Effect of Phenanthroline Substituents on the Rate of Replacement of Coordinated Water in Nickel(II) Complexes

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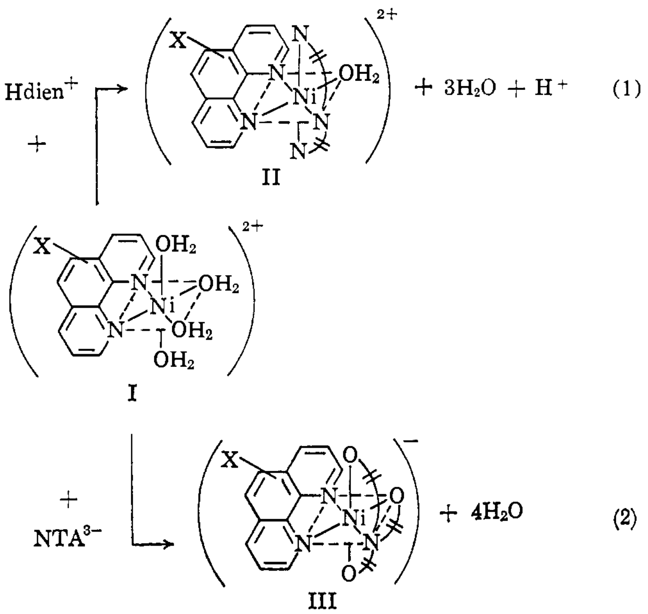
Abstract: The rates of reaction of diethylenetriamine and of nitrilotriacetate ion with mono(5-X-1,10-phenanthroline)nickel(II) complexes are influenced by substituents (X) on the 1,10-phenanthroline. In each case a mixed complex is formed without displacement of the 5-X-1,10-phenanthroline. The substituents are quite remote from the reaction site and their kinetic effect cannot be due to steric factors. The rates of formation of the mixed complexes increase slightly with increasing electron-donating properties of the substituent. The reactions fit a Hammett linear free-energy relationship with $\rho = -0.089$ for the reaction with $Hdien^+$ and $\rho = -0.264$ for the reaction with NTA^{-3}. The rate-determining step in each reaction is attributed to the loss of a coordinated water molecule which is influenced by changes in metal–ligand electron density. The nitrilotriacetate reaction is more sensitive to the substituent effect. This suggests that equatorially coordinated water molecules (in the plane of Niphen) may be influenced to a greater extent than the axial waters. For the formation reaction with $Ni(phen)^{2+}$, NTA^{3-} reacts 7900 times faster than $H(dien)^+$. This indicates the importance of electrostatic attraction in bringing the reactants together.

Characteristic rate constants for water substitution in the inner coordination sphere of aquometal ion complexes are known for many divalent metal ions, and splitting of the metal–water bond has been assigned as the rate-limiting step.[2] A little is known about the effect which other coordinated ligands have upon the rate of water loss of metal complexes.[3,4] The type of coordinated group rather than the charge on the complex has been shown to have the greater effect on the rate of water substitution in nickel complexes.[4] Substituents on the coordinated ligand, which are far removed from the reaction site, are shown in the present study to affect the rate of water replacement in nickel–1,10-phenanthroline complexes. The reactions studied are given in eq 1 and 2, where dien is diethylenetriamine and NTA^{3-} is the nitrilotriacetate ion. The phenanthroline substituents, X, were 5-NO_2, 5-Cl, 5-CH_3, 5,6-diCH_3, and the unsubstituted 1,10-phenanthroline. The reactions with the 5-SO_3^- group also were investigated. The substituents were well removed from the reaction site to eliminate any steric problems. Therefore, changes in the formation rate of the mixed complexes II and III are believed to be caused by the electron-donating or electron-withdrawing properties of the substituents. The effect is not large, but it definitely follows a Hammett free-energy relationship using the pK_a values of the substituted 1,10-phenanthrolium ions. This is believed to be the first example of such an effect upon the rate of substitution of coordinated water. Previously it had been shown that increased basicity of substituted pyridines in $[Co(en)_2(X\text{-}py)Cl]^{2+}$ resulted in a slight increase in the rate of acid hydrolysis.[5] This was attributed to inductive effects of the inert ligand and an SN1 mechanism was assigned to the acid hydrolysis. In the present case although the leaving group is neutral rather than negative and the metal ion is a comparatively labile one, a larger effect is observed. The fact that the effect fits the Hammett equation and gives negative ρ values supports the assignment of rate of water loss as the rate-determining step.



