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Spectrophotometric Studies on Organometallic Complexes Used in Analytical Chemistry On the Germanium Complex with 3-hydroxytropolone*

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Synopsis

An investigation was made by the authors to find soluble colored complexes of germanium. As a series of the study, examinations were made of several tropolones. And it was found that germanium formed water soluble complexes with them suitable for the determination of germanium.

The features of the absorption spectra of tropolones and its complexes with germanium are discussed. The composition and formation constant of 3-hydroxytropolone-germanium complex in aqueous solution were also evaluated. The composition of the complex was found to be 1:3.

I. Introduction

The authors examined(1) various organic compounds which would form soluble colored complexes with germanium. In the present paper, the reaction of the troplones with germanium were studied.

Informations on the metallic complexes of tropolones are rare. Bryant and co-workers investigated(2) potentiometrically the composition and stability of the complexes of bivalent metals, such as Cu (II), Be, Pb, Zn, Ni, Co (II), Mg and Ca. They also studied(3) them in the infra-red region spectrophotometrically. The authors studied the behavior of troplones in aqueous solution and several factors necessary for the formation of the germanium complexes. The composition and formation constant of 3-hydroxytropolone complex were evaluated from the absorption spectra in the visible and the ultra-violet regions.

Spectrophotometer used was that of EPB-U type made by Hitachi Works. All pH measurements were made with a Beckman glass electrode assembly.

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* The 78th report of the Research Institute of Mineral Dressing and Metallurgy.

(1) Y. Oka and S. Matsuo, J. Chem. Soc. Jap., **76** (1955), 610.

(2) B.E. Bryant, W.C. Fernelius and B.E. Douglas, Jour. Am. Chem. Soc., **75** (1953), 3784; B.E. Bryant and W.C. Fernelius, ibid., **76** (1954), 1696; 3783; 4864.

(3) B.E. Bryant, J.C. Pariaud and W.C. Fernelius, J. Org. Chem., **19** (1954), 1889.

II. Absorption spectra of troplones and their germanium complexes

The structure of tropolones, tropolone, 3-hydroxytropolone, 3-methoxytropolone and 3-aminotropolone used are illustrated in Fig. 1.

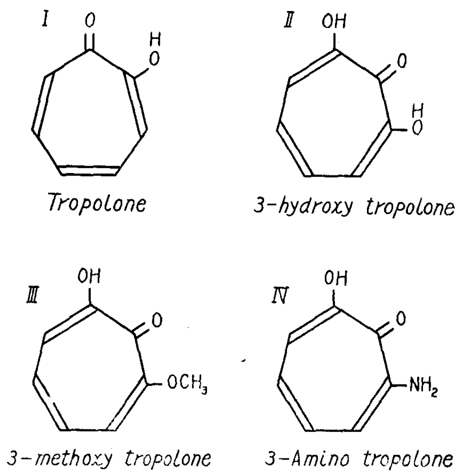


Fig. 1. Structual formulas of tropolones.

Their spectral absorbancy curves and those of germanium complexes are shown in Figs. 2 and 3. The concentrations of the tropolones were kept at 1×10^{-4}M/l and that of germanium at $1.3_5\ \gamma$/ml. As seen from curves I and III in Fig. 2 and curves I and III in Fig. 3, the spectrum of tropolone showed the absorption bands at the shortest wavelengths, and they showed a bathochromic shift when hydroxy, methoxy and amino groups were substituted for the hydrogen atom of the third position in tropolone. The shift of the bands was greatest when the substituent was $-NH_2$. In case hydroxy and methoxy were substituted, shifts in the absorption bands were smaller and almost identical with one another.

According to Matsen[4], ionization potentials of -OH and $-NH_2$ are given as 10.8 and 12.6 respectively. The shifts of the absorption bands caused by substitution may be explained as being due to the electron migration from the substituent radicals toward the seven-membered ring of the tropolone. Therefore, the lower the ionization potentials of the substituent radicals are, the greater the extent of the electron migration should be, and consequently, the greater the shift in the absorption band will be. The results mentioned above are in accord with this view[5].

