is sterically blocked for coordinate bond formation may still engage in hydrogen-bond formation as required for the ICB mechanism and that the strength of such a hydrogen bond parallels the basicity of the nitrogen donor atom.

Mechanism II. Initial Bonding to an Alcoholic Oxygen Donor Atom.—Mechanism II takes into consideration the fact that alcoholic oxygen donor atoms are also available for coordinate-bond formation. Such bonds are known to be weak relative to metal–water bonds, as evidenced by the strong preference of metal ions for water molecules in mixed water–alcohol solvents,[18-20] and would normally be of little consequence in aqueous solutions. In addition, kinetic evidence has been accumulated from studies in mixed solvents to support the fact that, in the case of metal ions with mixed solvation in the inner coordination sphere, metal–alcoholic oxygen bonds break much more rapidly than metal–water bonds.[21-24]

Despite the foregoing evidence for the relative lability of the nickel–alcoholic oxygen bond, it is apparent from molecular models that, in branched poly(amino alcohols) such as TKED and THPED, metal bonding to an oxygen facilitates subsequent bonding to a nitro-

gen donor atom. Therefore, mechanism II could become a significant reaction path if the direct attack of the nickel ion on a nitrogen donor atom, as discussed under mechanism I, is greatly hindered.

Using HTKED$^+$ as a model to avoid the possible complication of an ICB effect, the application of the steady-state approximation to the singly bonded intermediate, IIa, yields the differential rate expression

$$-\frac{d[\mathrm{Ni}^{2+}]}{dt} = \frac{K_{os}k^{\mathrm{Ni-H_2O}}k_2{}^{\mathrm{Ni-H_2O}}}{k^{\mathrm{Ni-OTKED}} + k_2{}^{\mathrm{Ni-H_2O}}}[\mathrm{Ni}^{2+}][\mathrm{HTKED}^+] \quad (12)$$

where $k^{\mathrm{Ni-OTKED}}$ represents the rate constant for nickel–alcoholic oxygen bond rupture (see Figure 4) and $k_2{}^{\mathrm{Ni-H_2O}}$ represents the rate constant for rupture of a nickel–water bond from a species which includes one alcoholic oxygen in the inner coordination sphere, modified by the rotational barrier inherent in rotating the nitrogen into position for second-bond formation.[6]

If $k^{\mathrm{Ni-OTKED}}$ were smaller than $k_2{}^{\mathrm{Ni-H_2O}}$, eq 12 would reduce to eq 3. However, the experimental rate constants in Table V clearly indicate that HTKED$^+$ reacts much more slowly than the rate predicted by eq 3 despite the fact that reaction path II represents an available route for complex formation. Since approach to the alcoholic oxygens is not sterically hindered, this sluggishness cannot be attributed to a steric factor. Therefore, it is concluded that $k^{\mathrm{Ni-OTKED}}$ must be greater than $k_2{}^{\mathrm{Ni-H_2O}}$ in accord with the mixed solvent studies cited above and, as a result, the second-bond formation must represent the rate-determining step in mechanism II.

Minimum Rate Constant for Nickel–Alcoholic Oxygen Bonding Rupture.—For the condition $k^{\mathrm{Ni-OTKED}} > k_2{}^{\mathrm{Ni-H_2O}}$, eq 8 and 12 combine to yield

$$k_{\mathrm{Ni}}{}^{\mathrm{HTKED}} = \frac{K_{os}k^{\mathrm{Ni-H_2O}}k_2{}^{\mathrm{Ni-H_2O}}}{k^{\mathrm{Ni-OTKED}}} \quad (13)$$

Using the known value for $k^{\mathrm{Ni-H_2O}}$ and calculated values for K_{os} and $k_2{}^{\mathrm{Ni-H_2O}}$, eq 13 can be used to estimate a minimum value for $k^{\mathrm{Ni-OTKED}}$ since the experimental value for $k_{\mathrm{Ni}}{}^{\mathrm{HTKED}}$ places an upper limit on the reaction rate *via* mechanism II.

Using molecular models to estimate the center-to-center distance of closest approach for an aquonickel ion adjacent to an alcoholic oxygen of HTKED$^+$ in the outer-sphere complex and the correlating repulsive distance between the nickel ion and the ligand proton (a = 7 Å, a' = 10.5 Å) gives an estimated K_{os} value of 0.22 (compare to ref 13). By comparison with estimates for ethylamine group rotation in the polyamines,[6,25] the rotational barrier for an ethanol group should decrease the rate of second-bond formation about 20–40 times relative to the value normally anticipated for nickel–water bond rupture—*i.e.*, $k_2{}^{\mathrm{Ni-H_2O}}$ $\approx 10^3$ sec^{-1}.[26] On the basis of these values, eq 3 yields a value of $k^{\mathrm{Ni-OTKED}} \approx 8 \times 10^5$ sec^{-1}. The fact that

(18) J. Bjerrum and C. K. Jørgensen, *Acta Chem. Scand.*, **7**, 951 (1953); C. K. Jørgensen, *ibid.*, **8**, 175 (1954).