Experimental Section

Crystalline salts of each of the substituted mono(1,10-phenanthroline)nickel(II) complexes were prepared. In every kinetic series freshly prepared solutions of these compounds were used to avoid bis- and tris(1,10-phenanthroline)nickel(II) complexes. The preparation procedures used were similar to those reported for 1,10-phenanthroline[6] and its 5-chloro derivative.[7] To a solution containing 0.05–0.06 mole of $Ni(NO_3)_2 \cdot 6H_2O$ in 50–75 ml of water was added 0.004–0.006 mole of the phenanthroline derivative. Complete solution was achieved by heating to the boiling point, and the solution then was evaporated using a water aspirator. With the 5-NO_2, 5-Cl, and 5-CH_3 derivatives, evaporation was stopped when crystals appeared. The other compounds were evaporated to a syrup. The crystals obtained after cooling were filtered on a 0.3-μ millipore filter, washed with *t*-butyl alcohol, and dried in a vacuum desiccator at 55°. Table I gives formulas of

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(1) Correspondence to be addressed to this author.

(2) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

(3) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

(4) D. W. Margerum and M. Eigen, "Proceedings of the 8th International Conference on Coordination Chemistry," Vienna, 1964, p 289.

(5) F. Basolo, J. G. Bergmann, R. E. Meeker, and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 2676 (1956).

(6) R. G. Wilkins and M. J. G. Williams, *J. Chem. Soc.*, 4514 (1957).

(7) P. Ellis, R. Hogg and R. G. Wilkins, *ibid.*, 3308 (1957).

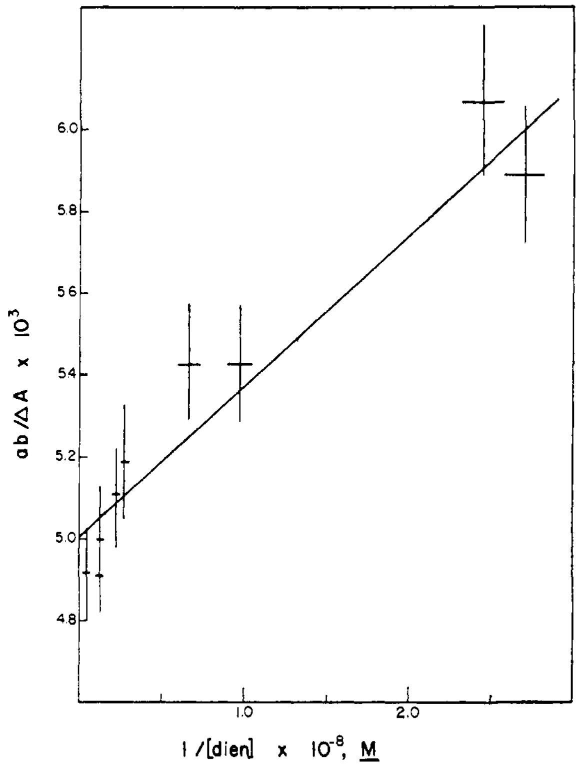

Figure 1. Resolution of absorbance data to obtain the stability constant and the molar absorptivity of the mixed complex: slope = $1/K_{II}\Delta\epsilon$, intercept = $1/\Delta\epsilon$.

the isolated crystals and elemental analysis results. Nickel was analyzed spectrophotometrically as $Ni(CN)_4^{2-}$ after the addition of cyanide solutions and chloroform extraction of the phenanthrolines.

