

New Substituted Hydroxamic Acid Derivatives as Spectrophotometric Reagents for Niobium (V)

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Methyl and halogen substituted derivatives of N-acetylsalicyloyl-N-phenylhydroxylamine (ASPHA) and N-p-nitrobenzoyl-N-phenylhydroxylamine are synthesised and used for the spectrophotometric determination of niobium (V). These reagents form deep yellow complexes with niobium (V) and thiocyanate in strong hydrochloric acid media which can be extracted into carbon tetrachloride or chloroform. The complexes absorb strongly around 400 nm and the sensitivities are about 0.005 $\mu\text{g. Nb per ml.}$ A large excess of associated ions including Ta(V) are tolerated.

N-ACETYLSALICYLOYL-N-phenylhydroxylamine (abbr. ASPHA) was introduced as a very selective analytical reagent for niobium (V)¹. This prompted us to modify the reagent properties by introducing suitable substituents in the benzene ring of the phenylhydroxylamine part of the molecule. Thus, out of the ten reagents tried, only five reagents formed complexes of sufficient sensitivity and stability for spectrophotometric work.

In 5-8 M hydrochloric acid media, the reagents form yellow complexes with niobium (V) and thiocyanate which can be extracted into carbon tetrachloride or chloroform. The sensitivities of the method are about 0.005 $\mu\text{g. Nb per ml.}$ at the chosen wavelength. The composition of the complexes is found to be 1 : 2 : 1 with respect of niobium, reagent and thiocyanate.

Experimental

Preparation of reagents: The reagents were synthesised by the condensation of acetylsalicyloyl chloride and phenylhydroxylamine derivatives in the presence of sodium hydrogen carbonate as described in a previous publication². N-p-nitrobenzoyl-N-phenylhydroxylamine was prepared from p-nitrobenzoyl chloride and phenylhydroxylamine. The method of preparation and purification of the compounds were described earlier³. The m.p. and elemental analyses data are given in Table I.

Reagent solutions: 0.25% (w/v) solutions of the reagents (except N-p-nitrobenzoyl-N-phenylhydroxylamine) were prepared in purified carbon tetrachloride. N-p-nitrobenzoyl-N-phenylhydroxylamine was prepared in chloroform.

TABLE I—NEW HYDROXAMIC ACIDS

No.	Reagent	M.P. °C	Formula	% Carbon		% Hydrogen		% Nitrogen	
				Found	Reqd.	Found	Reqd.	Found	Reqd.
I.	N-acetylsalicyloyl-N-o-tolyhydroxylamine	146	C ₁₆ H ₁₆ O ₄ N	68.37	67.37	5.92	5.26	5.21	4.91
II.	N-acetylsalicyloyl-N-m-tolyhydroxylamine	127	"	68.32	67.37	5.18	5.26	5.39	4.91
III.	N-Acetylsalicyloyl-N-p-chlorophenylhydroxylamine	154	"	68.25	67.37	5.13	5.26	5.50	4.91
IV.	N-acetylsalicyloyl-N-o-chlorophenylhydroxylamine	144	C ₁₅ H ₁₂ O ₄ NCl	59.43	58.92	3.53	3.93	4.81	4.58
V.	N-acetylsalicyloyl-N-m-chlorophenylhydroxylamine	94	"	59.20	58.92	3.80	3.93	5.02	4.58
VI.	N-acetylsalicyloyl-N-p-chlorophenylhydroxylamine	147	"	59.82	59.92	4.29	3.93	5.05	4.58
VII.	N-acetylsalicyloyl-N-o-bromophenylhydroxylamine	129	C ₁₅ H ₁₂ O ₄ NBr	52.80	51.44	3.50	3.43	4.16	4.00
VIII.	N-acetylsalicyloyl-N-o-iodophenylhydroxylamine	145	C ₁₅ H ₁₂ O ₄ NI	46.39	45.35	3.20	3.02	4.00	3.53
IX.	N-acetylsalicyloyl-N-p-iodophenylhydroxylamine	129	"	45.90	45.35	3.00	3.02	3.50	3.53
X.	N-p-nitrobenzoyl-N-phenylhydroxylamine	158	C ₁₃ H ₁₀ O ₄ N ₂	60.52	60.47	4.02	3.88	10.57	10.85

Standard niobium solution: Approximately 1 g. of pure niobium pentoxide (BARC, Bombay) was fused with 10 g. of fused sodium bisulphate in a silica crucible with a few drops of concentrated sulphuric acid. The cold cake was extracted with 500 ml. of 10% tartaric acid solution. The niobium content was estimated gravimetrically⁴. This solution was further diluted to contain 0.025 mg of the metal per ml.

Ammonium thiocyanate solution: A 4 M solution of AnalaR NH_4SCN was prepared just before use.

All other chemicals and apparatus were the same as used earlier¹.

