Results and Discussion

All runs were kinetically first order with respect to NO pressure. The pseudo-first-order rate constant for disappearance of dissolved NO depends on the concentration of sulfite as illustrated in Figure 1, corresponding to a rate law $k = 0.132 + 0.45[SO_3^{2-}]$ sec^{-1}. At 50° the values are $k = 0.12 + 1.32[SO_3^{2-}]$ sec^{-1}. Within the range of concentration 0.1 to 1.0 M, the rate is independent of hydroxide.

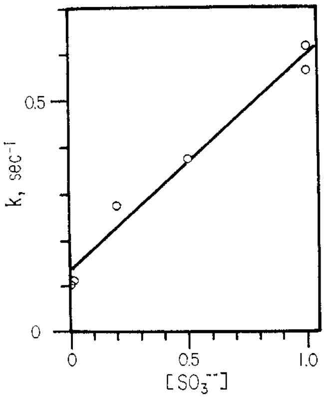


Figure 1.—Pseudo-first-order rate constant for the reaction of aqueous NO with sulfite at 25°.

This form of rate law is consistent with a mechanism involving two parallel paths. The sulfite-dependent term corresponds to direct combination of dissolved NO with sulfite ion, while the sulfite-independent term corresponds to a rate-determining reaction of dissolved NO with water to form a hydrolyzed species, followed by the relatively fast reaction of that species with sulfite

$$\text{NO(dissolved)} \xrightarrow{SO_3^{2-}} {}^-O_3SNO^-$$

$$\text{NO(dissolved)} \xrightarrow{xH_2O} NO(H_2O)_x \xrightarrow[\text{fast}]{SO_3^{2-}} {}^-O_3SNO^-$$

In either case, the primary product must be supposed to react rapidly with a second molecule of NO to yield the final product.

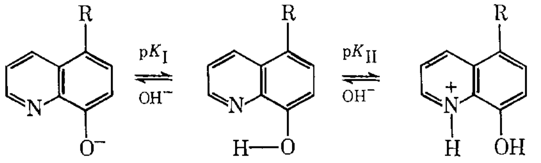
Contribution from the Department of Chemistry,
State University of New York at Buffalo,
Buffalo, New York 14214

The Kinetics of Complexing of Nickel(II) Ion with 8-Hydroxyquinoline and 8-Hydroxyquinoline-5-sulfonate

By William A. Johnson and R. G. Wilkins

Received December 8, 1969

The kinetics of formation of nickel(II) complexes with a large number and variety of ligands have been studied.[1] In our investigations of the effect of protonation of a ligand on its reactivity, a striking result has been the low rate constant for reaction of the zwitterion form of amino acids with nickel(II).[2] This may result from the internal hydrogen bonding present in the zwitterion, and in this connection it seemed worthwhile to examine the behavior of 8-hydroxyquinoline. This important ligand can exist in three forms, I–III, R = H, pK_I = 9.9 and pK_{II} = 5.1.[3] II has been reported to exist in the H-bonded form,[4] although its high rate constant for reaction with OH$^-$ ($\gtrsim 1.5 \times 10^9$ M^{-1} sec^{-1}) does not support this idea.[5] It was therefore of interest to study the complexation kinetics of I–III. We also examined the 5-sulfonated derivative, in which R = SO_3^- over the whole pH range of our study (pK_I = 8.4, pK_{II} = 3.8).[3] The kinetics of complex formation of a number of magnesium complexes with 8-hydroxyquinoline have been investigated previously.[5]



I II III

Experimental Section

Materials.—These were commercially available, reagent grade. 8-Hydroxyquinoline was recrystallized three times from aqueous ethanol and 8-hydroxyquinoline-5-sulfonic acid dihydrate was recrystallized twice from water, using decolorizing charcoal. 2,6-Lutidine was redistilled and a center fraction, bp 142°, was used.

Kinetic Experiments.—The concentration of nickel and copper ions was estimated by EDTA titrations, and that of the ligand by direct weighing. The formation and dissociation of the complexes were followed spectrally in the region of 370 mμ, using a glass–Lucite stopped-flow apparatus. In the formation experiment, metal ion at the appropriate pH (using acid alone, or buffer if necessary) was mixed with ligand at the correct pH, both solutions containing sodium nitrate to bring to the ionic strength used in all the studies (0.30 M). A large ratio of metal ion (usually 5×10^{-3} M) to ligand concentration (10^{-4} M) ensured pseudo-first-order kinetics and halted the reaction at the monocomplex stage, thus preventing precipitation of the sparingly soluble bis compound. The observed second-order rate constants [$k_{obsd} = 0.693/(t_{1/2}[Ni^{2+}])$, where $t_{1/2}$ is the half-life for the first-order reaction] are shown in Table I, and are the means of several runs.