Table I. Elemental Analysis of Phenanthroline Complexes

Compound	C	H	N	Ni
$Ni(phen)(H_2O)_2(NO_3)_2$				
Theoretical	36.1	3.0		14.7
Found	36.9	3.0		14.8
$Ni(5\text{-}Clphen)(H_2O)_2(NO_3)_2$				
Theoretical	33.3	2.6	12.9	13.6
Found	33.3	2.8	13.2	13.4
$Ni(5\text{-}NO_2phen)(H_2O)_2(NO_3)_2$				
Theoretical	32.5	2.5		13.2
Found	30.4	3.2		12.9
$Ni(5\text{-}CH_3phen)(H_2O)_2(NO_3)_2$				
Theoretical	37.8	3.4	13.6	14.2
Found	37.6	3.3	13.6	13.9
$Ni(5,6\text{-}diCH_3phen)(H_2O)_4(NO_3)_2$				
Theoretical	36.3	4.4	12.1	12.7
Found	36.7	4.6	12.0	12.7
$Ni(5\text{-}SO_3phen)(H_2O)_3(NO_3)$				
Theoretical	33.2	3.0	9.7	
Found	35.4	3.3	9.9	

Acid dissociation constants of the 5,6-dimethyl and 5-sulfo derivatives were determined spectrophotometrically (240–300 mμ) at 25.0° and 0.10 ionic strength and gave p*K* values of 4.3 and 5.6, respectively.

dien solutions were prepared from the dihydrochloride salt. Hydrogen chloride gas was bubbled into a solution of the pure amine in absolute ethanol, and the crystals were collected and recrystallized from hot 95% ethanol.

Nitrilotriacetic acid was prepared by recrystallizing the acid from a hot solution by the addition of HCl.

Reactions were buffered with purified 2,6-lutidine and its perchlorate salt (0.05 *M* salt).

An ionic strength of 0.13 for the dien reactions and 0.16 for the NTA reactions was held constant using sodium chloride.

dien reacts with $Niphen^{2+}$ to form a mixed complex, which was characterized by spectrophotometric and pH measurements. The addition of dien to $Niphen^{2+}$ causes a shift in its absorption peak from 610 to 590 mμ. Even more pronounced is an increase in the molar absorptivity of a shoulder peak at 342 mμ. Similar spectral changes between 300 and 350 mμ were found for the dien reaction with each derivative of mono(1,10-phenanthroline)nickel(II). dien does not absorb at these wavelengths and nickel–dien complexes have a negligible absorbance. In all cases the uncomplexed phenanthroline had a lower molar absorptivity than its complexed forms at the wavelengths used. Therefore the absorbance increase on addition of dien could be attributed only to the mixed complex. Figure 1 is a plot of eq 4 from which the stability constant of the dien mixed complex (II) and its molar absorptivity were determined.

$$\Delta A = A_{\text{mixture}} - A_{\text{Niphen}^{2+}} \tag{3}$$

$$\frac{ab}{\Delta A} = \frac{1}{\Delta\epsilon K_{II}[\text{dien}]} + \frac{1}{\Delta\epsilon} \tag{4}$$

where a = initial $Niphen^{2+}$ concentration, b = cell length, $\Delta\epsilon$ = the difference between the mixed complex and reactant molar absorptivities, and

$$K_{II} = \frac{[\text{Ni(phen)(dien)}]}{[\text{Niphen}][\text{dien}]} \tag{5}$$

The slope of Figure 1 gave a stability constant of 1.4×10^9 for the addition of dien to $Niphen^{2+}$. This is reasonable when compared to $K_1 = 5.0 \times 10^{10}$ and $K_2 = 1.6 \times 10^8$ for $Nidien^{2+}$ and $Ni(dien)_2^{2+}$, respectively.

Nitrilotriacetic acid was shown to form a mixed complex with $Niphen^{2-}$ by spectrophotometric measurements. As in the case with dien, the addition of NTA to $Niphen^{2+}$ caused a pronounced increase in molar absorptivity of a shoulder peak at 342 mμ. For each nickel–1,10-phenanthroline derivative the same wavelength that was affected by dien was affected by NTA.