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(23) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 1058, 1066, 2686 (1964).

(24) W. J. MacKellar and D. B. Rorabacher, Abstract INOR-38, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, F. R. Shu and D. B. Rorabacher, to be submitted for publication.

(25) D. B. Rorabacher, Ph.D. Thesis, Purdue University, 1963.

(26) The threefold difference between the rate constants for HTKED$^+$ and HTHPED$^+$, as noted in Table V, is then attributed to the difference in the potential energy barriers for rotation about the bonds in a 2-propanol group relative to an ethanol group. This correlates directly with the threefold difference cited for methyl rotation in isobutane relative to propane: J. G. Aston, *Discussions Faraday Soc.*, **10**, 73 (1951).

this value is approximately 25 times larger than the experimental aqueous value for $k^{\text{Ni-H}_2\text{O}}$ [27] is in very good agreement with the equilibrium data for mixed inner-sphere solvation in alcohol–water solvents, presuming that the latter values correlate to the relative rates of bond rupture for the two types of nickel–oxygen bonds.[18–20]

The use of data for the unprotonated TKED and THPED ligand species results in smaller values for $k^{\text{Ni-OTKED}}$. This discrepancy is attributed to the same factor cited for the ΔE_s values noted in Table VI, namely, that an ICB effect is actively promoting the bonding of the first donor atom—in this case an alcoholic oxygen.

Comparison with EDTA Systems.—Although the current data do not permit a conclusive choice to be made as to whether mechanism I or II predominates in the formation of the poly(amino alcohol) complexes, information on related ligands indicates that mechanism II is preferred. For example, preliminary investigations indicate that aquonickel ion reactions with species such as N,N,N',N'-tetraethylethylenediamine, for which reaction path II is not available, proceed at rates slower than the poly(amino alcohol) reactions despite the smaller steric factors involved.[28]

Studies on ligand-substitution[29] and metal-substitution[30] reactions involving metal complexes of EDTA and related poly(aminocarboxylate) ligands have indicated that the rate-determining step in both cases involves the formation of a metal–nitrogen bond in a species which already has a carboxylic oxygen bonded to the metal ion. In addition, theoretical values calculated *via* eq 13 for the formation rate constants of aquonickel ion reacting with monoprotonated and diprotonated EDTA are in good agreement with the experimental values as shown in Table VII.[31–33]

TABLE VII
COMPARISON OF EXPERIMENTAL RATE CONSTANTS AND VALUES
PREDICTED FOR NICKEL–EDTA COMPLEX FORMATION *via*
MECHANISM II AT 25° AND $\mu = 0.1$[a]

Rate constant	Predicted values	Exptl values	
		Ref 32	Ref 33
$k_{\text{N}_1}^{\text{HEDTA}}$	4.7×10^5	3.0×10^5	1.8×10^5
$k_{\text{Ni}}^{\text{H}_2\text{EDTA}}$	4×10^3	1×10^3	2×10^3

[a] All rate constant values in M^{-1} sec.$^{-1}$

Since the steric factors for TKED and EDTA are essentially identical, the minimal E_s value calculated in Table VI must apply to the latter ligand as well. Application of this value results in predicted nickel–

EDTA formation rate constants *via* mechanism I which are much smaller than the experimental values listed in Table VII. Therefore, EDTA complex formation reactions are presumed to proceed by mechanism II. Assuming that the experimental rate constants for TKED and THPED also represent reaction by mechanism II, the larger rate constants for EDTA are then attributed to a combination of favorable factors including (a) a more favorable electrostatic factor, (b) a reduced rotational barrier in the formation of the second bond,[25] and (c) the slower bond rupture of the nickel–carboxylic oxygen bond relative to the nickel–alcoholic oxygen bond.[34]

Conclusions

Both of the mechanisms discussed represent valid paths for the reaction of the poly(amino alcohols) with the aquonickel ion and, on the basis of previous studies, these appear to represent the most favorable reaction paths available. Since kinetic theory dictates that the most favorable reaction path will dominate, it is obvious that neither mechanism is capable of promoting complex formation at a rate faster than that which has been observed experimentally. Therefore, the E_s and $k^{\text{Ni-OTKED}}$ values calculated can be regarded as minimum limiting values.

Regardless of which mechanism is the more favorable, the following conclusions can be drawn.

(1) Tertiary substitution of bulky groups (equivalent to three or more carbon or oxygen atoms per group) on a nitrogen donor atom results in severe steric hindrance toward its reaction with an aquometal ion. This amounts to a minimum rate decrease of 60 and 200 times for TKED and THPED, respectively, relative to theoretically anticipated rate constants.

(2) Despite the steric blocking effects of the substituted alkanol groups in TKED and THPED, comparisons of the rate constants for the unprotonated and monoprotonated ligands give evidence that hydrogen bonding in the outer-sphere complex is actively accelerating complex formation according to the previously proposed ICB mechanism.

