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Kinetics of the Formation and Dissociation of Some Nitrosonaphtholsulfonate Complexes of Nickel(II)

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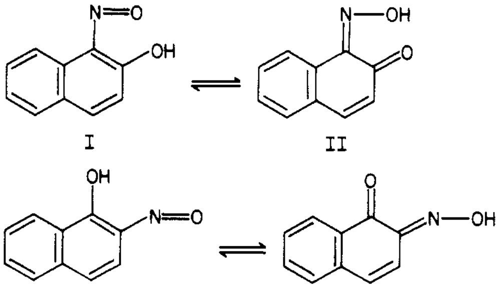
The kinetics of the reaction of $Ni(OH_2)_6^{2+}$ and 2-nitroso-1-naphthol-4,6-disulfonate and 1-nitroso-2-naphthol-3-sulfonate, -4-sulfonate, -5-sulfonate, and -7-sulfonate have been studied at 20, 25, and 30 °C in 0.10 M $LiClO_4$. The complex formation rates have been measured in the range of pH from $\sim$3.8 to $\sim$7.5. The dissociation of the complexes has been studied for $[H^+]$ between $\sim$0.02 and 0.10 M. The results do not agree with a simple one-step mechanism but can be fitted to models that include monodentate intermediates. The analysis indicates that the rate-controlling step changes from chelate ring opening and closing to first bond formation and dissociation as the pH increases. The effect of the sulfonate substituents on the tautomeric equilibrium between the nitroso–naphthol and oxime–quinone forms is used to rationalize the reactivity patterns for these ligands.

The *o*-nitrosonaphthols and their sulfonate derivatives are well-known complexing agents. These ligands form fairly strong, highly colored complexes that are useful in metal ion separation and analysis. Kinetic studies on these systems should establish the general reactivity patterns and rate-controlling steps in the chelate formation. Other factors with possible kinetic influence are the intramolecular hydrogen bond, the charge effect of the sulfonate groups in various positions, and the tautomeric equilibrium between nitroso (I, III) and oxime (II, IV) forms.



The electronic[1] and NMR spectra[2] indicate that 1-nitroso-2-naphthol actually exists essentially entirely in the oxime form (II). However, the NMR spectrum of 2-nitroso-1-naphthol[2] indicates a mixture of the two forms III and IV. The crystal structures of 1-nitroso-2-naphthol[3] and its 6-*tert*-butyl derivative[4] show the shortened N–C and C–O and lengthened C(1)–C(2) bond expected of the oxime (II). Similar results have been reported for 2-nitroso-1-naphthol derivatives.[3] The oxime is in the syn configuration relative to the quinone oxygen, as expected if there is intramolecular hydrogen bonding. The structure of potassium 1-nitroso-2-naphthol-7-sulfonate monohydrate[5] also has bond lengths expected for the oxime form, but the oxime is in the anti position. This configuration seems to be imposed by the potassium ion, which is within $\sim$3 Å of the quinone O and oxime N atoms.

These ligands have the potential to complex in either tautomeric form, through either the N or O atom of the nitroso (oxime) group. A five-membered chelate ring is usually assumed with coordination to the N atom, and this is consistent with the structure[6] of tetraaquo(1-nitroso-2-naphthol-6-sulfonato)nickel(II). The ligand bond lengths are similar to those expected of the oxime form but are generally shifted somewhat toward those of the nitroso form relative to typical values for the free ligands.

The acid dissociation constants and complex formation constants (K_f) with nickel(II) for a number of these ligands have been determined by Saarinen and co-workers[7] and Lalor and co-workers,[8] with generally good agreement.[9] The K_f values are generally smaller for the 2-nitroso-1-naphthol derivatives when ligands of similar proton basicity are compared. This difference in K_f may reflect some inherent, but not obvious, preference in the 1-nitroso-2-naphthol system or could be ascribed to a difference in the position of the tautomeric equilibrium. If the latter is the case, then the results imply that complexing is more favorable with the oxime tautomer, which appears to be dominant for the 1-nitroso-2-naphthol ligands.

Chart I

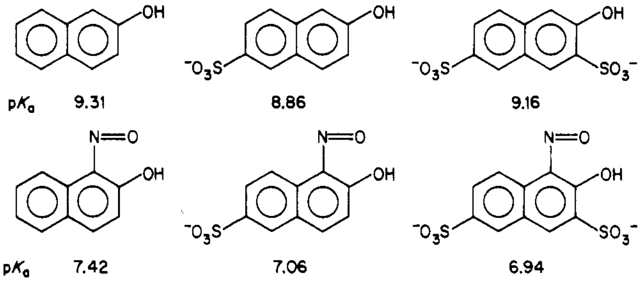
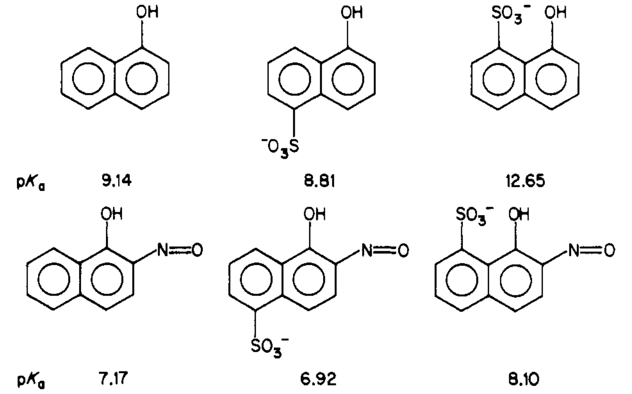


Chart II



The comparison of pK_a values[9] of naphthols and corresponding nitrosonaphthols depicted in Chart I shows that the addition of the 3-SO_3^- substituent increases the pK_a, relative to that of the

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(1) Buraway, A.; Cais, M.; Chamberlain, J. T.; Liversedge, F.; Thompson, A. R. *J. Chem. Soc.* **1955**, 3727.

(2) Shono, T.; Hayashi, Y.; Shinara, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3179.

(3) Saarinen, H.; Konvenranta, J. *Finn. Chem. Lett.* **1978**, 223.

