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Reactions of Nickel Ions with Nitroso-Naphthols. I. Equilibria and Dissociation Kinetics of some Nickel Complexes

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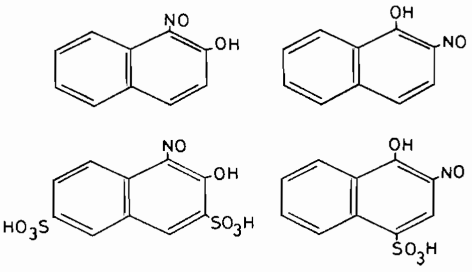
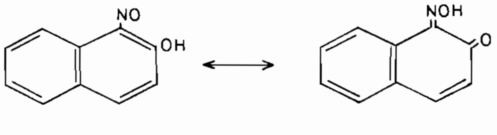
The formation constants and dissociation kinetics of NiL, (HL = 1-nitroso-2-naphthol, 1-nitroso-2-naphthol-3,6-disulphonate, 2-nitroso-1-naphthol and 2-nitroso-1-naphthol-4-sulphonate) are reported in the temperature range 15–30° C, at 0.100 M ionic strength. The formation constants appear to be temperature independent. The observed reaction rates vary markedly with the relative positions of the –NO and –OH groups and on substitution in the rings by sulphonate groups. The mechanism of the dissociation reaction is discussed and activation parameters are reported.

Introduction

Ortho-nitroso-naphthols are useful complexing agents[1]. The parent compounds 1-nitroso-naphthol ($\alpha\beta$H) and 2-nitroso-1-naphthol ($\beta\alpha$H) and two sulphonic acid derivatives 1-nitroso-2-naphthol-3,6-disulphonic acid and 2-nitroso-1-naphthol-4-sulphonic acid are well known. Some new derivatives have been reported recently[2].



Studies on these compounds are complicated by: (1) nitroso–oxime equilibria, illustrated here for 1-nitroso-



2-naphthol, which has been examined by numerous authors with sometimes conflicting results[3–11]; and (2) the uncertainty of whether 5- or 6-membered chelate rings are formed on coordination[10]. Nevertheless, these ligands form so many metal complexes and can be subjected to so many structural changes in the number, type and position of nonreacting substituents that equilibrium and kinetic studies appear eminently worthwhile. This paper reports the first of a projected series of studies on nickel/nitroso systems and deals with the kinetics of the back reaction and equilibrium constants of reaction (1).

$$\mathrm{Ni}^{2+} + \mathrm{HL} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \mathrm{NiL} + \mathrm{H}^+ \qquad (1)$$

Experimental

Reagents

Glass distilled water was used throughout. The sulphonated ligands, in the form of potassium salts, were purified and analysed as previously reported[12]. 1-nitroso-2-naphthol and 2-nitroso-1-naphthols were recrystallised several times from water, and dried over sodium hydroxide. The materials were shown to be chromatographically pure; the melting points agreed with literature values. A.R. grade nickel nitrate was used throughout. The concentration of the nickel stock solution was determined gravimetrically by dimethyglyoxime. All other reagents were of A.R. grade. Ionic stregths were held constant with $NaClO_4$.

Equilibrium Measurements

The equilibrium constants of reaction (1) were measured using a modified spectrophotometer previously described[13]. To ensure that only the mono-complex was formed [Ni^{2+}] exceeded [HL] by a factor of at least 50. In any particular series of experiments [Ni^{2+}] and [HL] were maintained constant and [H^+] varied by addition of $HClO_4$ from a micrometer burette. The ionic strength was kept constant at 0.1 *M*. The pH of each reaction solution was determined by use of an Orion 701 pH meter and corrected for the ionic strength of the solution in converting to [H^+][14].

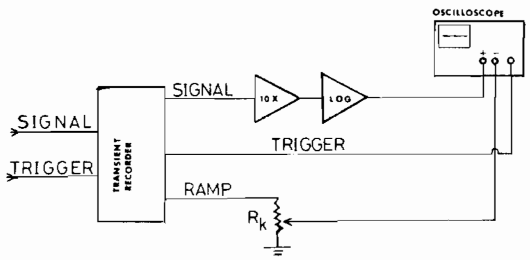


Figure 1. Block diagram of analog computer.

