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Stability of Tropolone Chelates of the Bi- and Tervalent Metal Ions

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The reaction of tropolone with several bi- and tervalent metal ions has been studied spectrophotometrically. Their stability constants (k_1) have been found to be 7.4_0, 3.8_2, 3.0_6, 2.4_5, 7.4_6, 4.6_0, and 6.2_5 for Be(II), Mg(II), Ca(II), Sr(II), Y(III), Cd(II), and La(III) respectively, at 25 ± 0.1°C and at an ionic strength of 0.10. A plot of $\log k_1$ against e^2/r gave a straight line for all the non-polarizable metal ions except Be(II) and Mg(II). The $\log k_1$ values for all the polarizable metal ions are large. The correlation of $\log k_1$ with the second or the third ionization potentials for bi- and tervalent metal ions gave a fairly straight line.

Several metal chelates of troponoid have been studied by many investigators.[1-7] Bryant *et al.* made their studies in 50 per cent dioxane because of the insolubility of metal chelates of troponoid in water.[1-2] The stability constants of copper and zinc chelates with 4-isopropyltropolone have been determined by Dryssen by the solvent extraction technique.[3]

Oka *et al.* have studied the effect of substitution on the stability of iron(III) chelates using 3-, 4- and 5-substituted tropolones.[8-11]

In a previous paper, the present authors have reported the results of their investigations of the tropolone chelates of manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II).[12,13] In this paper their studies of the beryllium(II), magnesium(II), calcium(II), strontium(II), cadmium(II), yttrium(III), and lanthanum(III) chelates with tropolone will be described. In these studies the stability constants have been spectrophotometrically determined.

Experimental

Materials. The tropolone was purified by sublimation at 40°C under reduced pressure, 20 mmHg. All the metal salt solutions were prepared as perchlorate from pure oxides, chlorides or nitrates. The water used was double-distilled. For the adjustment of the ionic strength (0.10), sodium perchlorate was used.

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Measurements. For the measurement of absorbance, Hitachi Model EPU-2 and EPS-2 spectrophotometers were used. The pH of the solutions was measured with a Hitachi-Horiba Model M-5 pH meter.

Results and Discussion

Acid Dissociation Constant of Tropolone. Tropolone is amphoteric, and its absorption spectrum changes with variations in the pH of the solution. In the pH range from 1.5 to 3.4, the spectrum I in Fig. 1 was obtained; this is the absorption spectrum of tropolone itself. Above pH 9.6, tropolone dissociates completely and gives the spectrum II. In a strong acidic solution, in a 2N $HClO_4$ solution for example, the spectrum III was obtained, indicating the formation of the dihydroxytropylium ion (I).

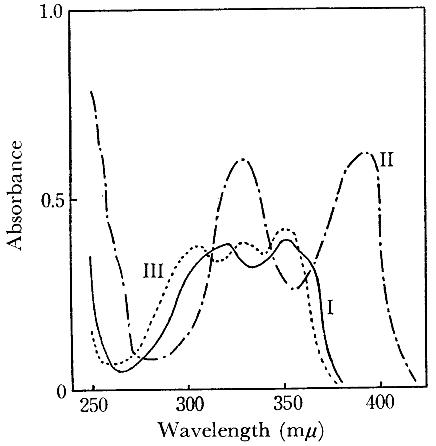
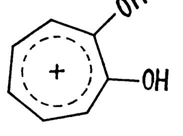


Fig. 1. Absorption spectra of tropolone.
tropolone: 6.06×10^{-5} mol/l
I; pH 1.5—3.4, II; pH >9.6, III; $HClO_4$ 3.2N

The acid dissociation constant, K_a, of tropolone was evaluated spectrophotometrically at an ionic strength of 0.10 and at 25.0±0.1°C.



(I) Dihydroxytropylium ion

When tropolone (HL) dissociates as follows:

$$HL = L^- + H^+$$

the following equation is derived, as has been reported previously:[14]

$$\frac{a}{(A-A')} = \frac{1}{(\varepsilon_2-\varepsilon_1)} + \frac{1}{(\varepsilon_2-\varepsilon_1)K_a}\cdot[H^+] \qquad (1)$$

where A is the total absorbance of the solution at various pH values, a is the analytical concentration of tropolone, ε_1 and ε_2 are the molar extinction coefficients of tropolone and the tropolonate ion respectively, and A' is equal to $\varepsilon_1 a$. Equation (1) shows that a plot of $a/(A-A')$ against $[H^+]$ may give a straight line. The acid dissociation constant, K_a, may, then, be calculated from the intercept and the slope of the straight line.