Typical kinetic runs with dien gave absorbance changes of about 0.2 unit in 2- to 5-cm cells. The reactions were studied at pH 6–7 where H_2dien^{2+} was the primary polyamine species present (dien K_a values: $K_1 = 8.7 \times 10^9$, $K_2 = 1.4 \times 10^9$, $K_3 = 2.2 \times 10^4$), but the kinetically reactive species was $Hdien^+$ (eq 1). Above pH 7 the reaction is too fast to measure by conventional means and the lower pH prevented any complications from metal hydroxide mixed complexes. A Cary Model 14 spectrophotometer was used and the reaction was followed after mixing a freshly prepared solution of Ni(phen-X) with an equal volume of dien and buffer solution. The total dien concentration was in tenfold or greater excess over the $Niphen^{2+}$ concentration to give pseudo-first-order kinetics.

The reactions of NTA with each derivative of $Niphen^{2-}$ were measured with a stopped-flow apparatus similar to that reported by Sturtevant.[8] Reaction conditions were identical with those for dien except all reactions were at pH 6.8 and 0.16 ionic strength. Reactions were displayed on a Tektronix Type 564 storage oscilloscope. The 0.2-cm absorption cell gave a change of about 4% transmittance with reaction times of 50 to 100 msec.

Insoluble salts of the mixed complexes slowly precipitated after the initial reactions. In reaction 1 this caused the solution to become slightly turbid after the reaction was complete and resulted in a slowly increasing absorbance near the end of the reaction and a considerable possible error in the evaluation of the equilibrium absorbance of the mixed complex. This is the reason for the large error limits indicated in Figure 1. To avoid this error in the kinetic plots, the Guggenheim method (to find a rate constant where the final reading is unknown) was used.[9] Kinetic data were not used beyond 75% of the extent of the reaction. Three or four reactions were run at each pH and the average rate constant was used. The precipitation did not interfere in the kinetic constants because it proceeded for many hours compared to half-times of less than 1 to 2 min for the reaction.

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[8] J. M. Sturtevant in "RapidMixing and Sampling Techniques in Biochemistry," B. Chance, *et al.*, Ed., Academic Press Inc., New York, N. Y., 1964, pp 89–103.

[9] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 49.

In the stopped-flow reactions involving NTA (eq 2), formation of the mixed complex was complete and the absorbance reading (A_∞) was taken before any precipitation. For these rates, a conventional first-order plot of $-\ln(A_\infty - A_t)$ against t was used to obtain the rate constant.

Results

The rates of formation of the mixed ligand complexes of nickel were first order in the concentration of nickel–1,10-phenanthroline and first order in either dien or NTA concentration. Excess dien and NTA were used to give pseudo-first-order kinetics.

$$\frac{-\mathrm{d}[\mathrm{Niphen}^{2+}]}{\mathrm{d}t} = k_0[\mathrm{Niphen}^{2+}] \qquad (6)$$

Excellent straight-line plots were obtained when the absorbance of the reaction product was known or when the Guggenheim method was used.

Table II. Reactant Concentrations and Observed First-Order Rate Constants for dien Reaction with Nickel–1,10-Phenanthroline Derivatives at Each pH

