Studies on Organic Reagents for Inorgänic Analysis. II[1]. Spectrophotometric Study on Phenylfluorone Chelates of the Fourth Group Metal Elements*

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Introduction

The study on the nature of the reaction of metals with organic reagents is very important for the purpose of selecting or sythesizing an organic reagent useful for the colorimetric determination of a metal. There are two groups of organic reagents used for this purpose; (1) For the first group, e. g. ethylene diamine or EDTA, the light absorption is attributed to the electronic transition from nonbonding orbital to antibonding orbital in a central metal atom as is usual with simple inorganic complexes[2]. (2) Most organic dyes used as the reagents for the colorimetric determination of metals belong to the second group, and their color changes are, as is stated in the following, ascribable to the shift of the $\pi \rightarrow \pi^*$ absorption spectra of the organic system caused by the bond formation between the metal and the donor atom of the reagent. For the investigation of such a color change, it is necessary to understand the general theory of light absorption of organic dyes. As is well known, there are essentially three methods, valency bond method, molecular orbital method, and free electron gas model method. Among them, the last method is much simpler than the others, and moreover its utility is almost comparable to that of the molecular orbital (L. C. A. O.) method which needs the cumbersome procedure of solving secular equations[3].

Recently, the free electron gas model method has been used extensively for calculating the wavelength of the absorption maximum in the spectrum of conjugated organic compound[4-11]. In particular, H. Kuhn has applied this method successfully to various organic dyes[7-11]. According to him, the electron gas in the cases of polyenes, unsymmetrical cyanines, oxanoles etc. suffers a disturbance, and the π-electrons are considered to be placed in a one-dimensional potential having a sine curve periodicity[8]. The wavelength of absorption maximum is expressed by the following equation.

$$\frac{1}{\lambda_{\max}}=\frac{V_0}{h\cdot c}\left(1-\frac{1}{N}\right)+\frac{h}{8mc}\cdot\frac{N+1}{L^2} \qquad (1)$$

where, L is the length of the path of the free π-electron measured along the conjugated chain, N, the number of π-electrons, m, the mass of the electron, c, the velocity of light, h, Planck's universal constant, and V_0 the amplitude of the sine-shaped potential along the chain. In the present study, this model was adopted to examine the relation between the nature of the chelating bond and the color change of reagent. 2,3,7-Trihydroxy-9-phenyl-fluorone was chosen as a suitable organic reagent, and is an excellent compound for such a purpose because of its symmetric structure and of the high stability of its chelates with fourth group metals.

Experimental and Results

Reagents and Apparatus. — The ethanolic solution of phenylfluorone (1 ml. contains 0.6 mg. of phenylfluorone*) was prepared by dissolving 0.120 g. of phenylfluorone in 150 ml. of ethyl alcohol containing 1 m. of 5.0 N hydrochloric acid, and the resulting solution was diluted to 200 ml. with ethyl alcohol.

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* This study was presented at the Meeting of the Chemical Society of Japan on Oct. 28, 1956 (Symposium on Chemistry of Complex Compounds).

1) K. Kimura and H. Sano, This Bulletin, **30**, 80 (1957).

2) H. Yamatera, *J. Inst, Polytechnics Osaka City Univ.*, **5**, 163 (1956).

3) H. H. Jaffé, *J. Chem. Phys.*, **20**, 1646 (1952); ibid, **21**, 1287 (1953).

4) N. S. Bayliss, *J. Chem. Phys.*, **16**, 287 (1948).

5) J. R. Platt, ibid., **17**, 484 (1949).

6) W. T. Simpson, ibid, **17**, 1218 (1949).

7) H. Kuhn, *Helv. Chim. Acta*, **31**, 1441 (1948); *J. Chem. Phys.*, **16**, 840 (1948).

8) H. Kuhn, *Z. Elektrochem.*, **53**, 165 (1949); *J. Chem. Phys.*, **17**, 1198 (1949).

9) H. Kuhn, *Helv. Chim. Acta*, **34**, 2371 (1951); *Z. Elecktrochem.*, **55**, 220 (1951).

10) W. Huber, H. Kuhn and W. Huber, *Helv. Chim. Acta*, **36**, 1957 (1953).

11) H. Kuhn, *Z. Naturforsch*, **9a**, 989 (1954); *Z. Elektrochem.*, **58**, 219 (1954).

* Abbreviation of 2, 3, 7-trihydroxy-9-phenylfluorone.