In the dissociation experiments, complex prepared from excess Ni^{2+} at pH ~5 was plunged into perchloric acid at the lower pH or into solutions containing Cu^{2+} at pH 4–5. From a knowledge of the formation constants for the complexes with the two ligands,[3] it could be shown (and was checked spectrally) that both formation and dissociation reactions went to ($\geq$95%) completion. The temperature was controlled to ±0.1°. Spectra were recorded with a Cary 14 in a thermostated room (25 ± 0.5°).

Results and Discussion

Complex Formation.—The major forms of the ligand

---

[1] M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, **No. 49**, 55 (1965); N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966); L. I. Budarin and K. B. Yatsimirskii, *Russ. Chem. Rev.*, **37**, 209 (1968); A. McAuley and J. Hill, *Quart. Rev., Chem. Soc.*, **23**, 18 (1969)

[2] J. C. Cassatt and R. G. Wilkins, *J. Amer. Chem. Soc.*, **90**, 6045 (1968).

[3] L. G. Sillén and A. E. Martell, Ed., "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964.

[4] A. Albert, "Heterocyclic Chemistry," The Athlone Press, London, 1968, p 91. The enol form is favored with respect to the charge-separated form, $^+NH\cdots O^-$, K_t = [zwitterion]/[enol] = 0.035: S. F. Mason, *J. Chem. Soc.*, 5010 (1957).

[5] D. N. Hague and M. Eigen, *Trans. Faraday Soc.*, **62**, 1236 (1966).

TABLE I

KINETIC DATA ($I = 0.3\ M$)

Formation of 8-hydroxyquinoline complex			Formation of 8-hydroxyquinoline-5-sulfonate complex			Dissociation of 8-hydroxyquinoline complex		
Temp, °C	pH	$10^{-3}k_{obsd}$, M^{-1} sec^{-1}	Temp, °C	pH	$10^{-3}k_{obsd}$, M^{-1} sec^{-1}	Temp, °C	pH	k_{obsd}, sec^{-1}
25.0	4.6	0.55	25.0	3.0^b	0.13	25.0	1.1	1.6
25.0	5.0^a	0.60	25.0	3.3	0.23	25.0	2.0	1.6
25.0	5.0	0.62	25.0	3.4	0.23	25.0	3.0^d	1.2
25.0	5.3	0.90	25.0	3.5	0.26	25.0	3.4	1.3
25.0	5.5	0.92	25.0	3.6	0.34	25.0	4.0^d	0.36
25.0	5.7	1.2	25.0	3.7	0.38	25.0	5.0^d	0.044
25.0	5.8	1.3	25.0	3.8	0.49			
25.0	5.9	1.3	25.0	3.9	0.53			
25.0	6.0	1.3	25.0	5.0	1.1			
25.0	6.0^b	1.2	25.0	5.0^a	1.3			
20.0	6.0	1.0	25.0	5.5	1.4			
30.0	6.0	2.0	25.0	5.5^b	1.4			
35.0	6.0	2.3	20.0	5.5	0.83			
40.0	6.0	3.6	30.0	5.5	2.0			
			35.0	5.5	2.3			
			40.0	5.5	3.1			
			10.0	2.0^c	~70			

[a] Acetate buffer; remainder 2,6-lutidine buffer. [b] Using $2 \times 10^{-2}\ M$ Ni^{2+}; all others $5 \times 10^{-3}\ M$ Ni^{2+} and $10^{-4}\ M$ total hydroxyquinoline. [c] Formation of Cu(II) complex; $10^{-3}\ M$ Cu^{2+} and $5 \times 10^{-5}\ M$ hydroxyquinoline. [d] Using $10^{-2}\ M$ Cu^{2+} as scavenger.

present in the range of pH studied are II and III, represented as HQ and H_2Q^+ in both the cases of R = H and R = SO_3^-. The equilibria and reactions involved in the production of the mono nickel chelate are shown in (1)–(3), for which the relationships 4 and 5 may be deduced. The linear plots appropriate to (5) are shown in Figure 1. The intercepts (k_1) are zero within experimental error and indicate, as might be expected, little reactivity associated with the diprotonated H_2Q^+ form. The slopes give the values of k_2, rate constant for reaction of the HQ form.