Kinetic Studies

A Durrum stopped flow spectrophotometer was used in the absorbance mode with the signal offset to make the output proportional to (A_t–A_∞). Data were obtained either photographically from a Hewlett–Packard 1207B oscilloscope screen or by using a Biomation 802 transient recorder for storage with analog processing somewhat similar to that described by Stuart[15], and shown in block form in Figure 1. The output of the transient recorder is normalized in amplitude (1 volt max.) and in time (2 msec sweep). This output, amplified by a factor of 10.00, is the input of a Burr–Brown Model 1664/16 logarithmic amplifier ($E_{out} = -10 \log E_{in}$; transfer accuracy better than 1%). The output of this amplifier is then equivalent to a repetitive (2msec) plot of log(A_t–A_∞) against time. The slope of this line can be measured directly on the oscilloscope screen or matched against the standard 2 msec ramp provided by the T.R., the amplitude of which is determined by R_k. In the latter case the first order rate constant k is given by equation (2)

$$k = R_k \times 0.2303/\text{T.R. input sweep time setting} \quad (2)$$

All amplifiers were exactly balanced and the accuracy of the individual units was adjusted to a few parts per thousand. The overall reproducibility of the system including the spectrophotometer, at this stage of development, is usually better than 5%.

Results and Discussion

Spectra

The observed spectra of the unsulphonated ligands and nickel complexes are in Figures 2 and 3. The spectra of the sulphonated compounds are similar to those.

The wavelengths selected for the studies were optimised for low absorption of HL and for a maximum difference in the molar extinction coefficients of the complex and ligand. A wavelength of 450 nm was selected for all systems except 2-nitroso-1-naphthol for which 474 nm was used. At 450 nm the extinction coefficients are:

	($\alpha\beta$)	[Ni$\alpha\beta$]	{$\alpha\beta(SO_3H)_2$}
ε_{450}	1311	4949	1170

[Ni{$\alpha\beta(SO_3H)_2$}]	{$\beta\alpha(SO_3H)$}	[Ni{$\beta\alpha(SO_3H)$}]
6830	4433	7090

For ($\beta\alpha$) and [Ni($\beta\alpha$)] the extinction coefficients at 474 nm are 953 and 6228 respectively.

Equilibria

The results obtained in the equilibrium studies are in Table I. 2 cm path lengths were used throughout.

The formation constants are insensitive to temperature. The values, together with pK_a values[16] at 25° C are collected together in Table II.

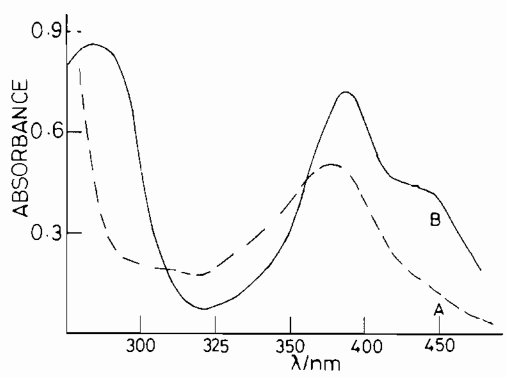


Figure 2. Spectra of 1-nitroso-2-naphthol (A) and Ni(1-nitroso-2-naphthol) (B). [HL] = $4.10 \times 10^{-5} M$, $[Ni^{2+}]_{Tot} = 1.04 \times 10^{-1} M$; 2 cm path length.