Metal solutions were prepared from their oxides (germanium, titanium), chloride (tin), or oxychloride (zirconium), and then standardized gravimetrically. These stock solutions contain enough hydrochloric acid to prevent the hydrolysis of metals, being free from foreign metal ions. The working solution was prepared by diluting an aliquot of each stock solution with water or diluted hydrochloric acid.

Gum arabic solution was prepared by dissolving 0.5 g. of gum arabic in 200 ml. of water by warming. The solution was filtered when necessary.

Cyclohexanol. — Analytical grade reagent was used without further purification.

Absorbance values of the sample and the blank solution were measured with a Beckman spectrophotometer Model DU, using 1-cm. glass cells and distilled water as a reference solution. From the difference the absorption spectrum of the dye or the chelate was obtained.

Absorption spectra of dyes.—The solution whose absorption spectrum is shown in Fig. 1, contains 20 ml. of ethanol, and 0.6 or 1.2 mg. of phenylfluorone. The desirable acidity or basicity in the final solution was maintained by adding the appropriate volume of hydrochloric acid or aqueous potassium hydroxide solution. The solution was diluted to 50 ml. with water.

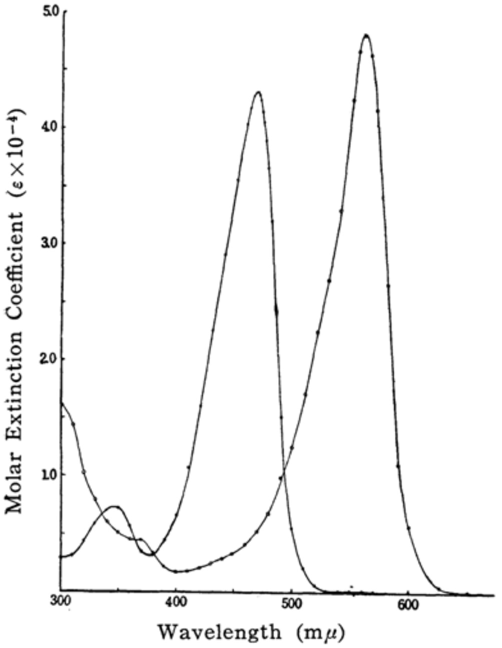

Fig. 1. Absorption Spectra of Phenyfluorone.

—●— in 0.5 N HCl solution

—○— in 1.0 N KOH solution

The absorption maximum of this dye is found at 468 mμ in an acidic solution, whereas it lies at 560 mμ in an alkaline solution. The value of molar extinction coefficient in alkaline solution might be slightly underestimated, because of the rapid fading of color due to the oxidation of the dye. With respect to the absorption maxima, the same results were obtained in the presence of either 5 ml. of cyclohexanol or gum arabic in the solution, although there was a slight difference in the detailed shape of their absorption curves. The solutions cause the precipitation of phenylfluorone in hydrochloric acic concentration below 0.04 N or in potassium hydroxide concentration below 0.01 N.

Reaction with Metals.—Phenylfluorone is one of the ortho-diphenol derivatives having the mesomeric group at its para position, which reacts remarkably with several metals, particularly titanium, germanium, zirconium, tin and thorium, giving striking color change[1,12].

Because the resulting complexes are insoluble in many solvents, the absorbance values were measured in the presence of a suitable stabilizer such as gum arabic or cyclohexanol*. The position and the intensity of absorption maximum is almost independent of the kind of the stabilizer used. On the other hand, the absorbance decreases with increasing acidity of solution. The effect of acidity is shown in Fig. 2. Beyond a certain value of acidity, the absorbance of chelate increases rapidly with the decrease in acidity. This specific value should be dependent on the stability of the chelate[13]. Then, the absorbance becomes nearly constant at lower acidity. In this range the molar extinction coefficients of the metal chelates are calculated, except for the case of titanium and tin chelate in which this range was not observed.

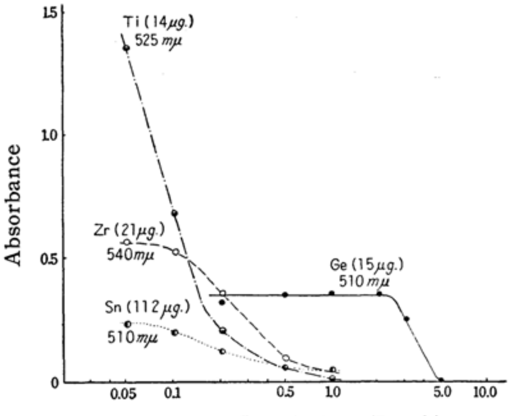

Fig. 2. Effect of Acidity. The solution contains 6 mg. of phenylfluorone, 20 ml. of ethanol, and 5 ml. of cyclohexanol or gum arabic solution in a final volume 50 ml.