(3) The rate constant for rupture of a nickel–alcoholic oxygen bond in the poly(amino alcohols) is at least 25 times greater than for a nickel–water bond in aqueous solution. This difference has important implications relating to the kinetics of reactions occurring in alcohol and alcohol–water solvents.[24]

(4) Owing to steric blocking of the nitrogen donor atoms, EDTA reacts with the aquonickel ion *via* mechanism II in which the first metal–ligand bond formation involves a carboxylic oxygen donor atom followed by second-bond formation to a nitrogen donor atom as the rate-determining step. Unprotonated EDTA (log $K_{\text{H1}} = 10.26$) should have an increased

(27) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).
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(29) D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, **3**, 382 (1964).
(30) D. W. Margerum and T. J. Bydalek, *ibid.*, **2**, 683 (1963); D. W. Margerum, D. L. Janes, and H. M. Rosen, *J. Am. Chem. Soc.*, **87**, 4463 (1965).
(31) The experimental stability constant for the mono(acetato)nickel(II) complex ion was used to estimate the quantity $K_{\text{os}}k^{\text{Ni}-\text{H}_2\text{O}}/k^{\text{Ni}-\text{OEDTA}}$ with a correction for the electrostatic forces arising between the metal ion and the charged sites in the EDTA species; *cf.* ref 25.
(32) C. M. Cook, Jr., and F. A. Long, *J. Am. Chem. Soc.*, **80**, 33 (1958).
(33) D. W. Margerum and B. A. Zabin, *J. Phys. Chem.*, **66**, 2214 (1962).

(34) This agrees with recent experimental data indicating that the rate constant for nickel–acetate bond rupture is only slightly larger than for the nickel–water bond: M. A. Pancholy and T. K. Saksena, *Acustica*, **18**, 299 (1967); H. Hoffmann, Case-Western Reserve University, to be submitted for publication.

rate constant for nickel complex formation due to the influence of the ICB effect. This, in turn, implies that the stability constant of the nickel–EDTA complex may be larger than would otherwise be anticipated.

Although mechanism II has been postulated previously for EDTA reactions, the evidence was largely circumstantial and the preference for this mechanism was primarily attributed to the favorable charge on the carboxylic oxygen atoms. It is now seen that reaction *via* mechanism I is sterically hindered to the extent that mechanism II represents the more favorable reaction path. This conclusion has far-reaching implications for all branched multidentate ligands and suggests that the substitution of selected donor atoms at ex-

terior sites on branched ligands might be utilized to improve kinetic selectivity.

Reaction of Tetrachloroplatinate(II) with Ethylene in the Presence of Chlorostannate(II) Ion

By ROSARIO PIETROPAOLO,[1] MAURO GRAZIANI, AND UMBERTO BELLUCO

Kinetic data are reported for the reaction of either tetrachloroplatinate(II) ion or Zeise's salt with $SnCl_3^-$. Data support a bimolecular attack of $SnCl_3^-$ upon the substrate. Data for the reaction of tetrachloroplatinate(II) with ethylene in the presence of chlorostannate(II) ion (at various Pt:Sn ratios) in acidic aqueous solution are also reported. The ethylene absorption by the metal complex affording $Pt(C_2H_4)Cl_3^-$ appears to involve both the *cis* and *trans* isomers, the *cis*-$Pt(SnCl_3)_2Cl_2^{2-}$ being the more active absorbing intermediate. No ethylene absorption is detectable at high Sn:Pt ratios, at which the predominant species is the five-coordinated $Pt(SnCl_3)_5^{3-}$. Results are discussed in terms of the high *trans* effect and of the pronounced π-acceptor character of $SnCl_3^-$ bonded to platinum(II).

Introduction

In recent years the chemistry of the tin–metal bond has attracted much interest because of its theoretical and practical implications exemplified by the investigations on the nature of the bond[2–8] and by the homogeneous hydrogenation, carbonylation, and double-bond migration on unsaturated compounds catalyzed by platinum–tin chloride systems.[9–13]

In the case of hydrogenation reactions, since the formation of a platinum–olefin complex is a necessary step

of the over-all process, the study of the factors governing the ease and occurrence of olefin coordination to transition metal ions appears most important.[2a,14,15] The maximum rate of homogeneous hydrogenation of olefins and acetylenes catalyzed by Pt–Sn complexes has been found for molar Sn:Pt ratios higher than 5.[16,17]

Among other chemical properties of tin–metal systems of d^8 transition metal ions, our attention has been drawn by the relevant observation of Cramer that whereas the formation of Zeise's salt from $PtCl_4^{2-}$ and ethylene is rather slow, it is markedly accelerated by stannous chloride.[18,19]

We have first examined the kinetic behavior of $PtCl_4^{2-}$ with $SnCl_3^-$ and then its role in the reaction of the ethylene absorption on tetrachloroplatinate(II) ion. The reactions studied are

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