# *Synthetic and Analytical Studies on Color Reagents. VIII. o-Halogeno-o'-hydroxyazo Compounds*

By Tadashi IWACHIDO*, Haruo MIYATA and Kyoji TOEI

(Received July 3, 1959)

In the previous papers[1-5], a series of *o*-substituted-*o'*-hydroxyazo compounds, having various groups in ortho position were synthetized and their identification limits for various metal ions were determined, and thus the usefulness of these reagents for metal indicators and colorimetric reagents was discussed.

The present paper describes the preparation of *o*-halogeno-*o'*-hydroxyazo compounds and their identification limits for calcium, magnesium and thorium. Especially absorption spectra of *o*-halogenophenylazo-chromotropic acids and their magnesium complexes are determined, and the relation between the absorption spectra and their structures is discussed.

## Experimental

**Syntheses of Reagents.**—*o*-Iodoaniline was prepared by the method of Baeyer[6]. *o*-Iodonitrobenzene was prepared from diazotized *o*-nitroaniline with iodine-potassium iodide solution, and then it was converted into *o*-iodoaniline by the reduction with stannous chloride and purified by the steam distillation. White needles, m. p. 59.5~60°C.

*o*-Bromoaniline[7] was obtained by the reduction of *o*-bromonitrobenzene which was prepared by Sandmeyer's reaction of diazotized *o*-nitroaniline, m. p. 33°C.

*o*-Chloroaniline and aniline were reagent grade products and *o*-fluoroaniline was kindly supplied from Dr. K. Inukai**.

Aniline and *o*-halogenoanilines were dissolved in 6 N hydrochloric solution respectively, cooled in ice, diazotized with an equivalent weight of sodium nitrite, and filtered off when necessary. Coupling reaction had to be carried out immediately. The stability of these diazonium salt solutions seems to decrease in the order of *o*-fluoro-, chloro-, bromo- and iodoaniline.

β-Naphthol, 2-hydroxy-3-naphthoic acid, Scheffer's acid and R-acid were dissolved in about 1 N sodium hydroxide solution, N-W-acid and chromotropic acid in a solution of sodium acetate and G-acid in concentrated aqueous ammonia. These solutions were separated from any insoluble matter by filtration, and then cooled below 5°C. Coupling reaction was carried out by adding the diazonium salt solution into the cooled naphthol or naphtholsulfonic acid solution and the azo compound thus obtained was recrystallized from acetic acid or dilute hydrochloric acid.

**Identification Limits.** — Identification limits for calcium, magnesium and thorium were determined by the method of the previous paper[1]. The reagents coupled with β-naphthol or G-acid indicate no color change with concentrations of 50 γ/ml. magnesium, calcium and thorium, whilst those with Scheffer's acid or N-W-acid change a littie or not at all. The identification limits of the reagents coupled with R-acid, 2-hydroxy-3-naphthoic acid and chromotropic acid are relatively low. R-acid reagents do not indicate any color change for 50 γ/ml. thorium, but the identification limits for calcium and magnesium are 5~50 γ/ml. Reagents prepared from 2-hydroxy-3-naphthoic acid for magnesium, calcium and thorium have a limit of 0.1~25 γ/ml. and those from chromotropic acid 0.1~10 γ/ml.

Identification limits of one series of these reagents increase with the atomic weight of the halogen atom at the ortho position. But the values for magnesium and calcium are far greater than those of *o,o'*-dihydroxyazo compounds[1], and are almost the same as those of *o*-trifluoromethyl- or *o*-methyl-*o'*-hydroxyazo[4] and *o*-sulfo-*o'*-hydroxyazo compounds[3]; for thorium they are larger than those of *o*-arsono-*o'*- hydroxyazo compounds[5].

**Absorption Spectra of *o*-Halogenophenylazo-chromotropic Acids and their Magnesium Complexes.** — *Reagent solution.* — The reagents being very hygroscopic, they were dried at 110°C in weighing bottles, cooled in phosphorus pentoxide desiccator, and weighed. A $2.5\times10^{-4}$ mol./l. solution was prepared and stored in the dark.

