2710 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2710—2712 (1971) [Vol. 44, No. 10

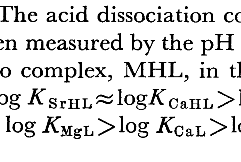
The Chelating Behavior of 1-(2-Phosphonophenylazo)-2-hydroxynaphthalene-3,6-disulfonic Acid with Alkaline Earth Metals

Kenyu Kina, Haruo Miyata, and Kyoji Tôei
Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama

(Received March 19, 1971)

A new chelating agent, *o*-phosphonophenylazo-2-hydroxynaphthalene-3,6-disulfonic acid, has been synthesized. The acid dissociation constants of this ligand and the chelate stability constants with alkaline earth metals have been measured by the pH titration method at an ionic strengh of 0.10 and at 25.0±0.1°C. This ligand forms the acido complex, MHL, in the pH 5—7 region. The stability constants of the acido complex decrease in this order: $\log K_{SrHL} \approx \log K_{CaHL} > \log K_{MgHL}$; whereas the decreasing order of the stability constants, $\log K_{ML}$, is as follows: $\log K_{MgL} > \log K_{CaL} > \log K_{SrL}$.

As a link in the chain of the studies of the *o*-substituted phenylazo compound, the present authors have attempted to introduce the phosphonate group into the *o*-position of the azo compound. For this purpose, it is necessary to prepare *o*-aminophenylphosphonic acid, which is produced by the reduction of *o*-nitrophenylphosphonic acid; however, it seemed difficult to introduce the phosphonate group into the *ortho* position of the nitro group. Recently Cadogan *et al.* presented a new method of synthesizing diethyl *o*-nitrophenylphosphonate;[1] the difficulty of the substitution is overcome by this synthetic manner, that is, *o*-nitrophenylphosphonic acid is obtained by the hydrolysis of diethyl *o*-nitrophenylphosphonate. The structural formula for *o*-phosphonophenylazo-2-hydroxynaphthalene-3,6-disulfonic acid disodium salt is:



The present paper will describe a method of synthesizing *o*-phosphonophenylazo-2-hydroxylnaphthalene-3,6-disulfonic acid disodium salt and the chelating behavior of this compound.

Experimental

Synthesis of o-*Phosphonophenylazo-2-hydroxynaphthalene-3,6-disulfonic Acid Disodium Salt.* The reagent was obtained by the coupling reaction of diazotized *o*-aminophenylphosphonic acid with the R acid [2-hydroxynaphthalene-3,6-disulfonic acid]. This reaction mixture was allowed to stand overnight, and then it was added, drop by drop to well-chilled concentrated hydrochloric acid. A reddish precipitate was obtained by this procedure. The azo compound thus obtained was recrystallized several times from an acidic solution by the salting-out method. The reagent, which is obtained as disodium salt, consists of fine, reddish needles. *o*-Aminophenylphosphonic acid was synthesized by using *o*-dinitrobenzene as the starting material; the procedure has been described in detail in a previous paper.[2]

Reagent Solutions. The stock solution of the ligand was prepared by dissolving it in distilled water; the concentration, 1.5×10^{-3} M, was standardized by potentiometric titration with standard 0.10 N potassium hydroxide before use. A carbonate-free potassium hydroxide solution was prepared by the method of ion exchange and was standardized titrimetrically by potassium hydrogen phthalate. The concentrations of the Mg(II) and Ca(II) solutions were determined by chelatometric titration, while the concentration of the Sr(II) solution was determined by the usual gravimetric method.

pH Titration Method. All the measurements were carried out by the use of a micro-titration vessel, the volume of which was 5 m*l*. The temperature was kept at 25.0±0.1°C during the titration by the circulation of water through the jacketed titration vessel; the ionic strength of the solution was adjusted to 0.10 with potassium nitrate. Alkali was added from a calibrated 0.50-m*l* micrometer syringe to the solution in an atmosphere of carbon dioxide-free nitrogen. Potentiometric measurements were performed by using an HRL-Model P pH meter (made by Horiba instruments, Inc., Kyoto), with a combined glass electrode (Metrohm, EA-125 U-type, Herisaw, Switzerland). Further details of the titration have been presented in the previous paper.[2]

Results and Discussion

Titration Curves. The titration curves are illustrated in Fig. 1 for the ligand in the presence and in the absence of alkaline-earth metal ions. The acid-dissociation constants of this ligand can be calculated by the use of the titration curve in the absence of alkaline earth metal ions. As can be seen from Fig. 1, the "ligand only" titration curve shows well-defined inflections at $a=1$ and at $a=2$, where a is equal to the number of moles of bases added per mole of the ligand. Since each of the dissociation steps is separated by such well-defined inflection points, the calculation of the acid dissociation constants can be performed separately, as in the case of monoprotic acid. The calculation formula is as follows:

$$(T_L - T_{OH} - [H] + [OH])/(T_{OH} + [H] - [OH])[H] = 1/K_a$$

where T_L represents the total concentration of the ligand species and where T_{OH} represents the total concentration of the base added to the system. The acid dissociation constants of the reagent are defined as follows:

$$K_{a1} = [H][H_2L]/[H_3L], \quad K_{a2} = [H][HL]/[H_2L],$$
$$K_{a3} = [H][L]/[HL],$$

---

[1] J. I. G. Cadogan, D. J. Sears, and D. M. Smith, *Chem. Commun.*, **1966**, 491.

