BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2815—2818 (1967)

A Spectrophotometric Study of the Thorium Complex of 2-(1, 8-Dihydroxy-3, 6-disulfo-2-naphthylazo)-mandelic Acid

Haruo MIYATA

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama

(Received June 9, 1967)

2-(1, 8-Dihydroxy-3, 6-disulfo-2-naphthylazo)-mandelic acid forms a stable violet complex with thorium ion at 1 : 1 molar ratio in an acidic solution. The acid dissociation constants of the reagent and the apparent stability constant of its thorium complex were estimated spectrophotometrically at 25°C and $\mu=0.1$. It was found that the thorium complex formed by the present reagent was more stable than those of the other phenyl-azo-chromotropic acid derivatives reported in the preceding papers.

The behavior of various functional groups in the complex formation with thorium has been reported using the derivatives of phenyl-azo-chromotropic acid. As has been described in a previous paper,[1] it was found that the derivative having hydroxyacetic acid group in the ortho position

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[1] H. Miyata, This Bulletin, **40**, 1875 (1967).

formed a very stable complex with thorium ion in an acidic solution. The –CH(OH)COOH group is therefore active with respect to thorium. The preparation of the reagent having –CH(OH)-COOH group, and the spectral properties of the reagent and its thorium complex were described in a previous short communication.²⁾ The application of the reagent as an indicator in the chelatometry for thorium was also reported in the previous paper.³⁾

This paper will report the results of more detailed studies of the acid dissociation of the reagnet, and of the stability of its thorium complex. The results indicate that the present reagent forms the most stable complex with thorium among the derivatives used in this and previous studies.

Experimental

Reagents. *2-(1,8-Dihydroxy-3,6-disulfo-2-naphthylazo)-mandelic Acid.* The acetylation of *o*-nitrotoluene with acetic anhydride afforded *o*-nitrobenzaldiacetate which by hydrolysis gave *o*-nitrobenzaldehyde.⁴⁾ The action of potassium cyanide upon *o*-nitrobenzaldehyde afforded the nitril derivative,⁵⁾ which was converted into *o*-nitromandelic acid⁵⁾ by hydrolysis with hydrochloric acid. *o*-Nitromandelic acid was converted into *o*-aminomandelic acid⁶⁾ by catalytic hydrogenation in the presence of palladium-charcoal catalyst.

The reagent, 2-(1, 8-dihydroxy-3, 6-disulfo-2-naphthylazo)-mandelic acid, was obtained from the diazotized *o*-aminomandelic acid which was coupled with chromotropic acid. To purify the reagent, the crude product which was obtained from coupling solution by adding concentrated hydrochloric acid, was dissolved in water and passed through a column filled with Amberlite IR-120 cation exchange resin (H-form) to remove sodium ion. The eluent was added drop by drop in concentrated hydrochloric acid saturated with hydrogen chloride gas. The pure azo compound was obtained in the acid form after the purification.

Thorium Perchlorate Solution. This solution was prepared by dissolving a purified thorium hydroxide⁷⁾ in perchloric acid.

All the other reagents were of the guaranteed reagent grade.

Apparatus and Procedure. The apparatus and the procedure have been mentioned elsewhere,¹⁾ and temperature and ionic strength of a solution are maintained, respectively, at 25°C and 0.1 with a sodium perchlorate solution.

Calculations

Acid Dissociation Constants of the Reagent. The reagent (Abbr. H_5R) is dissociated in water as follows:

$$H_3R^{2-} \overset{K_1}{\rightleftharpoons} H_2R^{3-} + H^+,$$

and

$$H_2R^{3-} \overset{K_2}{\rightleftharpoons} HR^{4-} + H^+$$

The constants of the above dissociation, K_1 and K_2, are:

$$K_1 = [H][H_2R]/[H_3R] \qquad (1)$$

and $$K_2 = [H][HR]/[H_2R] \qquad (2)$$

respectively, the ionic charge being neglected for the sake of convenience. If the two dissociation steps are separated widely enough, these dissociation equilibria can be treated independently. Therefore