A 0.25 M magnesium sulfate solution was made from recrystallized $MgSO_4\cdot7H_2O$.

*Procedure and apparatus.*—A series of the reagents and their magnesium complex solutions of varying pH were prepared in the following manner. All solutions were made in a dark room, for the absorption of reagents was retarded by the daylight, especially at a higher pH.

---

* Present address: The Electrical Communication Laboratory, Musashino-shi, Tokyo.

[1] K. Emi, K. Toei and H. Miyata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 78, 736 (1957).

[2] K. Emi, K. Toei and N. Takemoto, ibid., 78, 741 (1957).

[3] K. Emi, K. Toei and H. Miyata, ibid., 78, 977 (1957).

[4] K. Emi, K. Toei and H. Miyata, ibid., 78, 979 (1957).

[5] K. Emi, K. Toei and K. Furukawa, ibid., 79, 681 (1958).

[6] A. Baeyer, *Ber.*, 38, 2760 (1905).

[7] F. Ullman, ibid., 29, 1880 (1896).

** Government Industrial Research Institute, Nagoya.

Five milliliters of the reagent solution was placed in a 50 ml. volumetric flask, followed by addition of an adequate volume of 1 N hydrochloric acid, 1 M aqueous ammonia, 1 M ammonium chloride or 0.1 N sodium hydroxide to adjust the pH to the desired value and then the volume was made up to 50 ml. with water.

Magnesium complex solutions were similarly prepared with 5 ml. of 0.25 M magnesium sulfate solution. Above pH 11, magnesium hydroxide was formed, so the determination could not be made. The pH was measured with Shimadzu Glass Electrode Model GU-1 pH meter and the absorbancy with Shimadzu Spectrophotometer QR-50 type, with 1 cm. cells. Absorption spectra over various pH values are shown in Figs. 1—5.

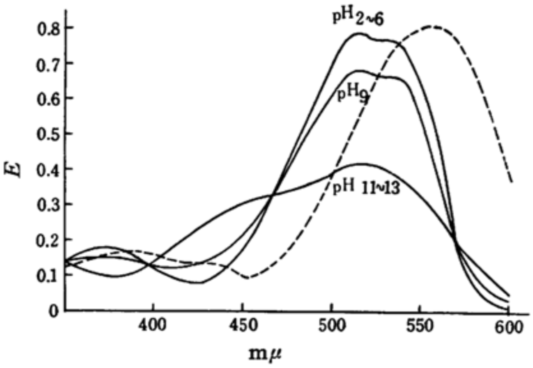


Fig. 1. Absorption curves of phenylazo-chromotropic acid and its magnesium complex (broken line).

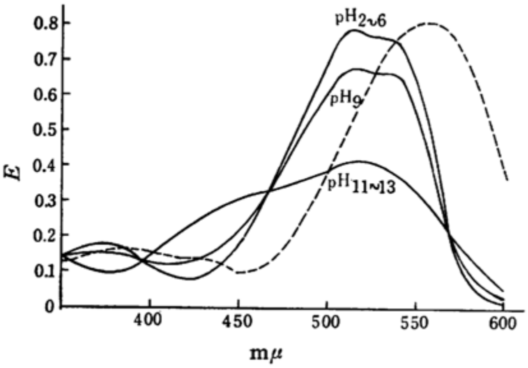


Fig. 2. Absorption curves of *o*-fluorophenylazo-chromotropic acid and its magnesium complex (broken line).

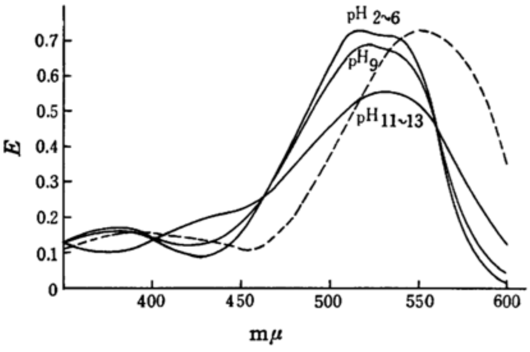


Fig. 3. Absorption curves of *o*-chloro-phenylazo-chromotropic acid and its magnesium complex (broken line).