[2] K. Kina, H. Miyata, and K. Tôei, This Bulletin, **44**, 1855 (1971).

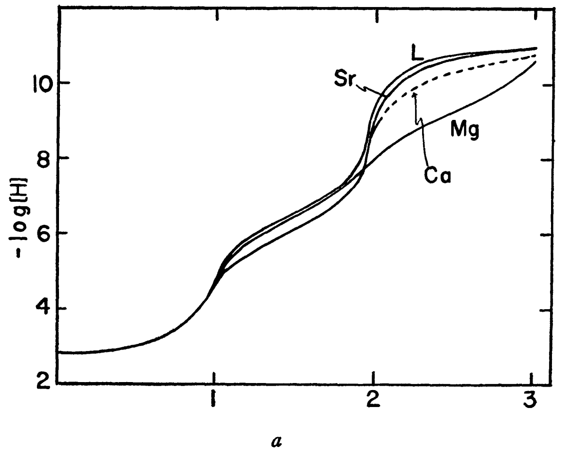


Fig. 1. Titration of 1-(2-phosphonophenylazo)-2-hydroxynaphthalene-3,6-disulfonic acid disodium salt and its chelate system at 25°C, $\mu=0.10$; L, Ligand only, [Ligand]$=1.555\times10^{-3}$ M, [Mg]$=2.216\times10^{-3}$ M, [Ca]$=2.256\times10^{-3}$ M, [Sr]$=2.078\times10^{-3}$ M,
a=moles of base added per mole of ligand

where the ionic charge is omitted for the sake of convenience. The first and the second steps of the titration curve correspond to the two phosphonic protons, while the third step corresponds to the naphtholic proton. Therefore, the pK_{a1} and the pK_{a2} values were assigned to the phosphonic group; the pK_{a3} value was assigned to the naphtholic hydroxyl group.

The titration curves in the presence of alkaline earth metal ions show a clear pH depression caused by the chelation; the chelate stability constants can be obtained from these curves by the algebraic method. No precipitates, except for the barium chelate system, were found throughout the titration. The calcium and the strontium chelate systems present the same degree of pH depression in the region of $a=1$—2, while this titration curve splits into two lines at $a=2$; the dotted and the solid lines indicate the titrations of the calcium and strontium chelate systems respectively. These chelate systems give well-defined inflections at $a=1$ and at $a=2$ similar to that of the ligand only. This indicates that different reactions occur in the two pH regions separated by such well-defined inflections. In the region of $a=1$—2, the metal-ligand equilibria may be expressed by:

$$\mathrm{M} + \mathrm{HL} \rightleftarrows \mathrm{MHL},\ K_{\mathrm{MHL}} = [\mathrm{MHL}]/[\mathrm{M}][\mathrm{HL}].$$

That is to say, the acido complex exists in this region; after $a=2$, the reaction may be expressed as:

$$\mathrm{MHL} \rightleftarrows \mathrm{H} + \mathrm{ML},\ K_a' = [\mathrm{H}][\mathrm{ML}]/[\mathrm{MHL}],$$

where the dissociation of the complex is observed. The order of the stability constant can be judged roughly by the extent of the pH depression. It is obvious that calcium and strontium ions form more stable acido complexes than does the magnesium ion; their values, $\log K_{\mathrm{SrHL}}$ and $\log K_{\mathrm{CaHL}}$, may be of much the same magnitude. The decreasing order of the stability constant, K_{ML}, with respect to the metal ions may be as follows: Mg(II)>Ca(II)>Sr(II). The titration curves of the calcium and strontium chelate systems show a clear inflection at $a=2$ similar to that of the ligand only. From this, it can be expected that the pK_a' values of the acido complex will differ little from the pK_{a3} value of the ligand.

