SHORT COMMUNICATION

*Synthesis of o-Phosphonobenzeneazochromotropic Acid as a New Reagent and its Thorium Complex**

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The present paper describes the preparation of *o*-phosphonobenzeneazochromotropic acid, and the spectrochemical properties of the reagent and its thorium complex.

Synthesis of the Reagent.—*o*-Bromobenzenephosphonic acid**,1) was prepared by the reaction of *o*-bromobenzenediazonium fluoborate with phosphorus trichloride in ethyl acetate, m. p. 198°C.

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** Identification of these samples were made by Doak.

1) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, 73, 5658 (1951); 74, 754 (1952); 75, 685 (1953).

o-Aminobenzenephosphonic acid** was prepared by the amination of *o*-bromobenzenephosphonic acid with ammonia by the procedure described by Doak and Freedman[2] and by Doak[3] who presented subsequently the following modified methods: Twelve grams of *o*-bromobenzenephosphonic acid, 9 g. of freshly prepared cuprous oxide and 200 ml. of ammonium hydroxide were heated for 18 hr. Nitrogen gas was then passed through the solution in order to remove free ammonia. It is not possible to remove all of the ammonia at this stage. Hydrogen sulfide was then passed into the solution. The precipitated copper sulfide was removed and the pH value of the filtrate was adjusted to 2.1 with concentrated hydrochloric acid. Pure *o*-aminobenzenephosphonic acid (1.1 g.), m.. 185~189°C, precipitated in a crystalline form, free from chloride ion. The mother liquors were evaporated to about 100 ml. and a second crop of 2.8 g. was obtained. This contained a trace of chloride ion.

o-Phsophonobenzeneazochromotropic acid was obtained from the corresponding diazonium salt by coupling with chromotropic acid. *o*-Phosphonobenzeneazochromotropic acid thus obtained was recrystallized from concentrated hydrochloric acid to give reddish brown needles. The reagent being very hygroscopic, it was stored in a phosphrus pentoxide desiccator.

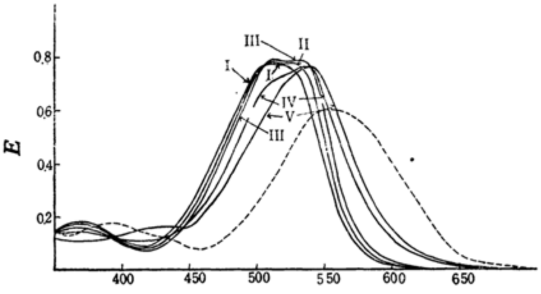

Fig. 1. Absorption curves of *o*-phosphonobenzeneazochromotropic acid (I—V) and its thorium complex (broken line pH 3.3).

I 2.8×10^{-5} mol./l., pH 1.1
II pH 6.3
III pH 8.0
IV pH 6.5
V pH 11.2

Spectrochemical Properties of the Reagent and its Thorium Complex.—Absorption spectra of the reagent solution (2.8×10^{-5} mol./l.) as well as its thorium complex (concentration of the reagent : thorium=1 : 2) are shown in Fig. 1 over various pH values.

On addition of thorium to the reagent solution, the absorption maxima shifted towards the longer wavelengths. The curve shows an absorption maximum at 555mμ.

Mole ratio of thorium to the reagent was confirmed by the mole ratio method (Fig. 2) and the result obtained indicates the formation of a 1 : 1 complex.

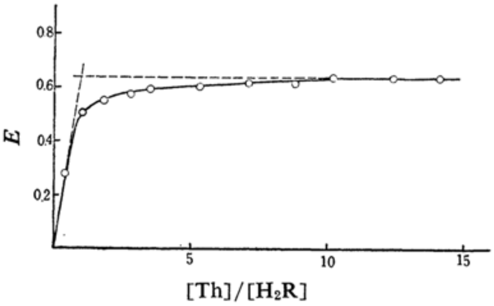

Fig. 2 Mole-ratio method.
pH 3.3, at 580 mμ.
The reagent concn.$=2.8\times10^{-5}$ mol., thorium concn. varied.

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[2] G. O. Doak and L. D. Freedman, ibid., **74**, 754 (1952).
[3] Private communication.