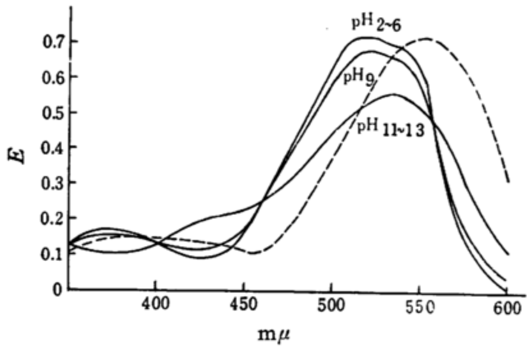


Fig. 4. Absorption curves of *o*-bromo-phenylazo-chromotropic acid and its magnesium complex (broken line).

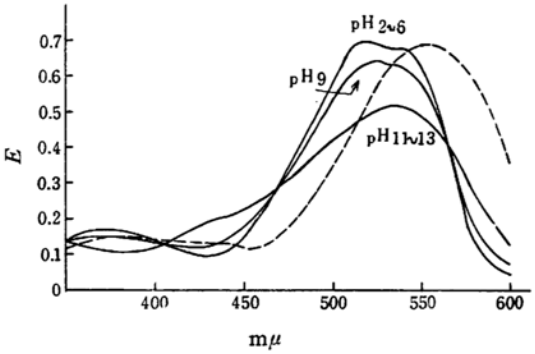


Fig. 5. Absorption curves of *o*-iodophenyl-azo-chromotropic acid and its magnesium complex (broken line).

## Results and Discussion

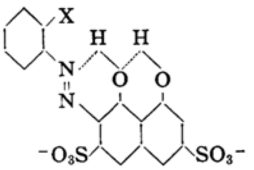
**Spectral Properties of the Reagents.**—Between pH 2 and 6, the same reagent gives the identical absorption spectra having two absorption maxima at 510~520 and 530~540 mμ (Fig. 1—5). It is considered that electrolytic dissociation of naphtholic OH does not occur. Above pH 7, these maxima shift to form one maximum (at pH≧12) with increasing pH.

From the presence of an isosbestic point in each figure, two structures are expected, and from the electrolytic dissociation of chromotropic acid[8,9] the following structures are presented.

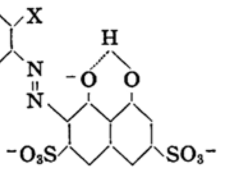
---

[8] H. Zollinger and W. Büchler, *Helv. Chim. Acta*, **34**, 591 (1951).

[9] J. Heller and G. Schwarzenbach, ibid., **34**, 1876 (1951).



(I)



(II)

X=H, F, Cl, Br and I.

Formula I corresponds to the acidic form and II exists at pH more than 12. Azo grouping seems to be *trans*-form. Structure I has two hydrogen bridges; the one between *peri*-oxygen atoms is too strong to dissociate even at pH 12, but the other begins to dissociate at pH 7~8 and completely dissociates at pH 12 to give II. Formula I has a higher co-planarity than formula II.

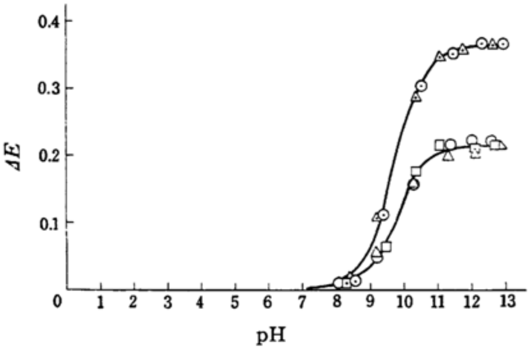


Fig. 6. Relationship between pH and absorption differences at 510 m$\mu$.