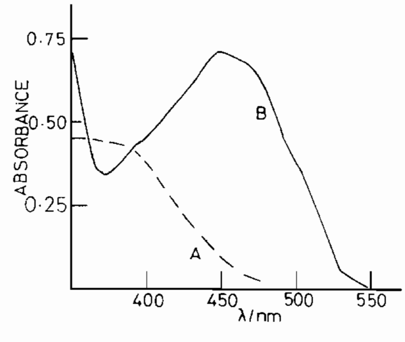


Figure 3. Spectra of 2-nitroso-1-naphthol (A) and Ni(2-nitroso-1-naphthol) (B). [HL] = 1×10^{-4}; $[Ni^{2+}]_{Tot} = 1.04 \times 10^{-1} M$; 1 cm path length.

TABLE I. Results of Equilibrium Studies.

Ni(1-nitroso-2-naphthol). $[HL]_o = 4.08 \times 10^{-5} M$, $[Ni^{2+}]_o = 4.14 \times 10^{-3} M$; 25.0° C.					
$10^4[H^+]$	1.29	4.72	7.57	9.53	11.8
absorbance	0.343	0.260	0.218	0.206	0.198
K	0.12_4	0.12_2	0.11_0	0.11_6	0.11_8
Ni(2-nitroso-1-naphthol). $[HL]_o = 3.85 \times 10^{-5}$, $[Ni^{2+}]_o = 4.14 \times 10^{-3} M$; 25.0° C					
$10^4[H^+]$	0.89	1.58	2.13	3.20	4.90
absorbance	0.318	0.258	0.232	0.220	0.149
K	0.033	0.032	0.033	0.045	0.027
15° C					
$10^4[H^+]$	1.1	1.81	8.3		
absorbance	0.292	0.233	0.127		
K	0.032	0.029	0.031		
Ni(1-nitroso-2-naphthol-3-6-disulphonate). $[HL]_o = 5.00 \times 10^{-5} M$, $[Ni^{2+}]_o = 2.588 \times 10^{-3} M$; 25.0° C					
$10^3[H^+]$	3.01	6.15	6.59	7.92	11.7
absordance	0.512	0.301	0.397	0.375	0.238
K	1.3_5	1.1_5	1.2_5	1.3_0	1.1_8
$[Ni^{2+}]_o = 5.175 \times 10^{-3} M$; 15.0° C.					
$10^3[H^+]$	2.56	5.73	6.43		
absorbance	0.515	0.398	0.398		
K	1.1_8	1.1_0	1.2_3		
Ni(2-nitroso-1-naphthol-4-sulphonate). $[HL]_o = 5.00 \times 10^{-5} M$; $[Ni^{2+}] = 5.18 \times 10^{-3} M$; 25.0° C.					
$10^3[H^+]$	1.32	1.35	2.94	5.74	
absorbance	0.455	0.455	0.332	3.45	
K	0.36_8	0.37_6	0.36_6	0.34_5	
$[Ni^{2+}] = 2.588 \times 10^{-3}$; 25.0° C.					
$10^3[H^+]$	0.792	3.62	3.71		
absorbance	0.342	0.218	0.221		
K	0.38_1	0.36_6	0.38_4		
$[Ni^{2+}] = 5.18 \times 10^{-3}$; 15.0° C.					
$10^3[H^+]$	1.4_7				
absorbance	0.441				
K	0.37				

TABLE II. Constants for NiL Formation and pK$_a$ Values of Nitrosonaphthol at 25° C, 0.1 *M* Ionic Strength.

	K_{NiL}	pK	$\log\beta_{NiL}$
1-nitroso-2-naphthol	0.118	7.63[a]	6.7
2-nitroso-1-naphthol	0.032	7.24[a]	5.98
2-nitroso-1-naphthol-4-sulphonate	0.37	6.10[b]	6.99
1-nitroso-2-naphthol-3,6-disulphonate	1.25	6.88[b]	7.64

[a] D. Dyrssen and E. Johansson, *Acta. Chem. Scand.*, *9*, 763 (1955). [b] O. Mäkitie and H. Saarinen, *Suomen Kemistilehti*, *B44*, 180 (1971).