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* The light scattering effect of the colloidal particle on the absorption spectra is negligible for several hours after the preparation of the solution.

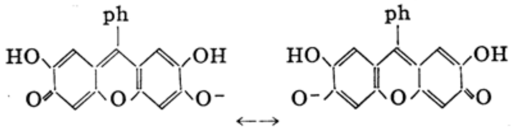
[12] F. Ihmura, H. Sano and M. Asada; Unpublished report.

[13] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", New York Prentice-Hall, Inc. N. Y. (1952) p. 119.

The absorption sepectra of metal chelates with phenylfluorone were measured at various acidities, but the position of the absorption maximum was constant. The ratio of reagent to metal was obtained by the gravimetric analysis of the chelate precipitate. Their results are shown in Table I, together with the several properties of the metal. These results show that the value of $\varepsilon_{\max}$ is roughly proportional to the ratio of the reagent to the metal in each chelate complex. This fact suggests that the absorption spectra in this wavelength range depend on the $\pi \rightarrow \pi'$ transition of the conjugated π-electron in the ligand.

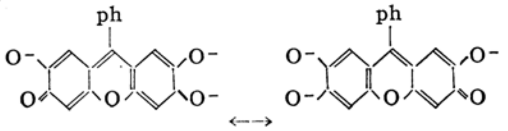
Discussion

The anionic phenylfluorone, which is responsible for the red-pink color observed in an alkaline solution, is considered to be resonating between two limiting structures, Ia and Ib, or IIa and IIb, each of which makes the same contribution to the normal state of the anion, because of its symmetrical structure. One form results from the other when the single and double bonds of the conjugated chain change over. This shows that each conjugated C—C bond has an equal bond length and bond order as a rough approximation. The value of V_0 is, therefore, considered to be zero. Then, the equation (1) is expressed as follows.



Ia Ib

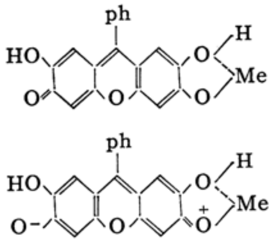
or



IIa IIb

$$\lambda_{\max}=\frac{8mc}{h}\cdot\frac{L^2}{N+1} \qquad (2)$$

In the equation (2), N, m, c and h are constants. But L, the length of the conjugated chain, has a somewhat arbitrary character. In the present study, L was calculated from the observed wavelength of absorption maximum of the phenylfluorone anion, and this value was used in the following calculation and discussion*. For the phenylfluorone metal chelates the two limiting structures, IIIa and IIIb, are not equal in energy and they will not have equal contributions to the normal state, unlike the case of the symmetrical phenylfluorone anion. V_0 has, therefore, a difinite value.



IIIa

IIIb

On the other hand, if we conventionally apply the ionic-covalent resonance to the chelating bond, it can be assumed as the first approximation that with increasing ionic character in the metal-oxygen bond, the value of parameter, V_0, decreases and the absorption maximum shifts toward a longer wavelngth. The ionicity is dependent upon the difference of electronegativity between the metal and the oxygen atom. When the chelating bond has a pure covalency, the conjugated system is considered to be similar to that of polyene which has the same number of conjugated double bond, whereas it becomes equal to that of symmetrical polymethine when the chelating bond is pure ionic. The values of V_0 calculated from the experimentally

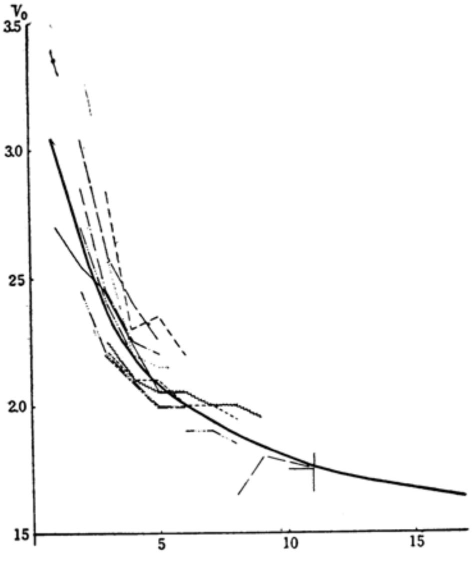


Fig. 3. Correlation between V_0 and Number of Conjugated Double Bond in Polyenes.