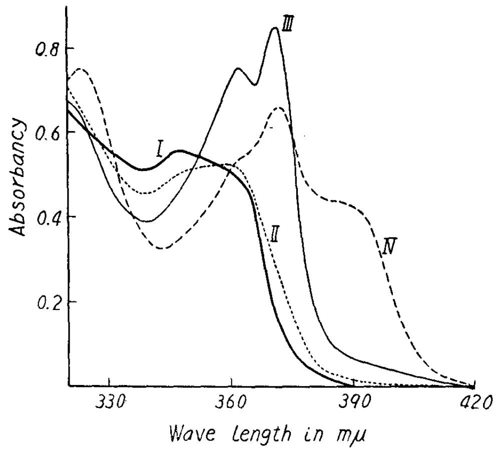


Fig. 2. Spectral absorbancy curves of tropolon, 3-hydroxytropolone and their germanium complexes.

I	tropolone : 1×10^{-4}M/l	pH 3.0
II	〃 : 1×10^{-4}M/l + Ge : $1.3_5\gamma$/ml	〃
III	3-hydroxytropolone : 1×10^{-4}M/l	pH 5.4
IV	〃 : 1×10^{-4}M/l + Ge : $1.3_5\gamma$/ml	〃

These tropolones react with germanium in neutral or weak acidic solution. As is seen in Figures 2 and 3, the shift in the absorption band was great when tropolone and 3-hydroxytropolone reacted with germanium, whereas the absorbancy

(4) F.A. Matsen, J. Am. Chem. Soc., **72** (1950), 5244.
(5) H. Baba and S. Nagakura, J. Chem. Soc. Jap., **72** (1951), 72, 74.

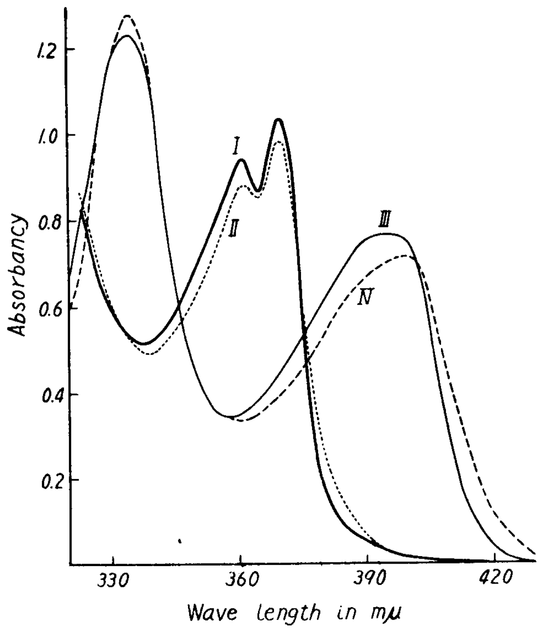


Fig. 3. Spectral absorbancy curves of 3-methoxytropolone, 3-aminotropolone and their germanium complexes.

I 3-methyoxytropolone :	1×10^{-4}M/l	pH 6.0
II ,,	: 1×10^{-4}M/l+Ge1.3$_5\gamma$/ml	,,
III 3-aminotropolone :	1×10^{-4}M/l	pH 6.5
IV ,,	: 1×10^{-4}M/l+Ge1.3$_5\gamma$/ml	,,

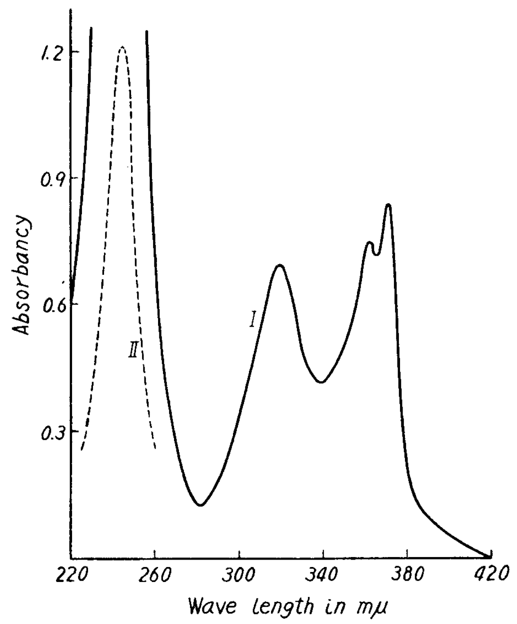


Fig. 4. Absorption spectrum of 3-hydroxytropolone.