$$H_2Q^+ \rightleftharpoons HQ + H^+ \qquad K_{II} = [HQ][H^+]/[H_2Q^+] \tag{1}$$

$$H_2Q^+ + Ni^{2+} \longrightarrow NiQ^+ + 2H^+ \qquad k_1 \tag{2}$$

$$HQ + Ni^{2+} \longrightarrow NiQ^+ + H^+ \qquad k_2 \tag{3}$$

$$[NiQ^+]/dt = k_{obsd}[Ni^{2+}]([H_2Q^+] + [HQ]) = k_1[Ni^{2+}][H_2Q^+] + k_2[Ni^{2+}][HQ] \tag{4}$$

$$k_{obsd}\frac{(K_{II} + [H^+])}{[H^+]} = k_1 + \frac{k_2K_{II}}{[H^+]} \tag{5}$$

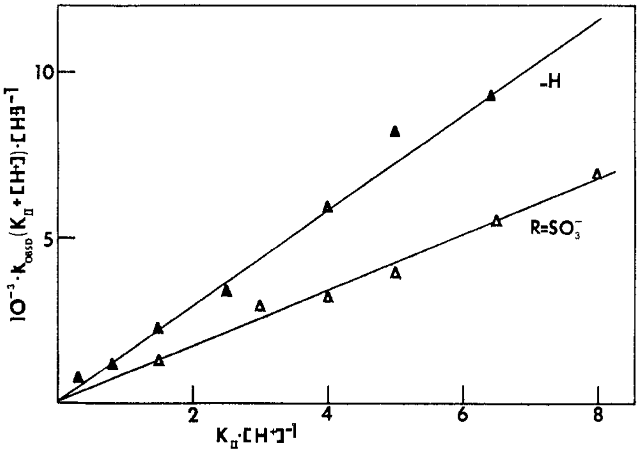


Figure 1.—Plot of $K_{II}/[H^+]$ against $10^{-3}k_{obsd}(K_{II} + [H^-])\cdot[H^+]^{-1}$ for 8-hydroxyquinoline complex formation at 25.0°. For 5-sulfonated derivatives ordinates are $10K_{II}/[H^+]$ and $10^{-2}k_{obsd}(K_{II} + [H^+])[H^+]^{-1}$.

We believe that over a wide range of pH the HQ form of the ligand is the sole contributor to the rate and that the rate law 6 holds. The equivalent rate term, $k_2'\cdot$

$$d[NiQ^+]/dt = k_2[Ni^{2+}][HQ] \tag{6}$$

$[Ni(OH)^+][H_2Q^+]$, we tend to discount because the concentration of $Ni(OH)^+$ will be low at the pH's used, and the H_2Q^+ would be expected to be very unreactive. The k_2 values are independent of the concentrations of nickel ion and total ligand and the nature of the buffer constituent. The values of k_{obsd} at pH 6.0 (R = H) and pH 5.5 (R = SO_3^-) are better estimates for k_2 than those derived from the plot (since they are independent of K_{II}) and these were determined at different temperatures so as to obtain the activation parameters. For the unsubstituted oxine, $\Delta H^* = 10.6$ kcal mol^{-1}, $\Delta S^* = -9$ eu, and $k_2 = 1.3 \times 10^3\ M^{-1}$ sec^{-1} at 25°, and for the substituted oxine (R = SO_3^-), $\Delta H^* = 10.1$ kcal mol^{-1}, $\Delta S^* = -10$ eu, and $k_2 = 1.4 \times 10^3\ M^{-1}$ sec^{-1} at 25°.[6] These values are very close to each other and to those observed for the reactions of nickel ion with neutral unidentate ligands.[1,7] They show (a) that there is no difficulty in effecting ring closure once the initial coordination has occurred, (b) that this initial coordination is controlled by the water-exchange process, and (c) that charge (in SO_3^-) relatively far removed from the potential donor sites modifies only slightly the rate compared with the unsubstituted ligand, as previously suggested.[2,8] In the event that (a) might not obtain with the more labile Cu(II) ion, an approximate value was obtained for the reaction of Cu^{2+} with 8-hydroxyquinoline-5-sulfonate. On the basis that II was the reactive form, $k_2 \approx 7 \times 10^6\ M^{-1}$ sec^{-1} at 10°, which suggests that ring closing is rate determining, *i.e.*, substitution is "sterically controlled."[9] The zwitterion forms of the amino acids are very much less reactive toward Ni(II)[2] and Cu(II)[10,11] than II, and this indicates that any hydrogen bonding in II is relatively weak or at least that masking of the reactivity of nitrogen by H^+ is less effective. The rate constants for reaction of Mg^{2+} with I and II (3.8×10^5 and $1.1 \times 10^4\ M^{-1}$ sec^{-1} at 25°) have led Hague and Eigen[5] to suggest that loss of water is not rate determining for the reaction of Mg^{2+} with II.