pH	[Niphen] × 10^4	$k_0 \times 10^2$, sec^{-1} (av)	pH	[Niphen] × 10^4	$k_0 \times 10^2$, sec^{-1} (av)
	5-CH$_3$[a]			5-H	
6.22	4.10	0.485	6.19	10.0[b]	0.794
6.28	3.97	0.637	6.21	10.3[b]	0.852
6.37	4.18	0.534	6.41	10.3[b]	1.05
6.50	4.18	0.665	6.49	10.3[b]	1.24
6.64	4.18	0.717	6.51	5.40[c]	0.656
6.72	4.17	0.846	6.51	5.45[d]	1.75
6.80	4.18	0.907	6.51	5.45[e]	2.76
6.82	4.17	0.997	6.68	9.85[b]	1.79
6.84	4.18	1.24	6.74	10.2[b]	1.76
6.91	4.19	1.11	7.01	5.30[f]	1.49
			7.01	4.01[f]	1.62
			7.22	4.41[f]	2.00
	5,6-diCH$_3$[f]			5-NO$_2$[a]	
6.18	4.45	0.962	6.16	4.43	0.450
6.19	4.15	0.745	6.21	4.11	0.299
6.29	4.45	0.971	6.28	4.21	0.311
6.30	4.10	0.819	6.41	4.22	0.395
6.38	4.05	0.942	6.49	4.15	0.391
6.39	4.36	0.889	6.59	4.11	0.425
6.51	4.41	1.19	6.70	4.38	0.544
6.51	4.35	1.00	6.82	4.23	0.675
6.55	4.33	1.11	6.88	4.09	0.770
6.58	4.40	1.01			
6.67	4.20	1.43			
6.70	4.61	1.22			
6.75	4.14	1.47			
6.78	4.16	1.52			
6.82	4.64	1.45			
6.91	4.38	1.78			
6.91	4.15	1.99			
7.02	3.95	2.02			
	5-Cl[f]			5-SO$_3^-$[c]	
6.17	4.85	0.372	6.76	5.26	1.61
6.17	4.84	0.450	6.81	5.35	1.83
6.32	5.01	0.374	6.86	5.13	2.01
6.39	5.30	0.452	6.91	5.79	2.09
6.48	5.01	0.494	6.99	5.14	2.63
6.59	5.10	0.592	6.95	5.93	2.27
6.65	4.97	0.786	7.07	5.24	2.84
6.70	5.26	0.754	7.14	5.27	3.82
6.78	5.25	0.933			
6.88	5.28	1.13			
6.93	5.23	1.06			

[dien$_t$] values: [a] 3.72×10^{-3}. [b] 9.92×10^{-3}. [c] 4.89×10^{-3}. [d] 1.47×10^{-2}. [e] 2.44×10^{-2}. [f] 4.46×10^{-3}.

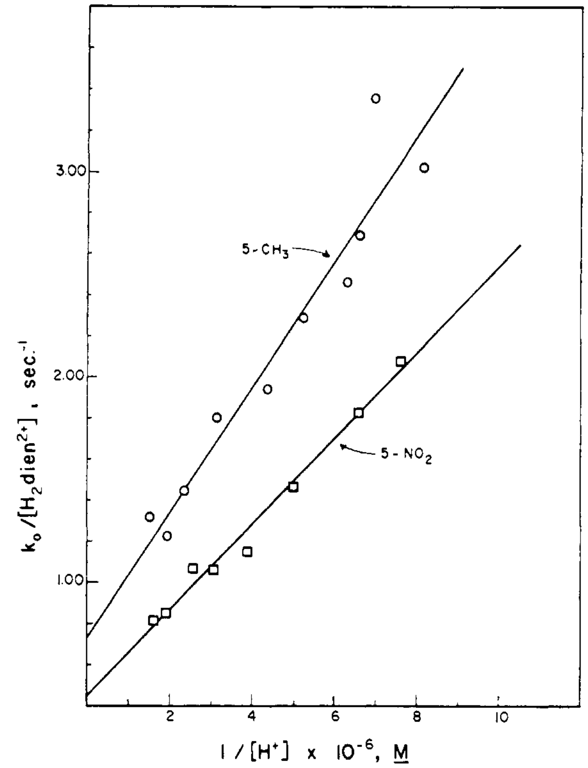

Figure 2. Resolution of observed reaction rate constant into rate constants for the Hdien$^+$ and H$_2$dien^{2+} reaction with Niphen-X. The intercept is $k^X{}_{H_2D}$ and the slope is $k^X{}_{HD}K_{H_2D}$.

The dien reactions were shown to be first order in total dien by running a series of reactions at pH 6.5 with 10-, 30-, and 50-fold excess total dien. Table II summarizes these data and the effect of pH for the reactions with 1,10-phenanthroline and its derivatives.