It is not yet known if under the relatively highly acidic conditions used in this study Ni^{2+} reacts with HL as written in equation (2) or whether the reaction proceeds via the acid–base equilibrium (equation 3):

$$HL \rightleftharpoons H^+ + L^- \tag{3}$$

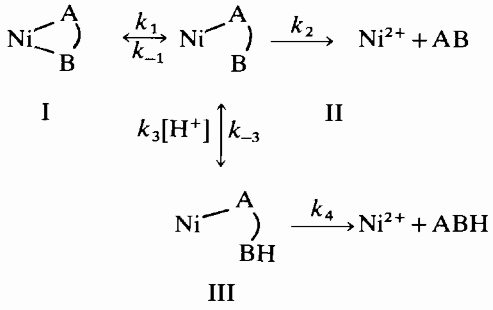
In the latter case, the formation constants for [NiL] should include the K$_a$ values of equation (3) as is done in the last column of Table II.

Kinetics

Pseudo-first order conditions with [NiL^{2+}] and [H$^+$] in large excess were used at 0.100*M* ionic strength. The results are in Tables III–IV. Each run was repeated at least three times.

Some of the data in these tables are plotted in Figure 4, which illustrates that $k_{\beta\alpha} >> k_{\alpha\beta} > k_{\beta\alpha(SO_3^-)} > k_{\alpha\beta(SO_3^-)_2}$ and that introduction of the sulphonate substituent lowers the reaction rate and reduces curvature in the k vs. [H$^+$] plots. The [H$^+$] dependence for Ni[$\alpha\beta$ $(SO_3^-)_2$] may be linear; the values of the $k_{obs}/[H^+]$ in Table IV may show a slight trend but this is within the experimental error.

The decomposition of chelates is generally considered to be a stepwise process which, in this case is shown, omitting solvent molecules in equation (4):



(4)

This scheme is kinetically identical to that proposed[16] for the dissociation of the tris(dipyridyl)cobalt(II) cation, with the same approximations leads to equation (5)

$$k = \frac{k_1(k_2 + k_3[H^+])}{k_{-1} + k_2 + k_3[H^+]} \tag{5}$$

by assuming stationary state kinetic conditions for II, and to equation (6)

$$k = \frac{k_1k_2 + K_3k_4[H^+]}{k_{-1} + k_2 + K_3k_4[H^+]} \tag{6}$$

if the stationary state conditions are assumed for both II and III, since it is reasonable to put $k_3/k_{-3} = K_3$. These hydrogen ion dependences are of the same for in that $1/k_{obs}$ can be linear with $1/_{[H^+]}$. k is identical with k_d in equation (1). This treatment yields excellent

TABLE III. Observed Pseudo-first Order Rate Constants(sec^{-1}) for the Acid Dissociation of Nickel-nitroso-naphthol Complexes.

Ni(1-nitroso-2-naphthol)							
	15° C						
$10^2[H^+]$	1.0	1.5	2.0	4.0	10.0		
k	16	23	29.4	49	83.1		
	25° C						
$10^2[H^+]$	2.0	4.0	5.0	8.0	10		
k	60 ± 2	107 ± 2	116	154	162		
Ni(2-nitroso-1-naphthol)							
	15° C						
$10^2[H^+]$	1.0	2.0	4.0	8.0			
k	77.6	120 ± 5	169	217 ± 7			
Ni(2-nitroso-1-naphthol-4-sulphonate)							
	15° C						
$10^2[H^+]$	1	1.5	2.5	3	4.94	5.0	10.0
k	10.2	15.4	24.3	28.0	39.2	45.2	78.1
	25° C						
$10^2[H^+]$	1	1.98	3.95	4.94	6.92	9.22	
k	21.2 ± .1	29.0 ± .8	67.9 ± .1	84.1 ± 1	112	142	
	35° C						
$10^2[H^+]$	1	1.98	3.95	4.94	6.92	9.22	
k	40	70	129	152	199	232	

TABLE IV. Rate Constants (sec–1) for the Dissociation of $[Ni\{\alpha\beta(SO_3^-)_2\}]$. $I = 0.100M$.