---

(6) When this work was completed we learned from Dr. R. H. Holyer that he was studying the reactions of Ni(II) with oxines and related ligands in mixed solvents. His activation parameters for Ni^{2+} with 8-hydroxyquinoline-5-sulfonate are $\Delta H^* = 9.2$, $\Delta S^* = -14$, and $k = 1.0 \times 10^3\ M^{-1}$ sec^{-1} at 25° in good agreement with ours.

(7) For example $Ni^{2+} + NH_3$ has $\Delta H^* = 10$ and $k_2 = 1.5 \times 10^3\ M^{-1}$ sec^{-1} at 25° and Ni^{2+} + py has $\Delta H^* = 13$ and $k_2 = 5 \times 10^3\ M^{-1}$ sec^{-1} at 25°.

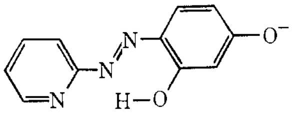
(8) The rate constants for the reactions of 1,10-phenanthroline and 1,10-phenanthroline-4,7-disulfonate with Ni^{2+} are 3.5×10^3 and $1.3 \times 10^3\ M^{-1}$ sec^{-1} at 25°, respectively: L. Smith and R. G. Wilkins, unpublished work.

(9) K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Amer. Chem. Soc.*, **88**, 4610 (1966).

(10) W. B. Makinen, A. F. Perlmutter, and J. E. Stuehr, *ibid.*, **91**, 4083 (1969).

(11) R. F. Pasternack, K. Kustin, L. A. Hughes, and E. Gibbs, *ibid.*, **91**, 4401 (1969).

Recently Funahashi and Tanaka[12] have measured the rate constant for reaction of nickel(II) with a ligand showing similar features to the oxines, namely, 4-(2-pyridylazo)resorcinol (IV). The value, 1.7 × 10^3 M^{-1} $\sec^{-1}$ at 25°, is interestingly close to that of II.



IV

Complex Dissociation.—A few experiments on the dissociation of the mono nickel chelate with 8-hydroxyquinoline gave interesting results. The first-order constant for dissociation (Table I) increased from pH 5 to 3 and was then independent of pH 3–1. More significantly, however, the reaction in the lower pH range was attended by a *small increase* in optical density at 360 mμ, whereas the spectra of NiQ^+ (ϵ 2.2 × 10^3) and H_2Q^+ (ϵ 1.6 × 10^3) would indicate that a *large decrease* should be observed. This indicated that NiQ^+ generated in neutral solution (pH 5–6) was rapidly (within milliseconds) converted into another species at pH 3 and lower and that the dissociation of this new species was pH invariant (7). We speculate that this

$$NiQ^+ + H^+ \underset{K\approx 3}{\overset{\text{rapid}}{\rightleftharpoons}} Ni(HQ)^{2+} \xrightleftharpoons{(+H^+)\ k\ =\ 1.6\ \sec^{-1}} Ni^{2+} + H_2Q^+ \tag{7}$$

species is $Ni(HQ)^{2+}$ in which a proton is attached to the oxygen, either maintaining a chelate structure or rupturing the nickel–oxygen bond to leave a unidentate ligand. The latter viewpoint tends to be supported by the relatively large value for the rate constant (1.6 $\sec^{-1}$ at 25°), which can be associated with the breakage of a unidentate rather than a bidentate ligand.[1] We attempted to obtain the spectra of the protonated species by lowering the pH and raising the nickel concentration of a solution containing 8-hydroxyquinoline. The absorption of the broad peak was markedly reduced as the pH of a solution containing 0.1 M Ni^{2+}–10^{-4} M $(Q)_{\text{total}}$ was lowered from 5.0 to 3.0, at which pH $\epsilon_{360\ m\mu}$ was ≃1.3 × 10^3 and below which substantial dissociation of the whole ligand occurred. Plunging the solution at pH 3 into a buffer at pH 6 on the flow machine gave little indication of a complex formation reaction. This confirms that the solutions at pH 3 have the oxine coordinated (as HQ) and that only a very rapid unobservable loss of a proton from $Ni(HQ)^{2+}$ occurs in changing the pH from 3 to 6.