Keeping the analytical concentration of tropolone $1.21_2\times10^{-4}$ mol/l, and varying the pH-values of the solution in the range from 6.40 to 6.91, the total absorbances were measured, the ionic strength being adjusted to 0.10. The plots of $a/(A-A')$ against $[H^+]$ are shown in Fig. 2. Good straight lines were obtained at various wavelengths. The acid dissociation constant calculated is shown in Table 1.

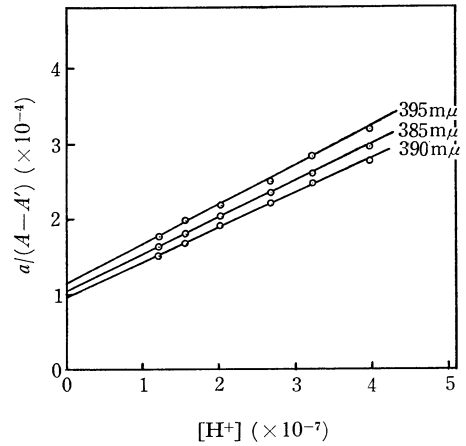


Fig. 2. Correlation of $a/(A-A')$ with $[H^+]$.
Tropolone: $1.21_2\times10^{-4}$ mol/l
25.0±0.1°C, ionic strength; 0.10, pH 6.40±6.91

TABLE 1. ACID DISSOCIATION CONSTANT OF TROPOLONE (K_a)
25.0±0.1°C, ionic strength: 0.10

Wavelength (mμ)	pK_a
385	6.68
390	6.68
395	6.68
mean	6.68

Stability Constants of Metal Chelates (1 : 1) with Tropolone. Each of the metal perchlorate solutions was added in excess into a tropolone solution, the ionic strength being kept at 0.10 with sodium perchlorate. The pH values of the solutions were varied in the range where the hydrolysis of metal ions does not occur in any appreciable extent. As an example, the absorption spectra of strontium(II)-tropolone system are shown in Fig. 3. At pH

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[14] a) Y. Oka and R. Tanaka, *Nippon Kagaku Zasshi*, **81**, 1846 (1960). b) H. A. Benesei and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

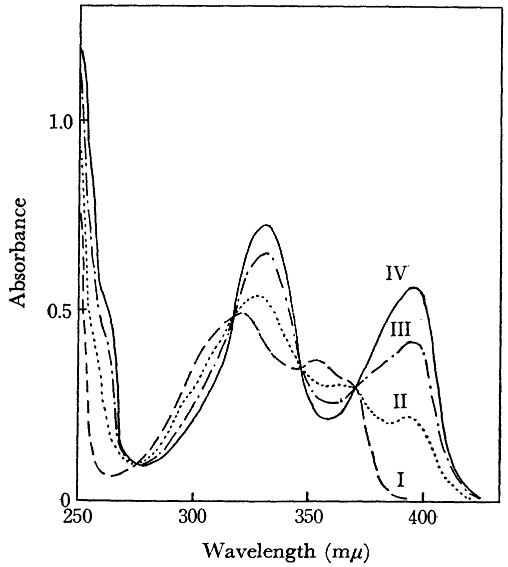

Fig. 3. Change of absorption spectrum of Sr(II)-tropolone system depends on pH in the presence of excess metal ion.
Tropolone: 6.01×10^{-5} mol/l
$Sr(ClO_4)_2$: 1.65×10^{-2} mol/l
I, pH 1.72; II, 5.93; III, pH 6.70; IV, pH 8.41

1.72 a spectrum I identical with that of tropolone was obtained. In this pH region, therefore, it may be considered that tropolone does not react with strontium. Above pH 5.9, the spectra II, III, and IV were obtained.

If, in the presence of an excess of the metal ion, tropolone (HL) reacts following Eq. (2):

$$M^{n+}+HL=ML^{(n-1)+}+H^+ \tag{2}$$

the equilibrium constant, K_1, can be expressed as follows:

$$K_1=\frac{[ML^{(n-1)+}][H^+]}{[M^{n+}][HL]} \tag{3}$$

Then,

$$K_1=\frac{x[H^+]}{(b-x)(a-x)} \tag{4}$$

where x is the equilibrium concentration of the metal chelate formed, and a and b are the total concentrations of the tropolone and the metal ion respectively. When the concentration of the metal ion is large enough, we may safely assume that $(b-x)\fallingdotseq b$.

Next, when measurements are made in the wavelength range where the molar extinction coefficient of the metal ion is zero, the total absorbance, A, is expressed as follows:

$$A=\varepsilon_1[HL]+\varepsilon_3[ML^{(n-1)+}]=\varepsilon_1(a-x)+\varepsilon_3x \tag{5}$$

where ε_1 and ε_3 are the molar extinction coefficients of the tropolone and the metal chelate respectively.