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(5) Saarinen, H.; Korvenranta, J.; Nasakkala, E. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 213 and references therein.

(6) Korvenranta, J.; Saarinen, H.; Nasakkala, E. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 689.

(7) Saarinen, H. *Ann. Acad. Sci. Fenn. Ser. A2* **1973**, 173.

(8) Bajue, S. A.; Dasgupta, T. P.; Lalor, G. C. *Rev. Latinoam. Quim.* **1979**, *10*, 9.

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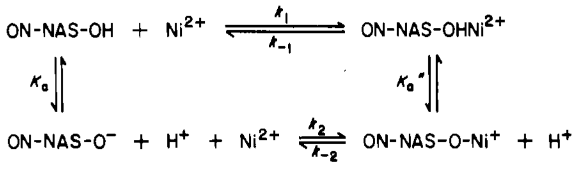
Table I. Nitrosonaphtholsulfonate Ligand Acid Dissociation Constants and Complex Formation Constants[a]

ligand[b]					
NO	OH	SO_3	pK_a[c,d]	$\log K_f(Ni^{2+})$[c,d]	K_aK_f
2	1	4, 6	5.90 (5.87)	5.56 (5.45)	0.45 (0.33)
1	2	3, 6	6.94 (6.88)	6.85 (6.90)	0.82 (1.05)
1	2	6	7.06 (7.22)	6.55 (6.64)	0.31 (0.26)
1	2	5	7.16 (7.23)	6.50 (6.56)	0.22 (0.21)
1	2	4	7.20 (7.15)	6.56 (6.43)	0.23 (0.19)
1	2	7	7.29 (7.31)	6.90 (6.73)	0.41 (0.26)
1	2	3	7.57	7.11	0.35

[a] Values at 25 °C and 0.10 M ionic strength. [b] Numbers give the position of the substituent on the naphthalene ring.
[c] Dasgupta, P. K.; Bajue, S.; Lalor, G., details to be submitted for publication. [d] Values in parentheses determined by H. Saarinen et al. and taken from ref 9.

Scheme I



6-SO_3 derivative, only for the naphthol system. This difference might be due to less intramolecular hydrogen bonding with the 3-SO_3^- nitrosonaphthol due to competition with the -NO···HO⁻ system or to less destabilization of the base because the O⁻ negative charge can be delocalized over the (O–N–C–C–O)⁻ system.

A similar comparison can be made with the 1-naphthol derivatives (Chart II). In this case the 8-SO_3^- substituent causes the pK_a to increase in both the 1-naphthol and 2-nitroso-1-naphthol systems, relative to that for 5-SO_3 derivative. These observations provide a meager indication that the 2-nitroso-1-naphthols are more similar to the naphthol, and may exist more as the nitroso tautomer, than the 1-nitroso-2-naphthols in aqueous solution. This qualitatively supports the NMR results of Shono et al.[2] in Me_2SO–dioxane and Me_2SO–acetic acid solvents.

In summary, the solid-state structures indicate the presence of the oxime tautomer in both the 1-nitroso- and 2-nitrosonaphthol systems. However, the spectroscopic and solution properties[10] indicate that there may be some differences in the position of the tautomeric equilibrium with more nitroso form for the 2-nitroso derivatives than for the 1-nitroso systems. However, the ratio of the tautomers in any one system remains uncertain.

Results and Discussion

The acid dissociation constants and nickel(II) complex formation constants for the ligands studied here, and some previously studied related systems, are summarized in Table I. For reasons of convenience and consistency with common nomenclature the ligands will be treated as nitroso–naphthols, but it should be acknowledged that the quinone–oxime tautomer is a significant form. If the nitrosonaphtholsulfonates are abbreviated as ON–NAS–OH, then the acid dissociation refers to the reaction

$$\text{ON–NAS–OH} \overset{K_a}{\rightleftharpoons} \text{ON–NAS–O}^- + H^+ \qquad (1)$$

and the complex formation refers to

$$\text{ON–NAS–O}^- + Ni(OH_2)_6^{2+} \overset{K_f}{\rightleftharpoons} \text{ON–NAS–O–}Ni(OH_2)_4 + 2H_2O \qquad (2)$$

Since the kinetic studies have been done under pseudo-first-order conditions with $[Ni^{2+}] >> [\text{ON–NAS–OH}]$, the formation of higher complexes can be neglected. The simplest description of the complex formation is shown in Scheme I. If it is assumed that the proton equilibria (K_a, K_a'') are rapidly established, then

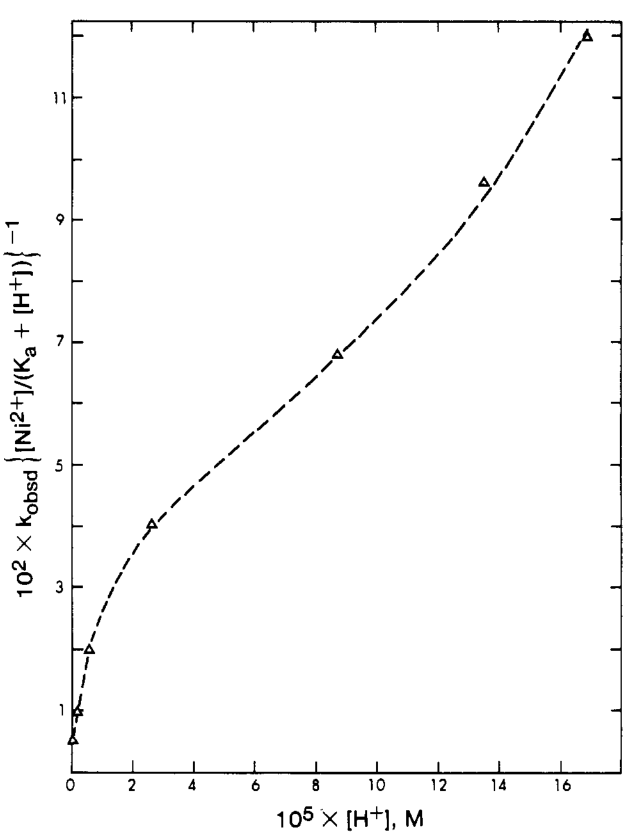


Figure 1. Variation of $k_{obsd}\{[Ni^{2+}]/(K_a + [H^+])\}^{-1}$ with $[H^+]$ for the formation reaction of $Ni(OH_2)_6^{2+}$ with 1-nitroso-2-naphthol-5-sulfonate.