$$\begin{aligned} pK_1 &= pH - \log\{[H_2R]/[H_3R]\} \\ &= pH - \log\{(E_{H_3R} - E)/(E - E_{H_2R})\} \qquad (3) \end{aligned}$$

where E_{H_3R}, E_{H_2R} and E represent, respectively, the absorbances of H_3R, H_2R and their mixture at a constant wavelength. And also

$$\begin{aligned} pK_2 &= pH - \log\{[HR]/[H_2R]\} \\ &= pH - \log\{(E'_{H_2R} - E')/(E' - E'_{HR})\} \qquad (4) \end{aligned}$$

where E'_{H_2R}, E'_{HR} and E' represent, respectively, the absorbances of H_2R, HR and their mixture at another wavelength.

Apparent Stability Constants of the Thorium Complex. Experimental results given in later sections indicate that the thorium complex of the reagent should be formulated as ThHR. The apparent stability constant, K', of the thorium complex may be obtained by assuming the formation of the complex in accordance with the following equations:

$$Th^{4+} + H_3R^{2-} \rightleftharpoons ThHR + 2H^+ \qquad (5)$$

and $$Th^{4+} + H_2R^{3-} \rightleftharpoons ThHR + H^+ \qquad (6)$$

$$K' = [ThHR]/[Th][H_3R + H_2R] \qquad (7)$$

The total concentrations of the reagent and thorium are given by:

$$C_R = [H_3R] + [H_2R] + [HR] + [ThHR] \qquad (8)$$

$$C_{Th} = [Th] + [ThHR] \qquad (9)$$

respectively. Under the experimental conditions studied, at pH values below 4, [HR] can be disregarded, judging from the pK_2 value.

The absorbance of the complex solution, E is given by Eq. (10). The thorium ion gives no absorption in the visible region, and $\varepsilon_{Th}[Th]$ can be neglected.

$$E = \varepsilon_{H_3R}[H_3R] + \varepsilon_{H_2R}[H_2R] + \varepsilon_{ThHR}[ThHR] \qquad (10)$$

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2) K. Tôei, H. Miyata and T. Mitsumata, This Bulletin **38**, 1050 (1965).

3) Y. Hosokawa and K. Tôei, *Japan Analyst,* **14**, 161 (1965).

4) S. M. Tsang, E. H. Wood and J. R. Johnson, "Organic Syntheses," Coll. Vol. 3, p. 641 (1955).

5) G. Heller, *Ber.,* **37**, 948 (1904).

6) E. J. Alford and K. Schofield, *J. Chem. Soc.,* **1952**, 2106.

7) R. L. Swan, *J. Chem. Soc.,* **125**, 781 (1924).

where ε_{H_3R} and ε_{H_2R} are the molar absorption coefficients of H_3R and H_2R, and ε_{ThHR} is that of the thorium complex, ThHR. Its value was calculated from the absorbance of the solution in which an excess amount of thorium was added to the reagent and the complete formation of the complex from the reagent could be assumed.

The apparent stability constant, K', was estimated from the following equation by substituting Eqs. (1) and (8)—(10) into Eq. (7):

$$K' = (C_R - A)/(C_{Th} - (C_R - A)\cdot A) \qquad (11)$$

where:

$$A = \frac{(1 + K_1/[H])(E - \varepsilon_{ThHR}\cdot C_R)}{\{\varepsilon_{H_3R} + \varepsilon_{H_2R}(K_1/[H]) - \varepsilon_{ThHR}(1+K_1/[H])\}}$$

Results and Discussion

Absorption Spectra. The absorption curves of the reagent and the thorium complex are shown in Fig. 1. The curve changes with variation of pH, but in each of the three limited pH ranges (below 1, from 5 to 7, and above 12), the curve remains unchanged (curves 1, 2, and 6).

Curve 1, with peaks at *ca.* 510 and 530 mμ and observed in the pH range below 1, corresponds to the species H_3R^{2-}. In this pH range, it seems that the dissociation of the carboxyl group does not occur.

