NOTES

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Preparation of Sodium *o*-(*N*-Hydroxy-*N*-phenylcarbamoyl)benzenesulfonate and Reactions with Metal Ions

S. P. BHARGAVA and N. C. SOGANI
Chemistry Department, University of Rajasthan, Jaipur, India

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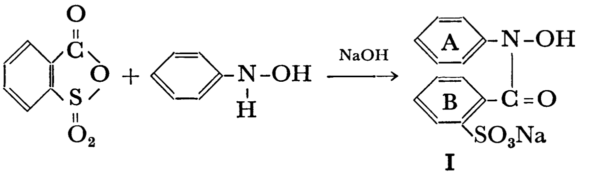
N-Benzoyl-*N*-phenylhydroxylamine (BPHA) has been recommended as a gravimetric reagent for 16 metal ions including copper, iron, aluminum, and titanium,[1] cobalt and nickel,[2] and uranium.[3] The interest in BPHA and its analogues can be judged from the number of papers and reviews.[4] Bass and Yoe[5] surveyed 33 hydroxamic acids and 3 *N*-substituted hydroxamic acids as reagents for metal ions and concluded that BPHA is the most popular compound for this purpose. We thought it worthwhile to study its sulfonic acid derivative, which should prove a useful spectrophotometric reagent for a number of metal ions. Thus, sodium *o*-(*N*-hydroxy-*N*-phenylcarbamoyl)benzenesulfonate (I) was prepared as water-soluble chelating reagent. The preparation could be easily accomplished by allowing *o*-sulfobenzoic anhydride to react phenylhydroxylamine.



I

With a view to preventing the possibility of steric hindrance in the formation of metal chelates by a sulfonic acid group ortho to the coordinating carbonyl group, attempts were made to introduce it in ring A or meta or para to carbonyl group in ring B, but with no success.

o-Sulfobenzoic anhydride is a weak acylating agent and gives only *N*-acyl derivative. In the preparation of BPHA, however, benzoylation of phenylhydroxylamine yields both *N*-and *o*-substituted products, which must be separated by using ammonium hydroxide solution.

There is no difference in the colours of metal complexes of BPHA and its sulfonic acid derivative, indicating that the sulfonic acid group has not altered the chelating properties.

Conventional procedures were adopted for studying the reactions of the reagent towards various metal ions. Results are recorded in Table 1.

The reagent did not give any colour reactions with Mn(II), Ni(II), Hg(II), Pb(II), Al(III), Sn(IV), Sn(II), Bi(III), Cd(II), Sb(III), Rh(III), Ir(III), Pt(IV), Tl(III), La(III), Ce(IV), Th(IV), Zr(IV), alkali and alkaline earth metals.

TABLE 1. REACTIONS OF THE REAGENT WITH METAL IONS

Metal ion	pH	Colour of complex
Fe(III)	below 1.5	Purple
	1.5—3.8	Wine-red
	3.8—9.5	Orange
Fe(II)	6—7	Brown
V(V)	1—3	Orange-red
Ti(IV)	1—3	Yellow
U(VI)	3.0—9.5	Orange
Mo(VI)	0.5—5.5	Yellow
Co(II)	6—7	Light pink
Cu(II)	4—6	Yellow-green
Ru(III)	3—4	Light violet
W(VI)	2—3	Yellow
Cr(III)	3—4	Dirty yellow
Pd(II)	2—4	Light yellow-orange

The application of I as a spectrophotometric reagent for iron(III), vanadium(V), molybdenum(VI), uranium(VI), *etc.* is in progress.

Experimental

Preparation. *O*-Sulphobenzoic anhydride was prepared by the reaction of ammonium *o*-sulphobenzoate and thionyl chloride.[6]

Dry phenylhydroxylamine (22 g,0.2 mol) was dissolved in 200 m*l* of dry benzene and *o*-sulphobenzoic anhydride 37 g,0.2 mol) in 150 m*l* of dry dioxane was run slowly under continuous mechanical stirring. After the addition was complete, stirring was continued for 15 min. A viscous mass appeared. With a vacuum pump the major bulk of the solvent was removed under reduced pressure. The viscous mass was dissolved in 10% ethanolic sodium hydroxide solution and the pH was maintained between 7.0 and 8.5. Sodium salt was precipitated by addition of ether. The crude material was crystallised by dissolving it in a minimum quantity of water and adding excess of ethanol. The compound came out as white cane-sugar like crystals. Yield: 50%. Dec. point: 118—120°C; $\lambda_{max}^{H_2O}$: 250—255 nm ($\varepsilon=5.51\times10^4$).

Found: C, 49.49: H, 3.10; N, 4.21; S, 10.02%. Calcd for $C_{13}H_{10}NO_5SNa$: C, 49.52; H, 3.17; N, 4.44; S, 10.15%.

The compound is highly soluble in water but insoluble in organic solvents. In solid state it is stable indefinitely, but in solution it starts decomposing in about 24 hr.

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