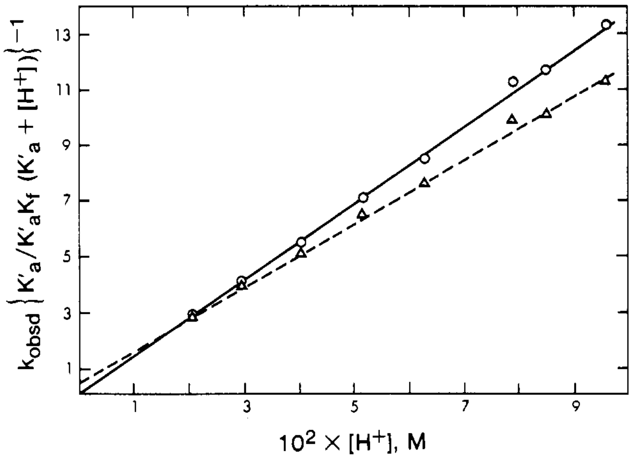


Figure 2. Variation of $k_{obsd}\{1/(K_a[H^+])\}^{-1}$ with $[H^+]$ for the dissociation of tetraaquo(1-nitroso-2-naphthol-5-sulfonato)nickel(II).

the observed pseudo-first-order rate constant for Scheme I is given by

$$k_{obsd} = \{k_1[H^+] + k_2K_a\}\left\{\frac{[Ni^{2+}]}{K_a + [H^+]} + \frac{K_a''}{K_aK_f(K_a'' + [H^+])}\right\} \qquad (3)$$

For the kinetic studies of the complex formation reaction (pH $\gtrsim 4$; $[Ni^{2+}] = 2.88 \times 10^{-3}$ M) it can be shown easily that the second term in braces in eq 3 is negligible compared to the first term, even if $K_a'' >> [H^+]$. Then the appropriate plot, shown in Figure 1 for the data for 1-nitroso-2-naphthol-5-sulfonate, should be linear, which clearly it is not. The curvature in Figure 1 occurs in a region where $[H^+] \approx 10^3 K_a$ and cannot be explained by any reasonable uncertainty in K_a.

The complex dissociation data (pH <2; $[Ni^{2+}] = 0$) for the 1-nitroso-2-naphthol-5-sulfonate can also be analyzed by eq 3. If it is assumed that $K_a'' >> [H^+]$, the plot is linear as shown

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(10) Dyrssen, D.; Johansson, E. *Acta Chem. Scand.* **1955**, *9*, 763.

Table II. Comparison of Observed and Best-Fit Results for the Nickel(II)-1-Nitroso-2-naphthol-5-sulfonate System[a]

$[\mathrm{H}^+]$, M	k_{obsd}, s^{-1}	k_{calcd}, s^{-1} eq 4[c]	k_{calcd}, s^{-1} eq 4-6[d]
9.60×10^{-2}	86.0[b]	58.2	86.2
8.50×10^{-2}	77.0[b]	56.5	77.8
7.40×10^{-2}	75.5[b]	54.4	69.1
6.30×10^{-2}	58.0[b]	51.8	60.0
5.17×10^{-2}	49.6[b]	48.4	50.3
4.05×10^{-2}	39.0[b]	43.9	40.2
2.95×10^{-2}	30.0[b]	37.9	30.0
2.05×10^{-2}	21.0[b]	31.1	21.2
1.69×10^{-4}	2.04	2.14	1.84
1.35×10^{-4}	2.05	2.07	1.99
8.73×10^{-5}	2.25	1.99	2.39
2.60×10^{-5}	4.50	2.08	4.64
6.10×10^{-6}	9.30	3.15	9.31
2.00×10^{-6}	13.5	6.05	13.6
7.28×10^{-7}	19.85	13.0	19.7
2.78×10^{-7}	32.7	27.8	30.8
1.14×10^{-7}	47.0	51.3	48.0
7.41×10^{-8}	58.1	64.9	58.0
5.05×10^{-8}	66.7	77.4	67.1
2.88×10^{-8}	78.0	94.1	79.3

[a] Conditions: $[\mathrm{Ni}^{2+}] = 2.88 \times 10^{-3}$ M; [ON-NAS-OH] $= 5 \times 10^{-5}$ M; at 25 °C and $\mu = 0.10$ M. [b] Dissociation rate. Conditions: initial [ON-NAS-ONi] $= 5 \times 10^{-5}$ M; $[\mathrm{Ni}^{2+}] = 2.4 \times 10^{-3}$ M. [c] The best-fit parameters are $k_1 = 5.71 \times 10^2\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, $k_2 = 4.60 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, and $K_a'' = 2.99 \times 10^{-2}$ M. [d] The fitting parameters are given in Tables III and IV.

in Figure 2, but the intercept (k_2K_a) of ~50 s^{-1} is totally inconsistent with the intercept of $\sim 2.5 \times 10^{-3}\ \mathrm{s}^{-1}$ in Figure 1. This inconsistency can be removed if it is assumed that $K_a'' \approx 0.5$ M. Then the intercept is indeterminant from zero, as expected if the correct value is $\sim 2.5 \times 10^{-3}\ \mathrm{s}^{-1}$.

The problems with Scheme I can be illustrated further by a comparison of the experimental and calculated values shown in Table II. Nine of the twenty calculated values are well outside a reasonable ±10% error limit on the experimental results, and the differences are a factor of 2-3 for $[\mathrm{H}^+]$ between 2.6×10^{-5} and 2.0×10^{-6} M.