I 3-hydroxytropolone :	1×10^{-4}M/l	pH : 5.5
II ,,	: $1/3\times10^{-4}$M/l	

of the complex was strong in 3-hydroxytropolone and 3-aminotropolone complex. Therefore, 3-hydroxytroxytropolone was most suitable for the determination of germanium. It was for this reason that examinations of the germanium complex of 3-hydroxytropolone was attempted in detail.

III. Absorption spectrum of 3-hydroxytropolone

The absorption spectrum of 3-hydroxytropolone in aqueous solution is shown in curve I in Fig. 4. The solution was adjusted to pH 5.5. The absorption maxima were found at 245 mμ, 320 mμ, 362 mμ and 371 mμ, the first being very strong in intensity. Of these, the bands at 245 mμ and at 320 mμ are characteristic of tropolone nucleus and are regarded to be related to the π-electrons extending along the entire system of conjugated seven-membered ring consisting of three C=C and one C=O. An absorption band at 320 mμ may be considered to be similar in nature to the band found at 306 mμ with octatrienal, which is explained by Mc Murry(6). It may be inferred from the fact that the bands showed a red shift on substitution of hydrogen atom with hydroxy group and that molar absorbancy indexes were of the order of 10^{4-5} that the absorption at 362 mμ and 371 mμ must be due to the N$\rightarrow$Vn transition(7).

Absorption spectrum of 3-hydrexytropolone changed its shape with acidity, as shown in Fig. 5. Curve III in the figure is that at pH 5.5. The absorption maxima were found at 320 mμ, 362 mμ and 371 mμ. Another absorption band appeared

(6) H.L. Mc Murry, J. Chem. Phys., **9** (1941), 231 ; 241.

(7) M.J.S. Dewar, Nature, **166** (1950), 790.

at 395 mμ with a decrease in the concentration of the hydrogen ion. And it increased pronouncedly as pH of the solution increased. Simultaneously, the absorption at 362 mμ and 371 mμ decreased.

The first dissociation constant of 3-hydroxytropolone was calculated from the absorption at 395 mμ and hydrogen ion concentration. In the calculation, the dissociation in the first step was assumed to be complete at pH 9.1. And $\varepsilon=6330$ was obtained from the absorbancy of it as the molar absorption coefficient of HT^{-}* at 395 mμ. A good agreement is seen among the individual dissociation constants.

By alkali titration method, Yui(8) obtained 1.91×10^{-7} and 3.02×10^{-12} as the first and the second dissociation constants respectively. The result given in Table 1 is in good agreement with his result.

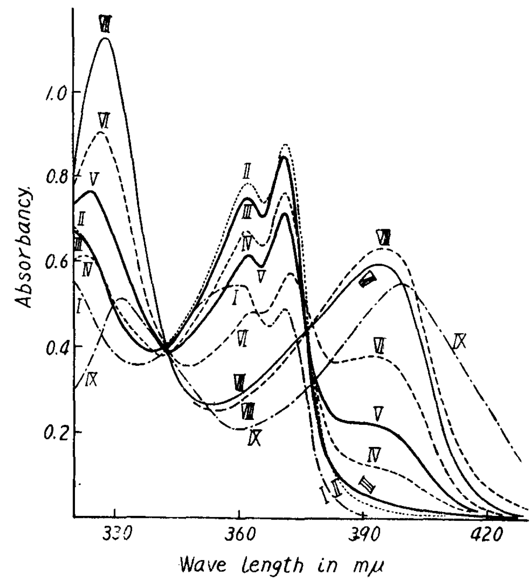


Fig. 5. Effect of acidity on the absorption spectrum of 3-hydroxytropolone.
3-hydroxytropolone : 1×10^{-4}M/l