The reaction rate decreases as the pH decreases because of the lower reactivity of the more protonated dien species. In this pH region H$_2$dien^{2+} is the primary species present with traces of Hdien$^+$ and even smaller traces of unprotonated dien ($\sim 10^{-9}$ *M*). The neutral dien molecule would be expected to react more rapidly than its protonated forms with the positive nickel–phenanthroline complex. However, its concentration is too small. If the reactant were dien, k_0 would vary with $1/[H^+]^2$ but instead k_0 varies with $1/[H^+]$. Therefore, Hdien$^+$ and H$_2$dien^{2+} are the reactive species in this pH range.

$$\frac{k_0}{[H_2D]} = \frac{k_{HD}}{K_{HD}}\frac{1}{[H^+]} + k_{H_2D} \qquad (7)$$

Typical plots of eq 7 are given for the 5-CH$_3$ and 5-NO$_2$ derivatives in Figure 2. In all cases the method of least squares was used to obtain the slope and intercept. The resolved rate constants are summarized in Table III. The general trend of the substituent effect is the same for both k_{H_2D} and k_{HD}, but the values for k_{HD} are more accurate because most of the reaction proceeds through Hdien$^+$ under the conditions of these experiments.

The reaction in eq 2 was shown to be first order in nitrilotriacetate ion concentration at pH 6.83 with 10-, 20-, and 30-fold excess NTA (Table IV). Values of the observed rate constant, obtained for the reaction of NTA with each derivative, are given in Table IV. The rate of the reaction increased with pH; however, com-

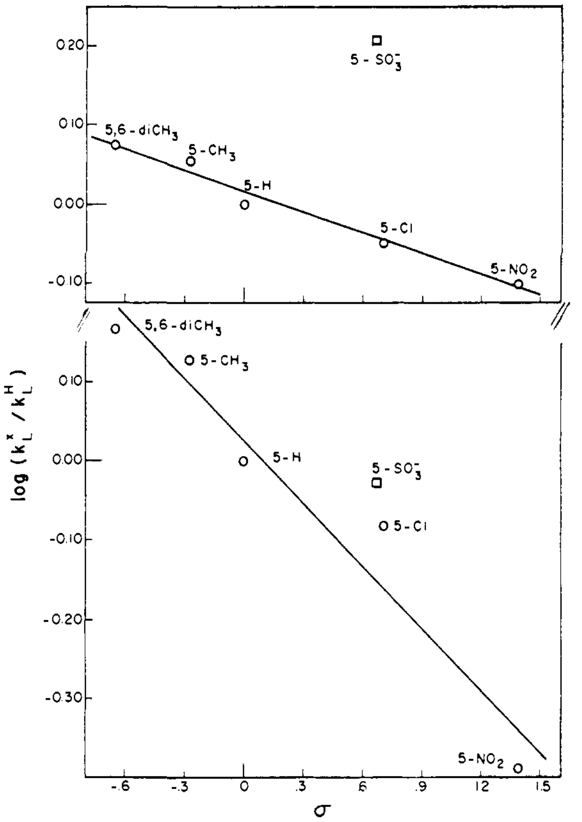

Figure 3. Hammett plots showing substituent effect for the Hdien$^+$ and NTA^{3-} reactions with Niphen-X. The 5-SO$_3^-$ derivative should not fall on the plot because of the difference in charge.

parative kinetic data were run at only one pH. The formation rate constant for the reaction of Ni^{2+} with NTA^{3-} is 4 × 10^4 larger than the rate constant for the reaction of Ni^{2+} with HNTA^{2-}. This is calculated from the values of the dissociation rate constants[10] and the stability constants.[11] Thus, the HNTA^{2-} ion with a proton on the nitrogen is very unreactive and under the experimental conditions should account for less than 1% of the reaction. The second-order rate constants k_{NTA} in Table IV were obtained by dividing the k_0 values by the concentration of unprotonated nitrilotriacetate ion and represent the specific rate constants for the reaction with NTA^{3-}. It is interesting to note that the phenanthroline group itself has relatively little effect on the rate of reaction with NTA^{3-}. Thus, the rate constant with aquonickel is 2.0 × 10^6 M^{-1} sec^{-1} (0.4 μ) while the rate constants in Table IV are from 1.2 × 10^6 to 4.2 × 10^6 M^{-1} sec^{-1}.