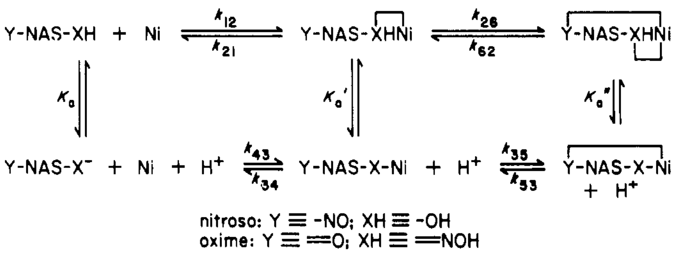
An empirical approach shows that the data can be fitted to the equation

$$k_{\mathrm{obsd}} = \frac{A[\mathrm{H}^+]^2 + B[\mathrm{H}^+] + C}{[\mathrm{H}^+] + D}\left\{\frac{[\mathrm{Ni}^{2+}]}{K_a + [\mathrm{H}^+]} + \frac{K_a''}{K_aK_f(K_a'' + [\mathrm{H}^+])}\right\} \tag{4}$$

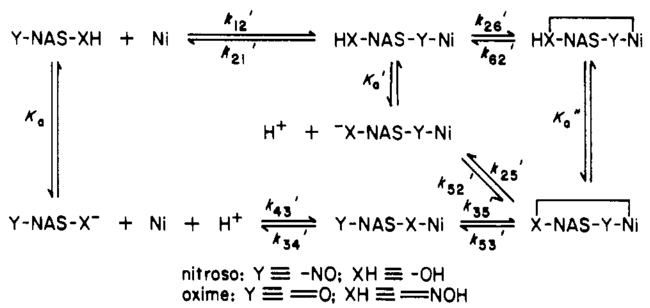
A least-squares fit of the results for 1-nitroso-2-naphthol-5-sulfonate gives $A = (2.39 \pm 0.10) \times 10^2\ \mathrm{M}^-\ \mathrm{s}^{-1}$, $B = (5.11 \pm 0.26) \times 10^{-2}\ \mathrm{s}^{-1}$, $C = (3.00 \pm 0.31) \times 10^{-8}\ \mathrm{M\ s}^{-1}$, $D = (1.17 \pm 0.10) \times 10^{-5}$ M, and $K_a'' = 0.50 \pm 0.19$ M. The observed and calculated values are compared in Table II and generally agree within ±10% over the whole range of acidities.

Previous experience[11-13] has shown that the failure of Scheme I and eq 2, and the complexity indicated by eq 3, can be explained if the chelation process is treated in more detail. The two possible tautomers for the ligand present an added complication. However, if the ligand is considered in general as Y-NAS-XH, where Y ≡ NO and XH ≡OH for the nitroso tautomer and Y ≡ =O and SH ≡ NOH for the oxime, then two general reaction pathways can be formulated as shown in Schemes II and III. In both schemes ligand-metal preassociation has been omitted for simplicity so that k_{12} and k_{43} are really products of a specific rate constant and an outer-sphere association constant. The deprotonated form of the ligand is assumed to react at the center carrying the most negative charge because of the influence of ligand charge on outer-sphere association. The schemes are simplified also by the assumption that the ligand is all in one tautomeric form, whereas the measured rate constants are the concentration-weighted averages of the reactivities of the two tautomers.

Scheme II



Scheme III



If the proton equilibria are assumed to be rapidly established, and a steady state is assumed for the monodentate intermediates, then the observed pseudo-first-order rate constant for Scheme II is given by

$$k_{\mathrm{obsd}} = \frac{k_{12}[\mathrm{H}^+] + k_{43}K_a}{1 + q}\left\{\frac{[\mathrm{Ni}^{2+}]}{K_a + [\mathrm{H}^+]} + \frac{K_a''}{K_aK_f(K_a'' + [\mathrm{H}^+])}\right\} \tag{5}$$

where

$$q = \frac{k_{12}[\mathrm{H}^+] + k_{43}K_a}{\dfrac{k_{26}}{k_{21}}k_{12}[\mathrm{H}^+] + \dfrac{k_{35}}{k_{34}}k_{43}K_a}$$

$$K_f = k_{43}k_{35}/k_{34}k_{53}$$

Similarly for Scheme III it is found that

$$k_{\mathrm{obsd}} = \left\{\frac{k_{12}'[\mathrm{H}^+]}{1 + q'} + \frac{k_{43}'k_{35}'K_a}{k_{34}' + k_{35}'}\right\}\left\{\frac{[\mathrm{Ni}^{2+}]}{K_a + [\mathrm{H}^+]} + \frac{K_a''}{K_aK_f(K_a'' + [\mathrm{H}^{+\prime})}\right\} \tag{6}$$

where

$$q' = \frac{(k_{21}'/k_{26}')[\mathrm{H}^+]}{[\mathrm{H}^+] + (k_{52}'/k_{62}')K_a''}$$

$$K_f = k_{43}'k_{35}'/k_{34}'k_{53}'$$

Both eq 5 and eq 6 can be rearranged to a form mathematically identical with eq 4 so that both Schemes II and III will fit the data and give identical fits as noted in Table II. In both cases one obtains four fitting parameters of kinetic interest in addition to K_a''. The four parameters and the K_a and K_f values can be used to calcuate k_{53} and k_{62}/K_a'' in Scheme II, and k_{52}' and k_{62}'/K_a'' in Scheme III.

The least-squares fit results for the ligands studied here at 25 °C are summarized in Tables III and IV for Schemes II and III,

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(12) Voss, R. H.; Jordan, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 6926.
(13) Chopra, S.; Jordan, R. B. *Inorg. Chem.* **1983**, *22*, 1708.