	15° C						
$10^2[H^+]$	3.02	4.05	6.04	8.06	8.14	9.06	1.07
k	7.9_5(±.05)	10.4(±.3)	14.9(±.4)	19.6(±.6)	20	22.3(±.0)	26.8(±1.2)
$k/[H^+]$	263	257	247	243	246	246	250
	20.5° C						
$10^2[H^+]$	4.05	8.06	1.01				
k	15.2(±.3)	29.7 ± 1	36.2 ± 1				
$k/[H^+]$	375	368	358				
	25.1° C						
$10^2[H^+]$	3.02	6.04	8.06	9.06	1.00		
k	15.6	30.1(±.3)	40.3(±.4)	44.7(±.2)	49(±1)		
$k/[H^+]$	517	498	500	493	490		
			30.0° C				
$10^2[H^+]$			8.11				
k			50.8(±1) av. of six runs				
$k/[H^+]$			626				

linear plots. The data in Table III were fitted to linear least squares equations with the following results:

1-nitroso-2-naphthol
At 15° C:

$$\frac{1}{k} = 6.962\times10^{-3} + 5.53\times10^{-4}\left(\frac{1}{[H^+]}\right) \qquad (7)$$

the standard deviations in the intercept and slope are 6.91×10^{-4} and 1.16×10^{-5} respectively.
At 25° C:

$$\frac{1}{k} = 3.20\times10^{-3} + 2.664\times10^{-4}\left(\frac{1}{[H^+]}\right) \qquad (8)$$

the standard deviations are 3.13×10^{-4} and 1.14×10^{-5} in the intercept and slope respectively.

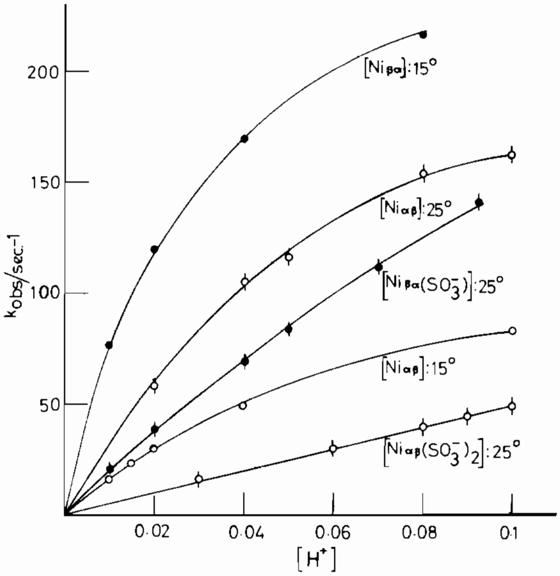


Figure 4. Variation of k_{obs} for decomposition of mono-nitroso nickel complexes with hydrogen ion concentration.

2-nitroso-1-naphthol
At 15° C:

$$\frac{1}{k} = 3.613 \times 10^{-3} + 0.31 \times 10^{-5}\left(\frac{1}{[H^+]}\right) \tag{9}$$

standard deviations: intercept, 4.33×10^{-5}; slope 7.51×10^{-7}.

2-nitroso-1-naphthol-4-sulphonic acid
At 15° C:

$$\frac{1}{k} = 4.348 \times 10^{-3} + 9.313 \times 10^{-4}\left(\frac{1}{[H^+]}\right) \tag{10}$$

standard deviations: intercept, 9.5×10^{-4}; slope, 1.87×10^{-5}.
At 25° C:

$$\frac{1}{k} = 2.748 \times 10^{-3} + 4.467 \times 10^{-4}\left(\frac{1}{[H^+]}\right) \tag{11}$$

standard deviations: intercept, 3.0×10^{-4}; slope, 5.3×10^{-5}.
At 35° C:

$$\frac{1}{k} = 1.80 \times 10^{-3} + 2.345 \times 10^{-4}\left(\frac{1}{[H^+]}\right) \tag{12}$$

standard deviations: intercept, 2.4×10^{-5}; slope 5.0×10^{-6}.