From Eqs. (4) and (5), Eq. (6) is derived:

$$\frac{a}{(A-A')}=\frac{1}{(\varepsilon_3-\varepsilon_1)}+\frac{1}{(\varepsilon_3-\varepsilon_1)k_1}\cdot\frac{[H^+]}{bK_a} \tag{6}$$

where k_1 is the stability constant.

In case when a chelate is formed in the pH range above 3.4, the dissociation of tropolone is not negligible. Then, Eq. (7) is derived:

$$\frac{a}{A}=\frac{1}{\varepsilon_3}+\frac{1}{\varepsilon_3k_1b}\cdot\frac{(A-A')[H^+]+(A-A'')K_a}{AK_a} \tag{7}$$

where $A'=\varepsilon_1a$, $A''=\varepsilon_2a$, and ε_1 is the molar extinction coefficient of tropolone, and ε_2, that of the tropolonate ion. A plot of $a/(A-A')$ against $[H^+]/bK_a$ or of a/A against $\{(A-A')[H^+]+(A-A'')\cdot K_a\}/AK_a$ will give a straight line.

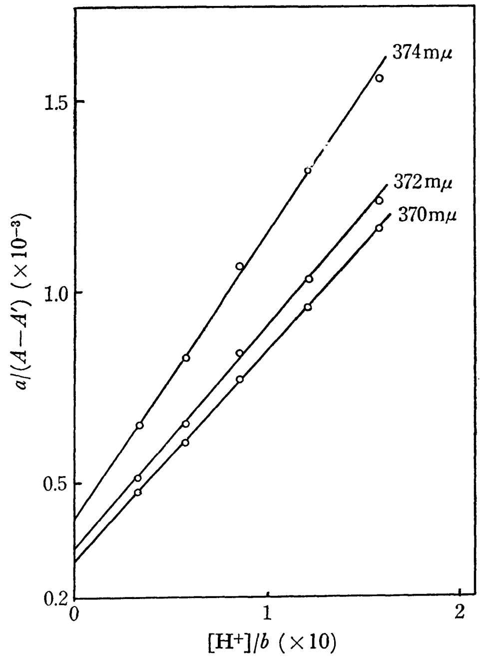

Fig. 4. Correlation of $a/(A-A')$ with $[H^+]/b$ (Be(II)-tropolone system).
Tropolone: $1.20_2\times10^{-4}$mol/l
$Be(ClO_4)_2$: $3.04_8\times10^{-3}$mol/l
25.0±0.1°C, ionic strength 0.10, pH 1.32—1.96

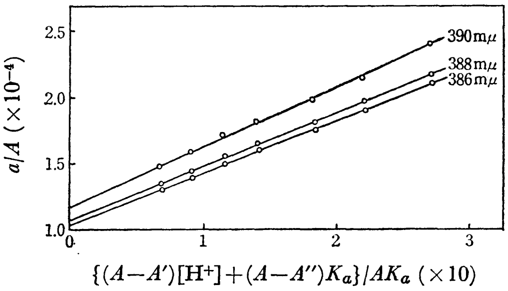

Fig. 5. Correlation of a/A with $\{(A-A')[H^+]+(A-A'')K_a\}/AK_a$ (Ca(II)-tropolone system).
Tropolone: $1.20_2\times10^{-4}$ mol/l
$Ca(ClO_4)_2$: $2.24_1\times10^{-2}$ mol/l
25.0±0.1°C, ionic strength 0.10, pH 5.22—5.82

For the beryllium(II)-, magnesium(II)-, yttrium(III)-, cadmium(II)- and lanthanum(III)-systems, Eq. (6) is used, while for the calcium(II)- and strontium(II)-systems, Eq. (7) is used. In all cases, good straight lines are obtained. Some sample results are shown in Figs. 4 and 5. Therefore, it can be safely concluded that 1 : 1 chelates are formed in such circumstances.

From the slopes and the intercepts of the straight lines, the stability constants are calculated to be as shown in Table 2.