Table III. Least-Squares Fitting Results for Scheme II at 25 °C[a]

position			$10^{-3}k_{12}$, $M^{-1}\ s^{-1}$	$10^{-4}k_{43}$, $M^{-1}\ s^{-1}$	$(k_{26}/k_{21})k_{12}$, $M^{-1}\ s^{-1}$	$(k_{35}/k_{34})k_{43}$, $M^{-1}\ s^{-1}$	K_a'', M	k_{53}, s^{-1}
NO	OH	SO_3						
2	1	4, 6	4.27 ± 0.80	5.03 ± 0.16	569 ± 51	11.5 ± 7.5	0.73 ± 0.65	3.2
1	2	3, 6[b]	2.63 ± 0.23	2.34 ± 0.10	436 ± 29	10.8 ± 1.6	1.73 ± 0.92	0.37
1	2	6[c]	2.19 ± 0.12	1.54 ± 0.05	564 ± 30	(7)[d]	0.83 ± 0.14	
1	2	5	4.60 ± 0.25	3.91 ± 0.10	252 ± 11	7.77 ± 0.40	0.50 ± 0.19	0.24
1	2	4	4.30 ± 0.20	5.15 ± 0.15	346 ± 16	19.6 ± 1.1	0.62 ± 0.29	0.54
1	2	7	4.42 ± 0.30	5.85 ± 0.19	746 ± 46	18.3 ± 2.3	0.44 ± 0.19	0.23
1	2	3	5.54 ± 0.44	13.2 ± 0.42	656 ± 38	24.0 ± 2.8	0.30 ± 0.09	0.19

[a] Data for $\mu = 0.10$ M unless otherwise indicated; error limits are one standard error. [b] Data from ref 14 at $\mu = 0.50$ M. [c] Data from ref 15 at $\mu = 0.10$ M, combined with dissociation data from ref 14 at $\mu = 0.50$ M. [d] This parameter was fixed at this probable value since it was not defined because the data do not cover pH 4–5.5

Table IV. Least-Squares Fitting Results for Scheme III at 25 °C[a]

position			$10^{-3}k_{12}'$, $M^{-1}\ s^{-1}$	$10^{-4}k_{35}'k_{43}'/(k_{34}' + k_{35}')$, $M^{-1}\ s^{-1}$	k_{21}'/k_{26}'	$10^3k_{52}'K_a''/k_{62}'$, M	K_a'', M	k_{52}', s^{-1}
NO	OH	SO_3						
2	1	4, 6	3.92 ± 0.55	4.82 ± 0.13	6.81 ± 0.83	2.44 ± 1.8	0.73 ± 0.66	3.12
1	2	3, 6	2.52 ± 0.21	2.29 ± 0.09	5.74 ± 0.65	0.52 ± 0.09	1.73 ± 0.92	0.28
1	2	6	1.99 ± 0.10	1.52 ± 0.04	3.49 ± 0.28	(0.40)	0.87 ± 0.13	
1	2	5	4.04 ± 0.22	3.75 ± 0.10	28.5 ± 2.1	0.38 ± 0.03	0.55 ± 0.26	0.25
1	2	4	4.05 ± 0.18	5.96 ± 0.14	11.6 ± 0.7	0.35 ± 0.03	0.62 ± 0.29	0.53
1	2	7	4.16 ± 0.26	5.67 ± 0.18	5.51 ± 0.50	0.12	0.44 ± 0.19	0.22
1	2	3	5.02 ± 0.4	12.5 ± 0.40	7.55 ± 0.66	0.093 ± 0.015	0.30 ± 0.09	0.18

[a] The data sources, ionic strengths, etc. are given in Table III.

respectively. In addition the published results on the 1-nitroso-2-naphthol-3,6-disulfonate[14] and 1-nitroso-2-naphthol-6-sulfonate[15] have been fitted and are included for comparison.

Any choice between Scheme II and III must be made on the basis of the rate constant magnitudes and variations between ligands, since both schemes give identical fits of the data. The k_{12} and k_{12}' values in Tables III and IV respectively are in the range of (2–4) × 10^3 $M^{-1}\ s^{-1}$, which is typical for a neutral ligand reacting with $Ni(OH_2)_6^{2+}$.[16] The negatively charged $-SO_3^-$ substituent does not seem to influence the rate of first-bond formation in the acid form of the ligand. Williams and Petrucci[17] have discussed a similar lack of influence of a remote $-SO_3^-$ in the 5-sulfosalicylate–nickel(II) system. The normal values of k_{12} or k_{12}' also imply that any hydrogen bonding in the (–N–O···H–O–) system has no detectable kinetic influence.

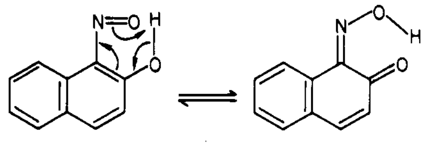
The values of k_{43} and $k_{35}'k_{43}'/(k_{34}' + k_{35}')$ are 10–20 times larger than k_{12} and k_{12}', respectively. This is typical of the effect of one more negative charge at the reacting center and has been rationalized[16] in terms of the dissociative ion-pairing mechanism. In the case of Scheme III the quotient $k_{35}'k_{43}'/(k_{34}' + k_{35}')$ probably reduces to $\sim k_{43}'$ because $k_{35}' > k_{34}'$, and this is consistent with the experimental magnitude of the quotient.

In Scheme III one might expect the values of k_{52}' to increase with the ligand K_a because chelate ring opening involves bond breaking at the same position as the proton ionization. On the other hand, the ring-opening step k_{53} in Scheme II is at the position not involved in the proton ionization and k_{53} might be expected to be relatively constant. In fact, the k_{53} or k_{52}' values are relatively constant in the range of 0.2–0.5 s^{-1} and show no trend with the ligand K_a value. This provides an indication that Scheme II gives a better means of rationalizing the results.

In Schemes II and III K_a'' refers to the same process and the values do parallel the K_a of the free ligand, as might be expected. The difference between K_a and K_a'' of a factor of $\sim 10^7$ might seem large for the effect of a nickel(II) ion. However, intramolecular hydrogen bonding is possible in the free ligand, but not in the complex, and this may accentuate the apparent acidity difference.