I	HCl 1N	VI	pH 7.0
II	pH 4.2	VII	8.0
III	» 5.5	VIII	» 9.1
VI	» 6.0	IX	NH_4OH 1N
V	» 6.4		

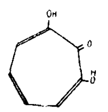
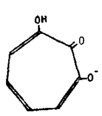
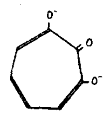
Table 1. Dissociation constants of 3-hydroxytropolone.
3-hydroxytropolone : 1×10^{-4}M/l

pH	A_{395}	C_{HT^-} ($\times10^{-5}$M/l)	C_{H_2T} ($\times10^{-5}$M/l)	K_1
5.5	0.0420	0.664	9.336	2.29×10^{-7}
6.0	0.1160	1.833	8.167	2.24×10^{-7}
6.4	0.2140	3.381	6.619	2.04×10^{-7}
7.0	0.3750	5.924	4.076	1.45×10^{-7}
8.0	0.5940	9.383	0.617	1.51×10^{-7}

The first and the second dissociation are to proceed to that of 99.59 per cent and 0.38 per cent respectively at pH 9.1, when it is calculated from Yui's data of pK_1 and pK_2. Therefore, the dissociation in the first step, $H_2T^{*}\rightleftarrows H^{+}+HT^{-}$, can be considered to be practically complete.

The absorption maximum at 395 mμ was transferred to 400 mμ when ammonium hydroxide was added to 1N. A calculation from Yui's data of $pK_2=3.02\times10^{-12}$ shows that 99.6% of T^{--}* exists in 1N ammoniacal solution, and therefore, the bnad at

(8) T. Yui and T. Nozoe, unpublished data ; c.f. Chem. Rev., **55** (1955), 15.

* H_2T anstds for  , HT^{-} for  , T^{--} for  ,

400mμ is considered to be due to ionization of 3-hydroxytropolone in the second step. The absorption bands at 395 mμ and at 400 mμ may be regarded to be due to the electron migration of the seven-membered ring system consisting of one C=O and containing ten and twelve electrons respectively. This is also due to N→Vn transition. 3-hydroxytropolone was gradually decomposed in 1N ammoniacal solution and the solution became colorless on being left standing.

It was also found that an increase in hydrogen-ion concentration resulted in a large decrease in absorbancy and a remarkable change in the shape of absorption spectrum. This is considered to be due to the addition of proton to oxygen atom of the carbonyl group of 3-hydroxytropolone.

Tropolone, 3-methoxytropolone and 3-aminotropolone showed behaviors similar to that of 3-hydroxytropolone with changes in acidity.

IV. Germanium complex of 3-hydroxytropolone

When an excess of 3-hydroxytropolone was added to germanium, the formation of the complex was comlete above pH 5.5. At pH 5.5 the complex showed absorption bands at 378 mμ and 325 mμ.

The absorption of the germanium complex increased with a rise of pH up to 7 and simultaneously, it shifted slightly toward longer wavelengths. Figure 6 represents the effect of acidity on the absorption of the germanium complex. At above pH 7, no noticeable change was observed in intensity. The absorption maximum, however, still showed a bathochromic shift.

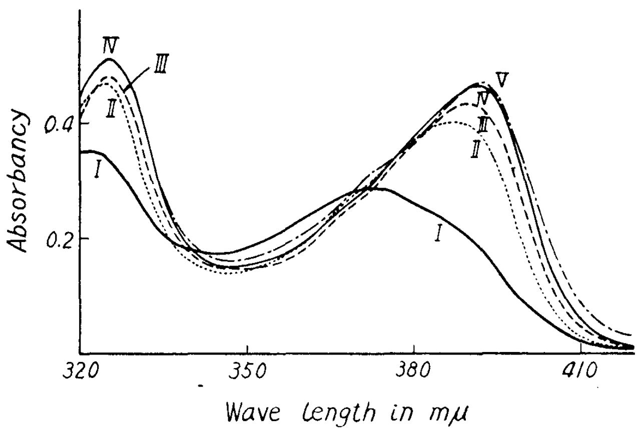


Fig. 6. Effect of acidity on the absorption of the 3-hydroxytropolone complex with germanium.
Germanium : $1.3_5 \gamma$/ml
3-hydroxytropolone : 1×10^{-4}M/l
I 4.2 II 5.5 III 6.0
IV 7.0 V 9.1

Next, changing the concentration of 3-hydroxytropolone from 9.9×10^{-6} M/l to 2.0×10^{-4} M/l, the composition of the complex was investigated by the molar ratio method (Fig. 7). Concentration of germanium was kept at 1.43 γ/ml and pH at 7.0. The curves broke sharply from the linear at a molar ratio of 3.1_0–3.1_5 of 3-hydroxytropolone to germanium. From the accuracy of this experiment, the complex might be concluded to be 1 : 3 compound. But, the absorbancy increased with increasing amounts of excess reagent, because of the absorption of 3-hydroxytropolone.