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* The value of L, 14.6₅ Å, is reasonable, because this value is comparable to that obtained in the same manner[9] for many cyanine dyes possessing the same number ot conjugated double bond. See also the references 8, 9 and 11 with respect to the propriety to apply the one dimensional free electron gas model method to the branched double bond system.

TABLE I

Metal	H	Ge	Sn	Ti*	Zr	ionic
$\lambda_{\max}$ (mμ)	468	510	510	525	540	560
$\varepsilon_{\max}$	4.3×10^4	8.5×10^4	1.2×10^4	4.7×10^4	15×10^4	4.8×10^4
Ratio, Reagent: Metal.	(1 : 1)	2 : 1**	—	2 : 1	4 : 1	—
Ionic Radius[13] (Å)	—	0.53	0.71	0.68	0.80	—
Electronegativity[14]	2.1	1.8—1.9	1.8—1.9	1.6	1.5	—
V_0(eV.)	0.49_0	0.23_6	0.23_6	0.16_2	0.094_5	0

* Ti is soluble as a true solution in 0.1 N or more concentrated hydrochloric acid.

** This value was gven by Dr. K. Saito.

determined absorption maxima of a number of polynes* have been collected in Fig. 3, showing the relationship between V_0 and number of conjugated double bond.

By the aid of the Pauling's[14] or Hannay-Smyth's empirical equation[15] or Dailey-Townes' empirical diagram[16], the ionic character of the chelating bond between the metal and the oxygen atom was estimated from the electronegativity of the atoms concerned**. The relationship between V_0 and ionic character I (or covalent character, C) will be expressed by the following equation,

$$V_0=F(1-I),\ \text{or}\ V_0=F(C). \qquad (3)$$

In this equation, the function F should have the property that V_0 increases up to the value of corresponding polyene with decreasing I or increasing C, whereas it becomes zero when I reaches unity or C comes to zero. The following n'th power function, one of the functions expected, is applied to examine the experimental results;

$$V_0=k(1-I)^n \quad \text{or} \quad V_0=k\cdot C^n \qquad (4)$$

where k and n are parameters to be determined by the experiment. The values of V_0 calculated from the experiments for the metal-phenylfluorone chelates are listed in Table I, together with other characters of the metal concerned. The value of n was determined from the relationship between the value of V_0 and the covalent character of the bond. The value of k is equal to that of V_0 obtained for the polyene which has the same number of conjugated double bond as phenylfluorone. These results were shown in Fig. 4a, b and c, in which all data met a straight line relation.

These results show that the shift of the wavelength of absorption maximum in the metal chelate depends on the ionic character of the bond between the metal and the functional atom of reagent. Conversely this fact makes it possible to estimate qualitatively the ionic character of the bond or the electronegativity of the metal concerned.

For many oragnic dyes used for the colorimetric determination of various metals, it is generally known that when the dye reacts with metal the absorption maximum shifts toward a longer wavelength. These phenomena will be explained as follows.

From equation (1), the following equation is derived,

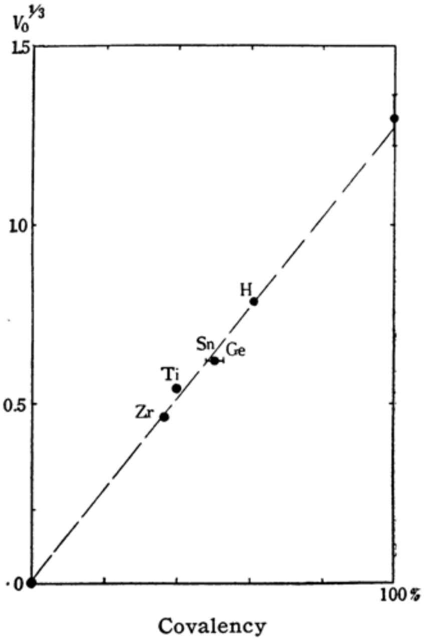

Fig. 4, a. Based on Pauling's equation.

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* The absorption maxima were taken from the following: A. E. Gillam and E. S. Stern "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold Ltd. London, (1954); Y. Urushibara, "Organic Chemistry II", Kyoritsu Shuppan, Tokyo, (1955).