Procedure: An aliquot of niobium solution containing 10–90 μg . of the metal was taken in a separatory funnel. Added 3–4 ml. of 4 M NH_4SCN solution followed by enough 10 M hydrochloric acid so as to make acid strength in the range 5–8 M. The solution was then gently extracted with 5 ml. of the reagent solution and 5 ml. of purified carbon tetrachloride or chloroform as the case may be. The golden yellow organic layer was collected in a small beaker containing 2 g. of anhydrous sodium sulphate. The aqueous layer was washed with 5 ml. of the solvent and added the washings of the beaker. The coloured solution was decanted to a 25 ml. volumetric flask. The sodium sulphate was washed with small portions of the solvent and combined the washings with the main solution. The solution in the flask was diluted to the mark with the solvent and the absorbance was measured at the recommended wavelength against reagent blank.

Discussion

Absorption spectra: All the complexes are yellow in colour and show no absorption maximum in the wavelength range 370–560 nm. The general nature of the absorbance curves is like that of the ASPHA complex¹. The most suitable wavelength for spec-

trophotometric work for each reagent is given in Table 2.

Effect of changing concentration of acid, thiocyanate and reagent: The minimum amount of reagent solution and thiocyanate solution for maximum colour intensity as well as the optimum hydrochloric acid strength are given in Table 2. Sulphuric acid was found to decrease colour intensity.

Effect of varying time and temperature: At room temperature the complexes slowly dissociated after about 12–24 hr. Afterwards a turbidity was formed. The colour intensity was not affected on changing temperature from 15° to 50°.

Solvents used: The complexes are soluble in common organic solvents. But for convenient extraction chloroform and carbon tetrachloride were tried. But it was found that all the complexes dissociated rapidly in chloroform except that of N-*p*-nitrobenzoyl-N-phenylhydroxylamine. Therefore, carbon tetrachloride was used for the study except for the latter reagent for which chloroform was used.

Sensitivity and optimum concentration range: The photometric sensitivity according to Sandell⁵, the molar absorptivity and optimum concentration range⁶ for the complexes of the reagents, which are of sufficient stability for the study, are given in Table 2.

Composition of the complexes: The stoichiometric composition of the complexes with respect to niobium, the reagent and thiocyanate were established by the method of continuous variations⁷ and molar ratio method⁸ as given in a previous paper².

For continuous variations method, two series of solutions were used. In one series, equimolar solutions ($0.5 \times 10^{-3} M$) of niobium and the reagent were used, keeping a constant excess of thiocyanate. From the maximum in the curve, the ratio of metal to reagent is found to be 1 : 2. In the other series,

TABLE 2—REAGENTS APPLIED FOR SPECTROPHOTOMETRIC DETERMINATIONS

No.	Name of Reagent	Sensitivity $\mu\text{g}/\text{cm}^2$	Wave length nm.	Optimum concentration Range $\mu\text{g}/\text{ml}$.	Molar absorptivity	Stability at room temperature, hrs.	Amount of 4M NH_4SCN solution ml.	Amount of 0.25% (w/v) Reagent solution ml.	Strength of HCl, M.
III.	N-acetylsalicyloyl-N- <i>p</i> -tolylhydroxylamine	0.0029	380	0. 2–2.8	28700	12	2	1	4–8
IV.	N-acetylsalicyloyl-N- <i>o</i> -chlorophenylhydroxylamine	0.0037	390	0. 25–3.5	22800	20	.2	2	4.5–8
VI.	N-acetylsalicyloyl-N- <i>p</i> -chlorophenylhydroxylamine	0.0055	390	0. 5–4.5	15200	18	3.5	2.5	5–8
VII.	N-acetylsalicyloyl-N- <i>o</i> -bromophenylhydroxylamine	0.0035	380	0.25–3.5	23650	24	1	3.5	4.5–8
X.	N- <i>p</i> -nitrobenzoyl-N-phenylhydroxylamine	0.0050	410	0. 5–4.5	17230	12	2.5	1	4–8

equimolar solutions ($2 \times 10^{-3} M$) of niobium and thiocyanate were used, maintaining a constant excess of the reagent. From the maximum in the curve the metal to thiocyanate ratio is found to be 1 : 1.

Similarly, molar ratio method was also applied to confirm the composition using two series of equimolar solutions.

Effect of diverse ions: Most of the associated cations do not interfere with the determination in very large excess. Thus, Tl^+ , Hg^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , Mn^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Fe^{2+} , B^{3+} , Ni^{2+} , Al^{3+} , Fe^{3+} , Cr^{3+} , Bi^{3+} , As^{3+} , Sb^{3+} , La^{3+} , Co^{4+} , V^{4+} , Th^{4+} , Zr^{4+} , V^{5+} , W^{6+} , Mo^{6+} and U^{6+} are tolerated in 1000 times excess. Cu^{2+} is masked by EDTA. Ta^{5+} can be tolerated upto 100 times excess. Ti^{4+} interferes. Of the various anions and complexing agents, F^- seriously interferes. Oxalate is tolerated upto 200 times excess. Acetate, citrate, tartrate and EDTA do not interfere at all.

Effect of substituents on reagent properties: The methyl and halogen substituents were introduced with a view to improve the reagent properties of ASPHA. However, reagents I and II form coloured complexes with niobium which are too insensitive for

spectrophotometric study. The failure of reagent VIII to form any complex with niobium is a vivid example of steric hindrance due to the large iodine; whereas the corresponding chloro and bromo derivatives do react well. Reagent V and IX are not forming stable complexes probably because of the weak conjugative effect of halogen at too far positions with respect to the coordinating centre.

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