⊙, *o*-H-compound; ◬, *o*-F-compound;
○, *o*-Cl-compound; △, *o*-Br-compound;
□, *o*-I-compound.

Absorption differences at 510 m$\mu$ are plotted against pH (Fig. 6). There are two series; the one consists of *o*-hydrogen and *o*-fluoro-compounds, and the other *o*-chloro, *o*-bromo and *o*-iodocompounds. The difference seems to spring from steric hindrance. Namely, in formula II, *o*-halogenophenyl group and chromotropic acid can rotate around each single bond of N-C axis, and hydrogen and fluorine atoms at ortho position are not hindered, but chlorine, bromine and iodine atoms are hindered by the sulfonic group of chromotropic acid according to Stuwart model.

**Spectral Properties of Magnesium Complexes.**—Absorption curves of the mixtures of the reagent and the magnesium solutions are the same as those of the reagent over pH 2~6. This indicates that magnesium complexes can not be formed in an acid medium. Absorption maxima of magnesium complexes at a higher pH are shifted to longer wavelength and to higher absorbancy with increasing amount of magnesium, and thus 1000 times magnesium

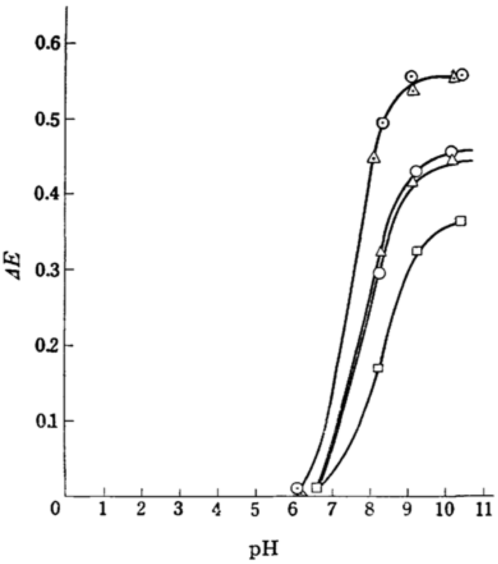


Fig. 7. Relationship between pH and absorption differences at 570 m$\mu$.

⊙, *o*-H-complex; ◬, *o*-F-complex;
○, *o*-Cl-complex; △, *o*-Br-complex;
□, *o*-I-complex.

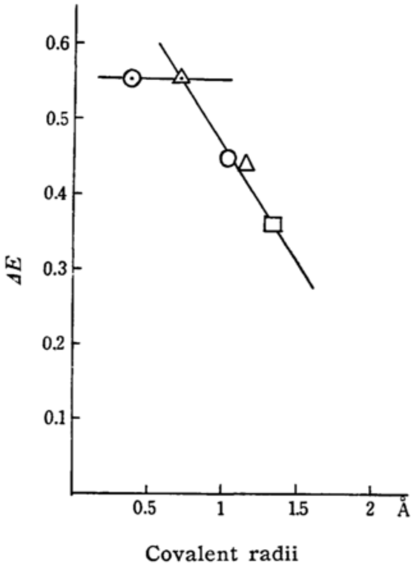


Fig. 8. Relationship between covalent radii of halogen atoms and absorption differences of magnesium complexes at 570 m$\mu$.

⊙, *o*-H-complex; ◬, *o*-F-complex;
○, *o*-Cl-complex; △, *o*-Br-complex;
□, *o*-I-complex.

was used for the measurement (broken lines in Figs. 1—5).

Absorption differences at 570 mμ are plotted against pH (Fig. 7) and against covalent radii of halogen atoms[10,11](Fig. 8). Absorption differences of *o*-hydrogen and *o*-fluoro-complexes are the same, and the others decrease with the atomic weight of halogen atoms. This also means the presence of steric hindrance.

The authors wish to express their thanks to Professor M. Ishibashi and Professor K. Emi for their encouragement. Also the authors express hearty thanks to Dr. K. Inukai who kindly supplied *o*-fluoroaniline.

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

---

[10] L. Pauling, "Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, N. Y. (1940), p. 164.

[11] V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).