** The value of electronegativity was taken from the Table presented recently by H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

14) L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, 1939.

15) N. B. Hannay and C. P. Smyth, *J. Am. Chem. Soc.*, **68**, 171 (1946).

16) B. P. Dailey and C. H. Townes, *J. Chem. Phys.*, **23**, 118 (1955).

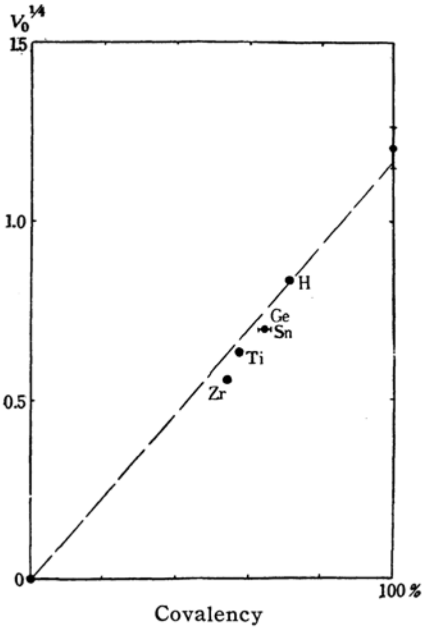

Fig. 4, b. Based on Smyth-Hanney's equation.

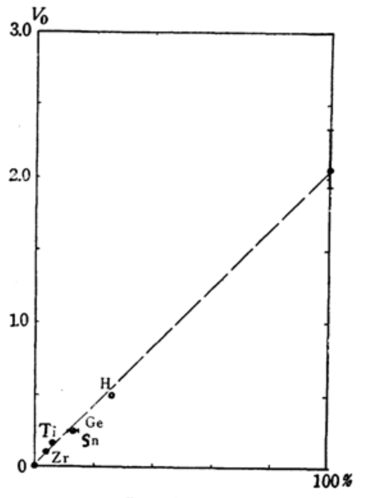

Fig. 4, c. Based on Dailey-Towne's diagram.

$$V_0=N\cdot h(\nu-\nu_i)/(N-1)=N\cdot h\{(\nu_H-\nu_i)-(\nu_H-\nu)\}/(N-1)=N\cdot h(\nu_0-\Delta\nu)/(N-1) \tag{5}$$

where ν is the frequency of absorption maximum observed with the metal chelate, ν_H and ν_i, the frequency of absorption maximum of the reagent in the acidic and the alkaline solution, respectively, and $\Delta\nu$, the shift ("red shift") of the frequency, which is equal to $(\nu_H-\nu)$. From the equation (4) and (5), $\Delta\nu$ can be derived as follows,

$$\Delta\nu=\nu_0-k(N-1)(1-I)^n/N\cdot h=\nu_0-k(N-1)\cdot C^nN\cdot h \tag{6}$$

where $\nu_0(=\nu_H-\nu_i)$ is constant for the reagent used. From equation (6), it is seen, that $\Delta\nu$ is affected with the covalent character of the bond, where k and n are chracteristic of the reagent used. In general, however, this relation will not always be satisfied because of their unsymmetrical structure, branched conjugated system, or uncertainty of the ionicity of the bond which is estimated empirically from the difference of electronegativity.

Summary

The absorption spectra of phenylfluorone and its chelates with the fourth group metal elements, titanium, germanium, zirconium and tin were studied. It was found that in acidic solutions the absorption maxima of these metal chelates shift towards a longer wavelength with increasing ionicity of the bond between the metal and the terminal oxygen atom of the ligand phenylfluorone. These absorption spectra were examined by the aid of free electron gas model method. Kuhn's theory was applied to the calculation of the value V_0 from the absorption maximum observed in each metal chelate. It was shown that there was a certain relationship between the value of V_0 obtained and the ionicity of the chelating bond which is estimated from the difference of electronegativity between the metal and the terminal oxygen atom. The relation can be expressed as follows:

$$V_0=k(1-I)^n \tag{4'}$$

where, n is a parameter depending on the method used for the estimation of the ionicity, k a parameter characteristic of the chelating dye used and equal to the value of V_0 for the polyene having the same number of the conjugated double bond. These results were applied to explain the "red shift" observed in acidic solutions of organic dyes in the colorimetric determinations of metals. A more detailed investigation concerning the nature of the chelating bond will be reported later.

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