Acknowledgment.—This work was supported by National Science Foundation Grant GP-8099. Dr. Johnson (Whitworth College, Spokane, Wash.) received a grant from the National Science Foundation Research Participation for College Teachers Program. We are grateful for these aids.

---

[12] S. Funahashi and M. Tanaka, *Inorg. Chem.*, **8**, 2159 (1969).

CONTRIBUTION FROM THE INSTITUTE OF PHYSICAL CHEMISTRY,
UNIVERSITY OF PERUGIA, PERUGIA 06100, ITALY

Photoionization Study of Tetramethylsilicon

BY G. DISTEFANO

Received January 20, 1970

Several mass spectrometric studies by electron impact[1-11] have been reported on tetramethylsilicon and/or related compounds. The agreement among the electron impact mass spectra[1-4] is satisfactory. However, discrepancies exist for the threshold[2,3,5,7] of the $(CH_3)_3Si^+$ ion and especially among the results regarding the bond dissociation energy $D_1[(CH_3)_3Si\text{–}CH_3]$ (ranging between 59[5] and 85[3] kcal mol^{-1}) and the ionization potential of the $(CH_3)_3Si$ radical (ranging between 6.94[3] and 7.97[5] eV). To our knowledge there are no published photoionization data for this molecule. For these reasons new data have been obtained by photon impact mass spectrometry on tetramethylsilicon.

The relative intensities of the positive ions in the photoionization mass spectrum at 21.22 eV (584 Å) are as follows: $(CH_3)_4Si^+$, 2.9; $(CH_3)_3Si^+$, 100.0; $HSi(CH_3)_2^+$, 1.6; $H_2SiCH_3^+$, 13.4; $(CH_3)_2Si^+$, $CH_2SiCH_3^+$, $HSiCH_3^+$, CH_3Si^+, H_3Si^+, HSi^+, Si^+, 0.4–0.7. They are in qualitative agreement with those of the electron impact mass spectra previously reported[1-4] considering the different nature and energy of the ionizing beam. A maximum number of three atoms and/or methyl groups attached to the silicon is (as by electron impact) the general rule: they account for 96% of the ion current in the present experimental conditions.

Photoionization efficiency curves from onset to 600 Å have been obtained for the three most abundant ions in the spectrum ($(CH_3)_4Si^+$, $(CH_3)_3Si^+$, and $H_2SiCH_3^+$). These curves are shown in Figure 1. All the three curves show a low-intensity tail near the threshold. As an example of this behavior, the threshold region of the ion-yield curve for $H_2SiCH_3^+$ is reported at high sensitivity in Figure 2. These tails begin at 0.17, 0.19, and 0.21 eV for $(CH_3)_4Si^+$, $(CH_3)_3Si^+$, and $H_2SiCH_3^+$, respectively, before the ion-yield curves start to rise quickly. The tail is probably due to hot bands, that is to the formation of ions from thermally excited mole-

---

(1) V. H. Dibeler, *J. Res. Nat. Bur. Stand.*, **49**, 235 (1952).

(2) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **65**, 2186 (1961).

(3) G. G. Hess, F. W. Lampe, and L. H. Sommer, *J. Amer. Chem. Soc.*, **87**, 5327 (1965).

(4) G. P. van der Kelen, O. Volders, H. van Onckelen, and Z. Eeckhaut, *Z. Anorg. Allg. Chem.*, **338**, 106 (1965).

(5) J. A. Connor, G. Finney, F. J. Leigh, R. N. Haszeldine, P. J. Robinson, R. D. Sedwick, and R. F. Simmons, *Chem. Commun.*, 178 (1966).

(6) I. M. T. Davidson and I. L. Stephenson, *ibid.*, 746 (1966).

(7) S. J. Band, I. M. T. Davidson, C. A. Lambert, and I. L. Stephenson, *ibid.*, 723 (1967).

(8) I. M. T. Davidson and I. L. Stephenson, *J. Chem. Soc. A*, 282 (1968).

(9) S. J. Band, I. M. T. Davidson, and C. A. Lambert, *ibid.*, *A*, 2068 (1968).

(10) M. F. Lappert, J. Simpson, and T. R. Spalding, *J. Organometal. Chem.*, **17**, 1 (1969).

(11) W. C. Steele, L. D. Nichols, and G. A. Stone, *J. Amer. Chem. Soc.*, **84**, 4441 (1962).