An attempt was further made to evaluate the formation constant of germanium complex. Figure 8 shows the absorption curves which were obtained by adding the reagent in the molar ratio of less than three times that of germanium at pH 5.5.

In addition to the absorption band of germanium, another one was found at 372 mμ, which corresponded to that of 3-hydroxytropolone. Consequently, at pH 5.5 it seemed that some amounts of reagents remained unreacted.

The amount of the complex formed and that of the reagent left unreacted were determined by measuring the absorbancy at 387 mμ and 372 mμ and the formation constant was calculated. The concentration of germanium was 1.3_5 γ/ml.

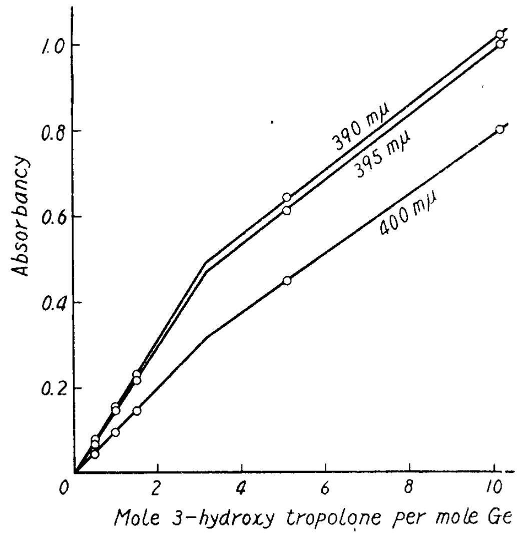


Fig. 7. Effect of ratio of reagent to germanium.
Germanium : $1.4_3\gamma$/ml
pH : 7.0

Taking the absorbancy Ax at any wavelength,

$$Ax=\varepsilon_x^C C_C+\varepsilon_x^R C_R,$$

where ε_x^C, ε_x^R = molar absorption coefficient of the complex and the reagent respectively at the wavelength x,

C_C, C_R = equilibrium concentration of the complex and the reagent,

C_C and C_R were calculated from the absorbancy at 387 mμ and 372 mμ.

The formation constant

$$K=\frac{[GeR_3]}{[Ge]\,[R]^3}$$

was then evaluated. In the equation [R] represents the concentration of germanium. The results are shown in Table 2. Concentration of germanium was 33.63 γ/25 ml. As seen in the table, the formation constants agreeded well with one another when the composition of the complex was taken as 1 : 3. By assuming the composition of the complex to be 1 : 4, the calculation was also made for comparison. The results are given in the last column, and they show a great disagreement.

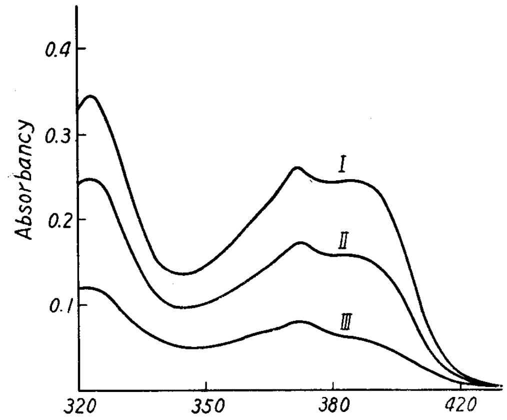


Fig. 8. Absorption spectra of solutions containing germanium and 3-hydroxytropolone in the ratios 1 : 0.8, 1 : 1.6, 1 : 2.4.
Germanium : $1.3_5\gamma$/ml
pH : 5.5
I 3-hydroxytropolone : 4.5×10^{-5}M/l
II " : 3.0 "
III " : 1.5 "

The absorption maximum of the complex showed a slight red shift with increasing pH, as shown in Fig. 6. This might be considered to be due to the stabilization of the excited state of the complex.