Table III. Second-Order Rate Constants for the Hdien$^+$ and H$_2$dien^{2+} Reaction with Nickel-1,10-Phenanthroline Derivatives

Substituent	pK_a	k^X_{HD}, M^{-1} sec^{-1}	Correlation coefficient[c]	$k^X_{H_2D}$, M^{-1} sec^{-1}
5,6-diCH$_3$	5.6[a]	426	(0.940)	1.30
5-CH$_3$	5.23[b]	408	(0.948)	0.91
5-H	4.96[b]	359	(0.983)	0.42
5-Cl	4.26[b]	327	(0.972)	0.43
5-NO$_2$	3.57[b]	281	(0.982)	0.42
5-SO$_3^-$	4.25[a]	590	(0.976)	...

[a] Constant measured in this study. [b] W. W. Brandt and D. K. Fullstrom, *J. Am. Chem. Soc.*, **74**, 3532 (1952). [c] The correlation coefficient was calculated for the least-squares fit of each k_0 value (from 24 to 63 values per substituent) to a linear relationship with 1/[H$^+$].

Table IV. Rate Constants Obtained for the Reaction of NTA with Nickel-1,10-Phenanthroline Derivatives

Substituent	[Niphen-X] × 10^3	[NTA$_t$] × 10^3	Av k_0 (at pH 6.83), sec^{-1}	% av dev	k_{NTA} × 10^{-6}, M^{-1} sec^{-1} [c]
5,6-diCH$_3$	1.00	9.72	54.3[a]	6.6	4.15
5-CH$_3$	1.01	9.72	47.3[a]	5.5	3.78
5-H	1.00	9.72	28.0[b]	3.9	
	1.00	19.4	57.1[b]	0.75	
	1.03	29.2	76.3[b]	3.0	
	1.02	9.73	35.2[a]	5.4	2.82
5-Cl	1.04	9.72	27.8[a]	4.1	2.34
5-NO$_2$	0.52	9.72	16.1[a]	5.0	1.15
5-SO$_3^-$	1.05	9.72	25.6[a]	1.3	2.64

[a] Ionic strength of 0.155. [b] Ionic strength of 0.173. [c] Reaction with NTA^{3-} using pK_a = 9.73.

Hammett σ constants were calculated using K_a, the acid dissociation constant of unsubstituted 1,10-phenanthroline as the reference value. Equation 8, which is plotted in Figure 3, where σ is log (K_a^X/K_a^H), gave a ρ value of −0.089 for Hdien$^+$ and of −0.264 for NTA^{3-}.

$$\log (k_L^X/k_L^H) = \rho\sigma \qquad (8)$$

The reaction of dien with the 5-SO$_3^-$ derivative does not fall on the Hammett plot because it is a +1 complex in solution as indicated by the formula of the solid (see Table I) and the fact that sulfonic acids are very strong acids. The over-all electrostatic repulsion for Hdien$^+$ is less, and hence this derivative would be expected to react more readily. However, the reaction of NTA^{3-} with the 5-SO$_3^-$ derivative was not suppressed as would be expected. There may be special interactions because this phenanthroline complex is a dipolar ion, but it is not clear if the reaction with dien or with NTA is abnormal.

Discussion

Substitution reactions for many octahedral complexes of nickel and other metals are governed by a characteristic first-order rate of loss of water as shown in a summary by Eigen and Wilkins.[12] Formation rate constants are considered to be a combination of outer-sphere association followed by a rate-limiting loss of an inner-sphere coordinated water.[2] Once the outer-sphere species exists, the rate constant appears to be independent of the incoming ligand.[13] The very large ratio (~8000) in formation rate constants for the reaction of NTA^{3-} compared to Hdien$^+$ with Niphen^{2+} illustrates the importance of electrostatic effects in bringing the reactants together. Al-

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(10) T. J. Bydalek and M. L. Blomster, *Inorg. Chem.*, **3**, 667 (1964).