The above discussion is concerned with the general reactivity patterns. A closer inspection of the results in Tables III and IV shows that the k_{12} and k_{43} (or k_{12}' and $k_{35}'k_{43}'/(k_{34}' + k_{35}')$) values are similar for the 2-nitroso-1-naphthol-4,6-disulfonate and 1-nitroso-2-naphthol-4-sulfonate, -5-sulfonate, and -7-sulfonate. The k_{12} for 1-nitroso-2-naphthol-3-sulfonate is only slightly larger than that for this group of ligands, but k_{43} (or $k_{35}'k_{43}'/(k_{34}' + k_{35}')$) is 2–3 times larger. This rate enhancement may be attributed to the proximity of the negative $-SO_3^-$ to the reaction site, thereby giving more effective ion pairing. However, the corresponding parameters are significantly smaller for 1-nitroso-2-naphthol-6-sulfonate and -3,6-disulfonates. The difference between the 3-sulfonate and the 3,6-disulfonate is especially remarkable, because in the other cases a remote $-SO_3^-$ substituent did not change the reactivity the way the 6-sulfonate group seems to have done.

A possible explanation for the dependence of rate constants on the position of the electron-withdrawing $-SO_3^-$ group may be formulated in terms of the substituent effect on the nitroso–oxime tautomeric equilibrium. The oxime formation involves electron donation from –OH to the aromatic ring, and from the ring to the nitroso group:



The ligands in the first group in the previous paragraph all have an $-SO_3^-$ substituent in conjugation with the –N=O group. This should favor the nitroso isomer. However, the 6-SO_3^- group is in conjugation with the –OH and this should favor the oxime. This simple movement of $-SO_3^-$ from the 4-, 5-, or 7-position to the 6-position changes the system from favoring the nitroso- to favoring the oxime tautomer.

The above arguments imply that a 3-sulfonate substituent should give the oxime tautomer, but this does not provide an explanation for the large reactivity difference between the 3-sulfonate and the 3,6-disulfonate. Intramolecular hydrogen bonding of the form $-O\cdots H\cdots OSO_2^-$ would favor the nitroso–hydroxy tautomer in the 3-SO_3^- system and counteract the normal substituent effect. There is an indication of this, as well as evidence of the differences between the 3-sulfonate and 3,6-disulfonate from the pK_a values. The 3-sulfonate (pK_a 7.57) is a weaker acid than 1-nitroso-2-naphthol (pK_a 7.42) but the 3,6-disulfonate (pK_a 6.94)

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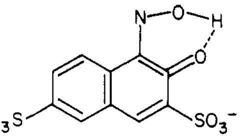
Table V. Activation Parameters from Kinetic Data at 20, 25, and 30 °C

position							
NO	OH	SO_3		k_{12}[a]	k_{43}	$(k_{12}/k_{21})k_{26}$	$(k_{35}/k_{34})k_{43}$[a]
2	1	4, 6	$\Delta H^\ddagger$	13.0 ± 3.4	11.2 ± 0.85	9.19 ± 1.1	−10.6 ± 10.7
			$\Delta S^\ddagger$	1.48 ± 1.6	5.39 ± 2.9	−15.1 ± 3.6	−65.7 ± 35.7
1	2	5	$\Delta H^\ddagger$	7.53 ± 2.1	10.83 ± 1.0	8.37 ± 0.7	4.47 ± 2.0
			$\Delta S^\ddagger$	−16.9 ± 7	−8.10 ± 3.4	−19.5 ± 2.3	−16.3 ± 6.8
1	2	4	$\Delta H^\ddagger$	7.90 ± 1.3	13.16 ± 0.63	8.16 ± 0.47	−0.16 ± 1.4
			$\Delta S^\ddagger$	−15.4 ± 4	7.45 ± 2.1	−19.5 ± 1.6	−30.3 ± 4.8
1	2	4	$\Delta H^\ddagger$	7.82 ± 1.74	14.0 ± 0.8	8.04 ± 0.61	12.9 ± 2.7
			$\Delta S^\ddagger$	−15.5 ± 5.8	10.1 ± 2.8	−18.4 ± 2.1	12.8 ± 8.9
1	2	3	$\Delta H^\ddagger$	13.8 ± 2.6	7.63 ± 1.1	7.82 ± 0.96	−1.38 ± 4.3
			$\Delta S^\ddagger$	4.39 ± 8.8	−9.72 ± 3.7	−19.3 ± 3.2	−3.38 ± 14.3

[a] These values are much less reliable because of parameter correlations noted in the text. [b] $\Delta H^\ddagger$ values are in kcal mol^{-1}, and $\Delta S^\ddagger$ values are in cal mol^{-1} deg^{-1}.

is a stronger acid than the 6-sulfonate (pK_a 6.94). If the 3-sulfonate is a weaker acid due to intramolecular hydrogen bonding, then the simplest explanation for the much greater acidity of the 3,6-disulfonate is that the tautomer equilibrium has been shifted to the oxime and the $-SO_3^-$ is no longer involved in hydrogen bonding:



The implications of the above analysis are that the 2-nitroso-1-naphthol-4,6-disulfonate and 1-nitroso-2-naphthol-4-sulfonate, -5-sulfonate, and -7-sulfonate ligands are predominantly in the nitroso–hydroxy form in solution. These systems show very similar reactivity. 1-Nitroso-2-naphthol-3-sulfonate may have less nitroso–hydroxy tautomer than the systems just mentioned, but the reactivity is enhanced by the proximity of the $-SO_3^-$ group to the reaction site. The 6-sulfonate also has less nitroso–hydroxy tautomer and shows lower reactivity. This may be due to stronger intramolecular hydrogen bonding in the protonated form, while the deprotonated form may be less reactive because the negative charge is delocalized over the $(O-N-C-C-O)^-$ system. The 3,6-disulfonate has a similarly low reactivity, and the adjacent $-SO_3^-$ has less rate-enhancing effect because of the charge delocalization just mentioned.