TABLE 2. STABILITY CONSTANTS (k_1) OF METAL CHELATES (1 : 1) WITH TROPOLONE
25.0±0.1°C; ionic strength, 0.10

Metal ion	Wavelength (mμ)	log k_1
Be(II)	370	7.39
	372	7.40
	374	7.40
	average	$7.4_0 \pm 0.0_1$
Mg(II)	386	3.82
	388	3.82
	390	3.81
	average	$3.8_2 \pm 0.0_1$
Ca(II)	386	3.05
	388	3.06
	390	3.06
	average	$3.0_6 \pm 0.0_1$
Mn(II)	average	$4.6_0 \pm 0.0_1$ 13)
Co(II)	average	$5.5_9 \pm 0.0_1$ 13)
Ni(II)	average	$5.9_7 \pm 0.0_1$ 13)
Cu(II)	average	$8.3_5 \pm 0.0_0$ 12)
Zn(II)	average	$5.8_4 \pm 0.0_0$ 13)
Sr(II)	386	2.45
	388	2.45
	390	2.46
	average	$2.4_5 \pm 0.0_1$
Y(III)	376	7.46
	378	7.47
	380	7.47
	382	7.46
	384	7.46
	average	$7.4_6 \pm 0.0_1$
Cd(II)	380	4.60
	384	4.60
	388	4.61
	390	4.59
	average	$4.6_0 \pm 0.0_1$
La(III)	380	6.24
	382	6.25
	384	6.25
	386	6.25
	average	$6.2_5 \pm 0.0_0$

The stability constants increase from strontium to copper in the following order:

Sr(II)<Ca(II)<Mg(II)<Cd(II), Mn(II)<Co(II)<Zn(II)<Ni(II)<La(III)<Be(II)<Y(III)<Cu(II)

For chelates of the primarily "ionic" type, the strength of chelation should increase with an increase in the ionic charge of both metal ion and donor, and with a decrease in the ionic radius of the metal ion. Martell *et al.* have discussed the

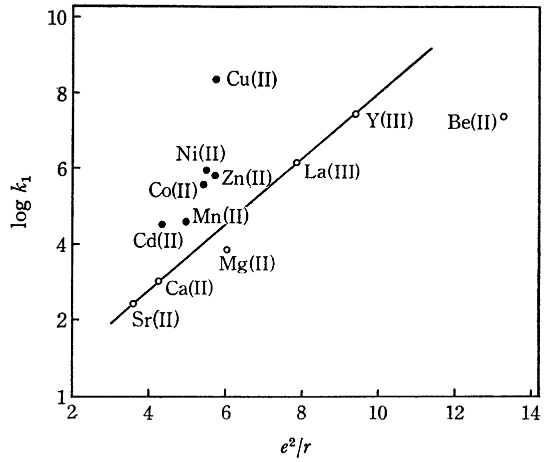

Fig. 6. Correlation of log k_1 with e^2/r for metal complexes (1 : 1) with tropolone.
○: non-polarizable metal ion
●: polarizable metal ion

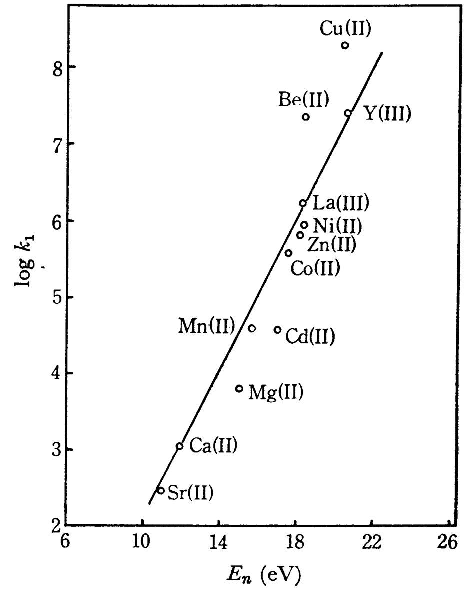

Fig. 7. Correlation of log k_1 with nth ionization potential for metal chelates (1 : 1) with tropolone.
E_n: nth ionization potential
n=2 for bivalent metal ion
n=3 for tervalent metal ion

stability constants with respect to charge(e)/radius(r) and e^2/r for a number of chelates which would be expected to form a primarily ionic bond.[15-17] They have found that e^2/r is superior. Where electrostatic interaction is predominant, $\log k_1$ may have a direct correlation with e^2/r. A similar treatment was attempted in the case of tropolone chelates; the results shown in Fig. 6 were obtained. A good straight line is observed for all the non-polarizable metal ions except beryllium(II) and magnesium(II). Their $\log k_1$ values are smaller than those expected. The ionic radii of these metal ions are small. It seems possible, therefore, that the steric effect hinders the stability. On the other hand, the values of $\log k_1$ for all polarizable metal ions are large. The polarization of the metal ion should be expected to enhance the stability of the chelates. Figure 7 shows the correlation of $\log k_1$ with the second and third ionization potentials for chelates of bi- and tervalent metals.[18] A fairly good correlation is observed.

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