Curve 2, in the pH values between 5 and 7, corresponds to the species H_2R^{3-}.

The change in the absorption spectra between pH values 1 and 5 seems to correspond to the dissociation of the carboxyl group. There are four isosbestic points at 360, 370, 406, and 510 mμ.

At pH values above 12, the reagent gives another constant curve, curve 6, corresponding to the species HR^{4-}.

Between the curves 2 and 6, three isosbestic points exist at 395, 462, and 557 mμ. The change in the absorption spectra between pH values 7 and 12 seems to correspond to the dissociation of one of the naphtholic hydroxyl groups of chromotropic acid.

On the addition of thorium to the reagent solution, the color of the solution changes from pink to violet, and the spectrum has a maximum peak at 575 mμ.

Acid Dissociation Constant. The acid dissociation constant reported here for the reagent were determined at 25°C, and at an ionic strength of 0.1 by sodium perchlorate. The values of pK_1 and pK_2 were measured at 568 and 510 mμ, respectively, and estimated from Eqs. (1) and (2) to be 3.10 and 9.55 respectively. The third dissociation constant, K_3, corresponding to the other naphtholic hydroxyl group, could not be obtained, because the dissociation occurs at pH above 14.

The Formation of the Thorium Complex. The color of the complex reached its maximum in a few minutes after mixing; then, the absorbance remained almost constant for at least 90 min.

The Composition of the Thorium Complex. Figure 2 shows the results obtained by the continuous variation method; the maximum absorbance of the complex was obtained at a molar ratio of 1 : 1. Figure 3 shows the results obtained by the mole-ratio method, and the results indicate again the formation of a 1 : 1 complex. These three experiments confirm that the molar ratio of thorium to the reagent in the complex formed is 1 : 1.

The Apparent Stability Constant of the Thorium Complex. The constant, log K', estimated from Eq. (11) is listed in Table 1. As shown in Fig. 4, the values of log K' are plotted

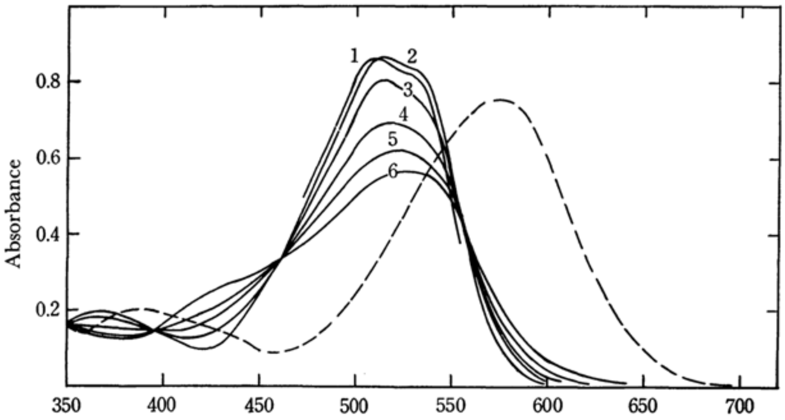

Fig. 1. Absorption spectra of the reagent, and its thorium complex (broken line). (1) 3.0×10^{-5} M reagent solution at pH below 1, (2) pH between 5 and 7, (3) pH 8.92, (4) pH 9.56, (5) pH 9.96 (6) pH above 12. Broken line: 3.0×10^{-5} M thorium + 3.0×10^{-5} M reagent, pH 3.08.

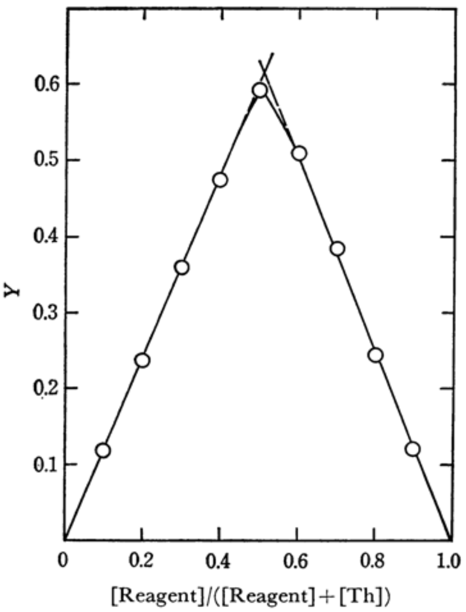

Fig. 2. Continuous-variation method.
at 590 mμ, pH 3.1
Thorium concn. + the reagent concn.= 5.0×10^{-5} M