Depending on which terms are dominant in eq 5 or eq 6, it can be seen that the rate-controlling step may be either first bond formation to form the monodentate intermediates or chelate ring closing. For the sake of illustration on analysis will be given for the variation in the rate-controlling step with acidity for eq 5 (Scheme II), but analogous conclusions can be obtained for eq 6. Rather than a discussion of each system some typical kinetic parameters (Table III) will be used; i.e., $k_{12} = 4 \times 10^3$ M^{-1} s^{-1}, $k_{43} = 5 \times 10^4$ M^{-1} s^{-1}, $(k_{26}/k_{21})k_{12} = 4 \times 10^2$ M^{-1} s^{-1}, $(k_{35}/k_{34})k_{43} = 2 \times 10^6$ M^{-1} s^{-1}, and $K_a = 6 \times 10^{-8}$ M. The observed rate constant is primarily determined by $(k_{26}/k_{21})k_{12}$ when $q > 1$ and $(k_{26}/k_{21})k_{12}[H^+] > (k_{35}/k_{34})k_{43}K_a$, which occurs for $[H^+] > 3 \times 10^{-4}$ M. Then complex formation consists of a rapid preequilibrium (k_{12}/k_{21}) and rate-controlling ring closing (k_{26}), and dissociation is controlled by ring opening (k_{62}). For $[H^+]$ between $\sim 3 \times 10^{-4}$ and $\sim 3 \times 10^{-5}$ M, still $q > 1$, but $(k_{35}/k_{34})k_{43}K_a > (k_{26}/k_{21})k_{12}[H^+]$, so that the determining factor is $(k_{35}/k_{34})k_{43}$ and chelate ring closing of the deprotonated ligand is rate controlling. If $q < 1$, and $k_{12}[H^+] > k_{43}K_a$, then k_{12} is rate controlling, and this occurs for $[H^+]$ between $\sim 3 \times 10^{-5}$ and 7×10^{-7} M. If $[H^+] < 7 \times 10^{-7}$ M, $q < 1$ and $k_{43}K_a > k_{12}[H^+]$, so that first bond formation with the deprotonated ligand (k_{43}) is rate limiting.

The above general analysis may be summarized as follows: the major kinetic terms are k_{43} for pH >6.2, k_{12} for pH 4.5–6.2, $(k_{43}/k_{34})k_{35}$ for pH 3.5–4.5, and $(k_{12}/k_{21})k_{26}$ for pH <3.5. These pH ranges will shift to lower values as the ligand K_a increases. The relatively narrow range over which $(k_{43}/k_{34})k_{35}$ is dominant explains why this value has a generally larger uncertainty in the present cases. It should be noted also that $(k_{12}/k_{21})k_{26}$ is determined from the dissociation rate data ($[H^+] \gtrsim 2 \times 10^{-2}$ M) in this study.

The temperature dependence of K_a and the formation and dissociation rates have been determined at 20, 25, and 30 °C. The resulting activation parameters for the model based on Scheme II (eq 5) are summarized in Table V. It is assumed that K_aK_f and K_a'' are temperature independent and have the values given in Table III. The activation parameters have somewhat larger than normal uncertainties because of the complexity of the model and inevitable parameter correlations, rather than because of poor fitting.

It should be noted that the small and even negative $\Delta H^\ddagger$ values for $(k_{35}/k_{34})k_{43}$ are not reasonable. These values are equal to $\Delta H^\ddagger$ for $k_{53}K_f$, but ΔH° for K_f is probably small and $\Delta H^\ddagger$ for k_{53} is unlikely to be less than 5 kcal mol^{-1}. This observation led to some quantitative tests of the parameter correlations. It was found, for example, that if $\Delta H^\ddagger$ for $(k_{35}/k_{34})k_{43}$ is fixed at 10.0 kcal mol^{-1} then the overall quality of the fit is not unreasonably affected, but the $\Delta H^\ddagger$ value for k_{12} can change by $\sim$5 kcal mol^{-1}, while the $\Delta H^\ddagger$ values for k_{43} and $(k_{26}/k_{21})k_{12}$ are affected by less than 0.6 kcal mol^{-1}. Thus it seems that only the last two values deserve further discussion.

For four of the ligands the $\Delta H^\ddagger$ values for k_{43} are in the range 11–14 kcal mol^{-1} as expected for a dissociative ion-pair mechanism for $Ni(OH_2)_6^{2+}$, for which water exchange has $\Delta H^\ddagger = 13.6$ kcal mol^{-1}.[18] The exception to this is 1-nitroso-2-naphthol-3-sulfonate, for which $\Delta H^\ddagger$ is almost half that of the other ligands. This reduction may be attributed to a more negative ΔH° for ion-pair formation due to the proximity of the $-SO_3^-$ and $-O^-$ functions in the basic form of the ligand.

The activation parameters for $(k_{26}/k_{21})k_{12}$ are remarkably constant and the same within their error limits. The average values are $\Delta H^\ddagger = 8.5$ kcal mol^{-1} and $\Delta S^\ddagger = -18.6$ cal mol^{-1} deg^{-1}. If k_{12} has $\Delta H^\ddagger \approx 14$ kcal mol^{-1} as expected for a dissociative mechanism, than it appears that $\Delta H^\ddagger$ for k_{21} is 5–6 kcal mol^{-1} larger than that for k_{26}. In the absence of other data for similar rate constant ratios further comparisons are not possible.

Experimental Section

Materials. Aqueous nickel(II) perchlorate was prepared from the reagent grade hydrated solid (J. T. Baker) and standardized gravimetrically with use of dimethylglyoxime. Lithium perchlorate was recrystallized by dissolving it in a minimum of water and filtering and partially evaporating the solution before collecting the solid by filtration. Stock solutions of $LiClO_4$ were standardized by titrating the hydrogen ion released from an ion-exchange resin in the H^+ form. The buffer, sodium cacodylate, was used as supplied.

The nitroso–naphthol ligands were prepared by standard methods,[7,19] except for 3-sulfonate, where the published procedure[20] was unsuccessful. A modified procedure was developed that involved conversion of 2-

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hydroxy-3-naphthoic acid to the methoxy derivative followed by conversion to the isocyanate and then to 2-methoxy-3-naphthylamine. Treatment with SO_2 and Cu yielded the sulfinic acid, which was oxidized with $KMnO_4$ to the sulfonic acid and then treated with aqueous HCl to give 2-naphthol-3-sulfonic acid. This was treated with $NaNO_2$ in aqueous HCl at 0–5 °C and then with sodium perchlorate to yield the sodium salt of 1-nitroso-2-naphthol-3-sulfonate trihydrate. The product was recrystallized from warm water by the addition of ethanol. The details will be published elsewhere.[21]

The ligands were characterized by C,H,N analysis and infrared and proton NMR spectroscopy.