V. Absorbancy and the concentrations of germanium

The relation between the absorbancy and the concentrations of germanium was examined. Spectrophotometric measurements were made at pH 7.0 over a concentration range of 0.5 to 2.2 γ/ml of germanium. 3-hydroxytropolone complex with germanium was found to conform to Beer's law within the range.

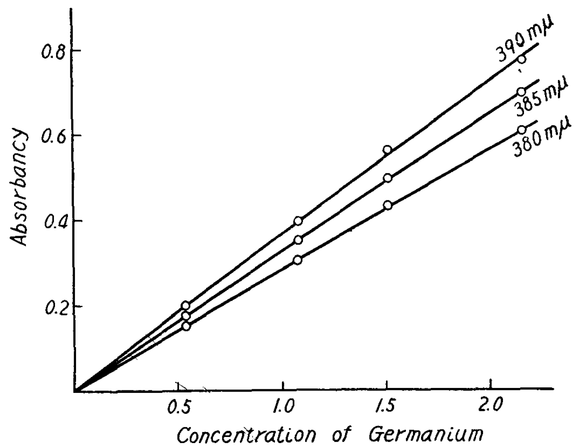


Fig. 9. Calibration curves.
3-hydroxytropolone : 1.5×10^{-4}M/l

But, at about pH 5.5 the formation of the complex was complete when the reagent was present in considerable excess. At this pH the reagent showed no appreicable absorption in the neighbourhood of 387 mμ. Accordingly, it would be desirable to determine germanium at this pH.

Table 2. Formation constant of germanium-3-hydroxytropolone

R/Ge (molar ratio)	Absorbancy		Molar absorption						Concentration of complex ($\times 10^{-5}$M/l)		Equilibrium concentration of Ge ($\times 10^{-5}$M/l)		Equilibrium concentration of reagent ($\times 10^{-5}$M/l)		Formation constant	
			Complex				Reagent									
			GeR_3		GeR_4											
	A_{387}	A_{372}	ε_{387}	ε_{372}	ε_{387}	ε_{372}	ε_{387}	ε_{372}	GeR_3	GeR_4	when GeR_3 was formed	when GeR_4 was formed	when GeR_3 was formed	when GeR_4 was formed	GeR_3	GeR_4
2.4	0.2449	0.2596	21883	15864	22584	24026	701	8153	1.085	1.085	0.768	0.768	1.073	−0.013	1.14×10^{15}	5.74×10^{27}
1.6	0.1561	0.1726	"	"	"	"	"	"	0.688	0.688	1.164	1.164	0.777	0.088	1.26×10^{15}	9.74×10^{23}
0.8	0.0600	0.0809	"	"	"	"	"	"	0.259	0.259	1.594	1.594	0.489	0.230	1.38×10^{15}	5.75×10^{21}

Summary

An investigation on the soluble colored complexes of germanium has been extended to include the complexes of tropolones. Absorption spectra of tropolone, 3-hydroxytropolone, 3-methoxytropolone and 3-aminotropolone were examined as well as those of their germanium complexes. Among the four reagents, the 3-hydroxytropolone proved to have the greatest difference in the spectra from its germanium complex. Therefore an extensive study was made on the germanium complex of 3-hydroxytropolone.

3-hydroxytropolone showed the absorption maxima at 320, 362 and 371 mμ. When the pH of the solution was

increased another absorption band appeared at 395 mμ. It increased with a rise of pH, accompanied by simultaneous decrease in absorption at 325 and 371 mμ. The observations were explained on the ground that 3-hydroxytropolone was ionized. The decrease in absorption at 362 mμ and at 371 mμ and the change in absorption spectra were also obserbed when the solution became extremely acidic, i.e. in 1N-HCl.

The formation of germanium complex of 3-hydroxytropolone was complete at above pH 5.5. With an increase of pH, the absorption of the complex increased and the spectrum showed a bathochromic shift without any noticeable affect on the composition of the complex. The composition of it was 1 : 3. The formation constant of the complex was 1.26×10^{15}. It obeyed Beer's law up to 2.2 γ/ml of germanium.

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