Stability Constants. The chelating reaction is separated into two steps; the calculation of the equilibrium constants, except for the case of the magnesium chelate system, can be treated separately as two steps, that is, the acido complex formation and the acid dissociation of this complex. The stability constant of the barium chelate system was not obtained because of the precipitation. At the formation step of the acido complex in the region of $a=1$—2, the calculation formula of the acido complex stability constant is:

$$K_{\mathrm{MHL}} = (T_{\mathrm{L}}-F)/[\mathrm{HL}](F+T_{\mathrm{M}}-T_{\mathrm{L}}),$$

where $[\mathrm{HL}] = K_{a3}/[\mathrm{H}](T_{\mathrm{L}} - T_{\mathrm{OH}} - [\mathrm{H}] + [\mathrm{OH}])$,

$$F = (1+K_{a2}/[\mathrm{H}])(T_{\mathrm{L}}-T_{\mathrm{OH}}-[\mathrm{H}]+[\mathrm{OH}]).$$

The acid dissociation constant of the acido complex was then obtained by the following equation:

$$1/K_a' = (T_{\mathrm{MHL}}-A)/[\mathrm{H}]A,\quad \text{here } A=T_{\mathrm{OH}}+[\mathrm{H}]-[\mathrm{OH}],$$

where T_{MHL} represents the total concentration of the acido complex species, which is almost equal to T_{L} when there is an excess of the metal ion. In addition, the following simple relationship holds among the equilibrium constants:

$$K_{\mathrm{MHL}}\cdot K_a'/K_{a3} = K_{\mathrm{ML}}.$$

Therefore, $\log K_{\mathrm{MHL}} - pK_a' + pK_{a3} = \log K_{\mathrm{ML}}$

The stability constant, $\log K_{\mathrm{ML}}$, of the calcium or strontium chelate system was obtained by the use of the above relationship. The results of these calculations are shown in Table 1. When we suppose the structural formula of the acido complex, first we consider that the metal ion makes a coordination bond with the phosphonate group alone; however, neither phenylphosphonic acid nor the *p*-isomer of the ligand showed a remarkable pH depression such as did the ligand in the region of $a=1$—2. As can be seen from this result, the metal ions form a coordination bond not only with the phosphonate group, but also with the azo group. The naphtholic hydroxyl group of the azo compound is known to make a hydrogen bond with the azo link;[3] the structural formula for the acido complex, therefore, may be represented by Structure I. The magnesium ion forms an unstable chelate, MgHL, therefore, the calculation of the K_{ML} can be adequately approximated by the following equation:

$$K_{\mathrm{ML}} = (T_{\mathrm{L}}-F)/[\mathrm{L}](F+T_{\mathrm{M}}-T_{\mathrm{L}})$$

where $[\mathrm{L}] = (2T_{\mathrm{L}}-T_{\mathrm{OH}}-[\mathrm{H}]+[\mathrm{OH}])/([\mathrm{H}]/K_{a3} + 2[\mathrm{H}]^2/K_{a3}K_{a2})$

$$F = [\mathrm{L}](1+[\mathrm{H}]/K_{a3}+[\mathrm{H}]^2/K_{a3}K_{a2})$$

In this manner, the stability constant of the magnesium chelate, $\log K_{\mathrm{MgL}}$, was obtained; it is also shown in Table 1. As can be seen from the titration curves and Table 1, the acido complex of the magnesium ion has a smaller pK_a' value than the other pK_a' values; it is considered that the acido complex of the magnesium ion, MgHL, has a tendency to become the stable

---

[3] S. Nakashima, H. Miyata, and K. Tôei, This Bulletin, **41**, 2632 (1968).

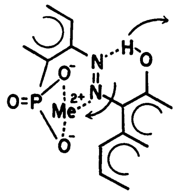
Table 1. Acid dissociation constants of *o*-phosphonophenylazo-2-hydroxynaphthalene-3,6-disulfonic acid disodium salt and stability constants of its chelate (t=25.0±0.1°C, μ=0.10; KNO_3)

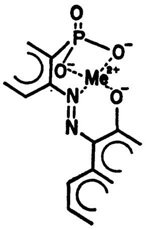
Ligand	pK_{a1} ***	pK_{a2} 6.49	pK_{a3} 11.10
	Mg	Ca	Sr
$\log K_{ML}$	4.83	3.80	3.06
$\log K_{MHL}$	—	2.98	2.97
pK_a'	—	10.28	11.01

where $K_{ML}=[ML]/[M][L]$, $K_{MHL}=[MHL]/[M][HL]$, $K_a'=[H][ML]/[MHL]$

*** too strong to be measured.

chelate form, MgL, through its own acid dissociation. In other words, since the electron-withdrawing tendency of the magnesium ion is larger than that of the calcium or strontium ion, the basicity of the naphtholic hydroxyl group was lowered by the magnesium ion which was coordinated to the azo link. This relation may be illustrated by Structure I.





Me^{2+}=Metal Ion

Structure I. MHL

Structure II. ML

The decreasing order of the pK_a' values with respect to the metal ions is as follows: Sr(II)>Ca(II)>Mg(II); that is, the electron-withdrawing tendency of the metal ions increases in this order: Sr(II)<Ca(II)<Mg(II). It seems reasonable that the metal ion forms a coordination bond with the dissociated naphtholic hydroxyl group after the dissociation of the acido complex (Structure II).