Kinetic Measurements. For the formation kinetics, stock solutions of nickel(II) ($\sim 6 \times 10^{-3}$ M) and ligand ($\sim 6 \times 10^{-5}$ M) were prepared in $LiClO_4$ (0.10 M) and 0.05 M sodium cacodylate, and the pH of each was adjusted by addition of perchloric acid. In the region of pH 3–4.5 only perchloric acid was used to establish the pH. The pH of the solution after mixing in the stopped-flow system was recorded.

For the dissociation kinetics, a stock solution containing $\sim 1 \times 10^{-3}$ M nickel(II) and 1×10^{-5} M ligand in 0.1 M $LiClO_4$ was mixed with the appropriate $LiClO_4$–$HClO_4$ solution in the stopped-flow system. The acid concentration was taken as half of that in the original $LiClO_4$–$HClO_4$ solution.

The reactions were monitored at or near an absorption maximum of the nickel(II) complex. The specific wavelengths for the 3-sulfonate, 4-sulfonate, 5-sulfonate, 7-sulfonate, and 4,6-disulfonate ligands are 446, 455, 436, 440, and 470 nm, respectively.

In each case the reported rate constant is the average of at least five determinations with a range of ±3%.

Instrumentation. The pH was measured with an Orion 801A digital pH meter standardized against appropriate borate, phthalate, and phosphate buffers.[22] The temperature was maintained within ±0.10 °C by water circulating through a double-walled container for the solution.

A Durrum-Gibson D-110 stopped-flow spectrophotometer was used in the absorbance mode, with the output stored on a Biomation 802 transient recorder. The analog unit for subsequent processing is described elsewhere.[23]

The spectral characterization of the ligands were done with a Cary 219 spectrophotometer, a Pye-Unicam SP3-3000 infrared spectrophotometer, and a JEOL JNM-PMX-60 NMR spectrometer. Elemental analyses were performed by the Pascher Mikroanalytisches Laboratorium, Bonn, West Germany.

Acknowledgment. We wish to acknowledge the financial support for this work from the Natural Sciences and Engineering Research Council of Canada and the University of West Indies.

Registry No. $Ni(OH_2)_6^{2+}$, 15365-79-4; 2-nitroso-1-naphthol-4,6-disulfonate, 94517-69-8; 1-nitroso-2-naphthol-3-sulfonate, 94517-70-1; 1-nitroso-2-naphthol-4-sulfonate, 94517-71-2; 1-nitroso-2-naphthol-5-sulfonate, 94517-72-3; 1-nitroso-2-naphthol-7-sulfonate, 94517-73-4.

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Kinetics and Mechanism of Chelation of Nickel(II) by a Tridentate α-[(2-Hydroxyphenyl)azo]-α-acetoacetonitrile and an α-(8-Quinolylazo)-α-acetoacetonitrile Dye

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The kinetics of formation of 1:1 tridentate chelates with the (2-hydroxyphenyl)azo (**1**) and 8-quinolylazo (**2**) dyes were studied over the pH range 4–9 and at an ionic strength of 0.1 M in buffers that do not complex nickel(II). Resonance-Raman and ^{13}C NMR spectra show that the predominant tautomers of **1** and **2** are the hydrazones at pH < pK_{a1} for **1** ($pK_{a1} = 6.11$) and at pH < pK_{a2} for **2** ($pK_{a2} = 7.32$). Ionization at the indicated pK_a's gives the arylazo enolates and eliminates tautomeric forms. Dye **1** has the azo enolate structure in the chelate. The ^1H and ^{13}C NMR spectra show separate lines for conformers that interconvert slowly ($\tau > 30$ ms) at room temperature. Under conditions of neutral and mildly basic pH and excess nickel, an intermediate accumulates, and its formation and decay were measured at wavelengths corresponding to appropriate isosbestic points. Estimated lower limits on the magnitudes of the formation constants for the intermediates indicate that they are bidentate. Rate constants for the final ring-closure step were independent of pH and nickel concentration and had values of 3.7 ± 0.2 and 0.044 ± 0.008 s^{-1}, respectively, for **1** and **2**. Overall formation rate constants for the chelates from the monoanions of **1** and **2** (6.2×10^2 and 1.15×10^3 M^{-1} s^{-1}, respectively) and for the undissociated dyes (<15 and 2.4 M^{-1} s^{-1}, respectively) are much smaller than expected from the water-exchange constant of Ni^{2+} and reasonable outer-sphere formation constants. The slow rates of ring closure and of formation of the intermediates are discussed in terms of steric effects and the presence of unreactive tautomers.

This paper is a continuation of our effort to understand the details of the kinetics and mechanism of the chelation of nickel(II) by tridentate metalizable dyes. In an earlier paper[2] we were able to estimate rate constants for partitioning of partially chelated intermediates from 2-(2-pyridylazo)-1-naphthol (α-PAN) dyes. Whereas one of the ring-closure steps was partially rate limiting, the overall rate constants for formation of 1:1 nickel:dye complexes from the various ionic species of the dyes were only about half the value calculated from the water-exchange rate of Ni^{2+} and reasonable values for the outer-sphere complex constant. We also showed that the 1:2 nickel:dye complex (MD_2) of the α-PAN dyes forms surprisingly rapidly from the 1:1 complex (MD) via a consecutive competitive pathway. Initial chelation gives a kinetically controlled mixture of complexes in which the 1:2 complex exceeds its equilibrium concentration. We suggested that complexation of the first dye served as a template to facilitate rapid addition of a second dye, following the concept advanced by Cayley and Margerum.[3]

In this paper we have sought to extend the generality of the earlier findings. Dyes **1** and **2** were selected for several reasons: (a) The dyes have fewer and smaller aromatic moieties than the α-PAN dyes and were expected to differ in their ability to form templates for facilitating 1:2 complex formation. (b) Space-filling

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(1) Present address: Coherent, Inc., Palo Alto, CA 94304.

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