Equations (5) and (6) yield the same value of $1/k_1$ for the intercept. The slope will give a collection of constants (C) the details of which depend on the mechanism chosen. The values of k_1 and C are in Table V.

TABLE V. Rate and Equilibrium Constants for the Decomposition of Nickel–Nitroso-naphthol Complexes in Acidic Aqueous Solutions.

° C	15.0	25.0	35.0
	k_1; C	k_1; C	k_1; C
1-nitroso-2-naphthol	144; 12.6	312; 12.0	–
2-nitroso-1-naphthol	277; 29	–	–
2-nitroso-1-naphthol-4-sulphonic acid	230; 4.67	364; 6.15	556; 7.6_8

TABLE VI. Arrhenius Parameters for Reactions.

	[Ni($\alpha\beta$)]	[Ni($\beta\alpha$SO$_3^-$)]
A(sec^{-1})	1.48×10^{12}	1.86×10^{8}
E_A(kcal)	13.2	7.79

Values of the terms A and E_A in equation (13) to which k_1 data

$$k = A \exp-(E_A/RT) \tag{13}$$

were fitted are in Table VI.

If equation (6) is applied and k_2 is assumed small as seems reasonable, $C = \frac{K_3 k_4}{k_{-1}}$. C is independent of temperature for the 1-nitroso compound but exhibits a significant temperature dependence for [Ni($\beta\alpha$SO$_3^-$)].

It has not yet been possible to obtain Arrhenius parameters for the 2-nitroso-1-naphthol complex. The dissociation rate is too rapid for studies above 15° C and we have not been too successful in obtaining reproducible kinetics below about 10° C, probably due to condensation of moisture on the optical surfaces or to the long times required for temperature equilibration.

The observed pseudo-first order rate constants for the decomposition of [Ni{$\alpha\beta$(SO$_3^-$)$_2$}] appear to increase linearly with [H$^+$] up to the highest acid concentration examined (0.25*M* at 10° C), indicating a rate equation

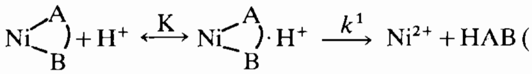
$$-\frac{d}{dt}[NiL] = k_{H^+}[NiL][H^+] \tag{14}$$

Average values of k_{H^+} are in Table IV. The temperature dependence of these rate constants is reasonably well reproduced by equation (15)

$$k_{H^+} = 2.997 \times 10^{10} \exp-(10.640/RT) \tag{15}$$

The spread in logA is ± 0.37 and in E_A is ± 515 cal. The observed kinetics would be explicable on the same general mechanism (equation 4) but with k_4 now rate determining.

Although the above treatment is based on a fairly generally accepted mechanism all the kinetics results are also explicable on the simpler mechanism in equation (16),



$$\mathrm{Ni}\overset{A}{\underset{B}{\langle\,\rangle}} + \mathrm{H}^+ \overset{K}{\longleftrightarrow} \mathrm{Ni}\overset{A}{\underset{B}{\langle\,\rangle}}\cdot\mathrm{H}^+ \xrightarrow{k^1} \mathrm{Ni}^{2+} + \mathrm{HAB} \quad (16)$$

in which case, k^1 and K are identical with the k_1 and C respectively of Table V.

The information presently available does not allow a choice between mechanisms (4) and (16). The mechanism may well depend on the structure of the nickel complexes. Saarinen and Korvenranta[17] have recently shown by X-ray methods that the copper complexes of both 1-nitroso-2-naphthol[17] and 2-nitroso-1-naphthol[18] have five-membered chelate rings *i.e.* the bonding to the metal is via the oxime nitrogen and the naphtholic oxygen. If this is applicable to these nickel complexes there would be an uncoordinated oxygen atom, attached to the nitrogen atom, which may be acidic enough to be engaged in the acid–base equilibria in equation (16). It may be possible to obtain information on this point by examining more robust complexes. Studies are now in progress on other dissociation reactions of similar ligands and on the formation reactions of these complexes.

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