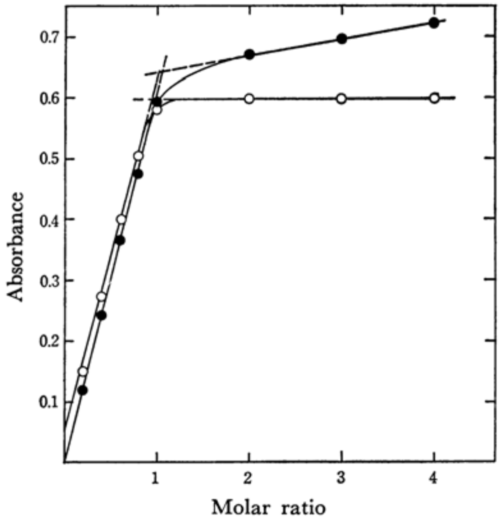

Fig. 3. Mole-ratio method.
at 590 mμ, pH=3.0
○ The reagent concn.=2.5×10^{-5} M, Thorium concn. varied.
● Thorium concn.=2.5×10^{-5} M, The reagent concn. varied.

Table 1. Apparent stability constant of the thorium complex 25°C, μ=0.1

pH	E	C_R $\times10^{-5}$ M	C_{Th} $\times10^{-5}$ M	log K'
1.07	0.193	2.5	2.5	4.04
1.45	0.328	2.5	2.5	4.77
2.00	0.509	2.5	2.5	5.91
2.69	0.585	2.5	2.5	7.18
2.78	0.590	2.5	2.5	7.38
2.89	0.592	2.5	2.5	7.47
3.16	0.599	2.5	2.5	7.90

$\varepsilon_{H_3R}=3.96\times10^3$, $\varepsilon_{H_2R}=5.13\times10^3$,
$\varepsilon_{ThHR}=2.44\times10^4$

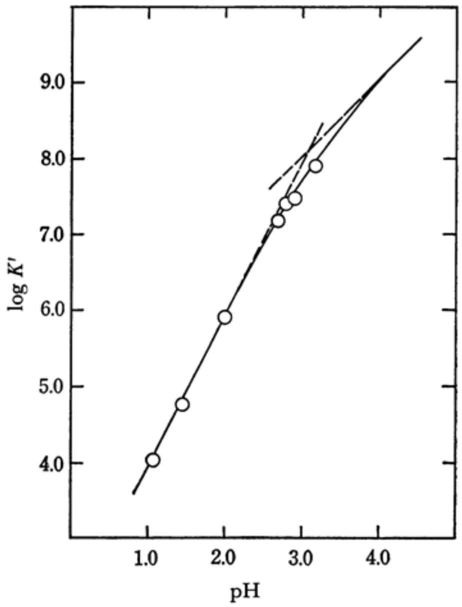

Fig. 4. Relationship between log K' and pH at 25°C, μ=0.1.

against the pH values. The slope of the curve is equal to 2 when pH $<\mathrm{p}K_1$, showing that in this pH range the complex is chiefly formed by the equilibrium (5). This situation is the same as in the case of the derivatives having $-COOH$[8] or $-OCH_2-COOH$[1] group, but the stability for the present complex higher than those for such derivatives. From this, it seems that the present reagent forms the most stable complex with thorium among the derivatives used in this and previous studies. At higher pH, the slope decreases, showing that the equilibrium (6) begins to take part in complex formation.

The author wishes to express his deep thanks to Dr. Kyoji Tôei for his guidance in the course of this study.

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[8] K. Tôei, H. Miyata and T. Harada, This Bulletin, **40**, 1141 (1967).