(11) G. Schwarzenbach and R. Gut, *Helv. Chim. Acta*, **34**, 1589 (1956).

(12) M. Eigen and R. G. Wilkins, "Mechanism of Inorganic Reactions," Summer Symposium, Division of Inorganic Chemistry, American Chemical Society, June 1964.

(13) L. DeMaeyer and K. Kustin, *Ann. Rev. Phys. Chem.*, **14**, 15 (1963).

though the same rate-limiting step may occur with Niphen,$^{2+}$ the amount of the other reactant in the immediate vicinity is determined by charge attraction or repulsion which greatly influences the rate of reaction.

Except for the sulfonic acid derivative, all the substituted 1,10-phenanthroline complexes have the same charge, and to a first approximation their outer-sphere association constants should not vary with the same reactant. Secondly, there is relatively little difference in the size of the various Niphen-X^{2+} complexes, and the substituents are quite remote from the reaction site. These factors again suggest an invariant association constant. Thirdly, it is difficult to understand why the association constant would follow a Hammett equation, but if this could be imagined then an electron-withdrawing substituent should favor association of NTA^{3-} in the vicinity of the nickel ion and have the opposite effect on Hdien$^+$. Actually, the electron-withdrawing substituents give smaller not larger rate constants with NTA^{3-}, and the ρ values are negative for both NTA^{3-} and Hdien$^+$. Therefore, the substituent effect is assigned to the substitution reaction itself and not to the prior association of reactants.[14] Finally, negative values for ρ are in accord with a decrease of electron density at the reaction center during the transition state. Thus, the rate-limiting step must involve the loss of a coordinated water molecule to a greater extent than it does the addition of another ligand.

Figure 3 shows an excellent fit of the free-energy relationship. In general, as the pK_a of the substituted 1,10-phenanthrolium ion increases, the strength of the corresponding nickel complex increases.[15,16] Derivatives with higher pK_a values can increase the electron density on the metal ion and increase the rate of loss of coordinated water. Earlier work[4] showed that it is not the charge of a nickel complex so much as the electron-pair-donating properties of the ligand which appear to govern the rate of water substitution.

In the reactions of polyamines with aquonickel ion, the rate-determining step is the formation of the first nickel–nitrogen bond.[17] As shown in eq 1 the two terminal nitrogens in dien are most likely to be coordinated to positions axial to the plane of nickel–1,10-phenanthroline. This minimizes the steric repulsion of the hydrogens on the phenanthroline ring with those on dien. When Hdien$^+$ is the reactant its initial coordination to nickel should be at a terminal nitrogen (with the proton at the opposite end) from both electrostatic and steric considerations. Therefore, the substituent effect observed in the reactions of Hdien$^+$ is believed to be for coordinated water molecules axial to the plane of nickel–1,10-phenanthroline.

On the other hand, the nitrogen bond in the nitrilotriacetate mixed complex must be in a position equatorial to the plane of nickel–1,10-phenanthroline as seen in species III. The rate of loss of water immediately preceding nitrogen bond formation to nickel is believed to be the rate-determining step in the reaction of NTA as is the case with EDTA.[18] Thus, the substituent effect for reaction 2 is believed to be for an equatorial position. An acetate group could bond first, but the Ni–N bond step appears to be rate–determining. If prior acetate bond formation significantly increased the electron density at the reaction center, a more positive ρ value would be expected.[19] Instead the reaction with the negatively charged nitrilotriacetate ion has a more negative ρ value than the reaction with the positively charged diethylenetriamine ion. Therefore, the difference in ρ values is attributed to the difference in axial and equatorial water substitution.

In conclusion, the manner in which the substituents influence the formation rate suggests that they affect the rate of water loss and that this effect is greater for the equatorial than for the axial positions. Admittedly, several assumptions are involved but other explanations tend to operate in directions opposite to the observed behavior.

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[14] This may not be the case when the substituted 1,10-phenanthroline is itself a reactant (see ref 15) because the second bond formation may be rate determining.

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