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Note

Preparation and Properties of *N*-Arylhydroxamic Acids. Spectrophotometric Determination of Vanadium(V) with *N*-Phenylphenylpropiolohydroxamic Acid

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Twenty *N*-arylhydroxamic acids, three of which contain a triple bond in the side chain, have been synthesized and characterised by elemental analysis, melting point, spectral characteristics in the infrared region, and reaction with vanadium(V). All the *N*-arylhydroxamic acids form chloroform extractable coloured complexes with vanadium(V) in a strong hydrochloric acid medium. The use of *N*-phenylphenylpropiolohydroxamic acid as reagent for vanadium(V) by spectrophotometric method is described.

The preparation and properties of a large number of *N*-arylhydroxamic acids have been reported in recent years[1-11], and they have been applied as analytical reagents for the estimation of metal ions[3,5,12-16]. The sensitivity and selectivity of hydroxamic acids can be altered by changing the substituent groups attached to the hydroxamic acid functional group[15,17-19]. The introduction of the side chain double bond increases sensitivity for the vanadium(V) colour reaction[3,20-21]. Twenty new *N*-arylhydroxamic acids have been synthesized for use as possible analytical reagents. Three of these, containing triple bond in the side chain, are derived from phenylpropiolic acid. Similarly, another three containing acetyl group in the side chain are derived from acetyl mandelic acid. The remaining fourteen derived from different carboxylic acids containing different substituents have been synthesized and reported here. Their melting point, elemental analysis, infrared spectra and reaction with vanadium(V) in strong hydrochloric acid medium are described and given in Table I.

N-Phenylphenylpropiolohydroxamic acid ($\lambda_{max} = 560$ mμ $\varepsilon = 5900 + 50$ l mol^{-1} cm^{-1}) is found to be a very sensitive reagent for vanadium(V). The bluish-violet coloured complex with vanadium(V) is extractable in chloroform and other organic solvents from a stron hydrochloric acid medium.

EXPERIMENTAL

Apparatus. — A Carl Zeiss UV VIS Specord and C. Z. Specol (Spectro Colorimeter) with 10 mm matched silica cells were employed for spectrophotometric measurements. IR Spectra have been recorded on a Perkin-Elmer Model 177 Infrared Grating Spectrophotometer.

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TABLE I

Properties of Hydroxamic Acids

Compound No.	Hydroxamic acid (Formula)	m. p./°C	Elemental Analysis % of Nitrogen		Infra red spectra			Spectral Characteristics of coloured vanadium (V)-*N*-aryl-hydroxamic acid complexes in chloroform.	
			calc'd	found	ν (O—H) cm^{-1}	ν (C=O) cm^{-1}	ν (N—O) cm^{-1}	λ_{max} mμ	E l mol^{-1} cm^{-1}
1.	*N*-Phenyl-y.2:4-Dichloro-Phenoxy-Butyro-($C_{16}H_{15}NO_3Cl_2$)	101	4.12	3.94	3160	1630	940	520	4100
2.	*N*-*p*-Tolyl-y.2:4-Dichloro-Phenoxy-Butyro-($C_{17}H_{17}NO_3Cl_2$)	96	3.95	3.62	3170	1620	950	520	4050
3.	*N*-Phenyl-Acetyl-mandelo-($C_{16}H_{15}NO_4$)	135	4.91	4.82	3180	1640	910	520	4000
4.	*N*-*p*-Chloro-phenyl-Acetyl-mandelo-($C_{16}H_{14}NO_4$)	136	4.38	4.20	3170	1645	925	520	3900
5.	*N*-*p*-Tolyl-Acetyl-mandelo-($C_{17}H_{17}NO_4$)	126	4.68	4.41	3140	1630	940	520	4050
6.	*N*-*p*-Chlorophenyl-y.-2:4-Dichlorophenoxy-Butyro-($C_{16}H_{14}NO_3Cl_3$)	139	3.74	3.37	3290	1640	—	520	4200
7.	*N*-*m*-Tolyl-y.2:4-Dichlorophenoxy-Butyro-($C_{17}H_{17}NO_3Cl_2$)	105	3.95	3.43	3180	1620	940	520	4050
8.	*N*-*o*-Tolyl-y.2:4-Dichlorophenoxy-Butyro-($C_{17}H_{17}NO_3Cl_2$)	93	3.95	3.72	3270	1650	930	520	3900
9.	*N*-*p*-Chlorophenyl-α-β-Dibromo-Cinnamo-($C_{15}H_{12}NO_2ClBr_2$)	144	3.23	3.32	—	—	—	540	4300
10.	*N*-*p*-Chlorophenyl-Phenyl-propiolo-[a]($C_{15}H_{10}NO_2Cl$)	130	5.15	5.29	3160	1615	935	560	5600
11.	*N*-Phenyl-α-β-Dibromo-Cinnamo-($C_{15}H_{13}NO_2Br_2$)	156	3.50	3.12	3250	1640	900	520	4200
12.	*N*-Phenyl-Phenyl-propiolo[b]-($C_{15}H_{11}NO_2$)	65	5.90	5.42	3180	1610	920	560	5900
13.	*N*-*p*-Tolyl-Phenyl-propiolo[c]-($C_{16}H_{13}NO_2$)	86	5.57	5.51	3150	1635	915	560	5800
14.	*N*-*p*-Chlorophenyl-Hepto-($C_{13}H_{18}NO_2Cl$)	92	5.47	5.74	3170	1630	910	520	4350
15.	*N*-*p*-Tolyl-Hepto-($C_{14}H_{21}NO_2$)	79	5.95	5.42	3180	1625	905	520	4450
16.	*N*-Phenyl-Hepto-($C_{13}H_{19}NO_2$)	63	6.32	5.70	3160	1620	895	515	4200
17.	*N*-*p*-Chloro-Phenyl-Undecamo-($C_{17}H_{26}NO_2Cl$)	90	4.49	4.78	3140	1620	895	520	4250
18.	*N*-Phenyl-Undecano-($C_{17}H_{27}NO_2$)	83	5.04	4.83	3180	1625	900	520	4150
19.	*N*-*m*-Tolyl-Undecano-($C_{18}H_{29}NO_2$)	62	4.80	4.61	3160	1615	900	515	4050
20.	*N*-*p*-Tolyl-Undecano-($C_{18}H_{29}NO_2$)	76	4.80	4.47	3170	1620	900	520	4200

[a] ν ($C\equiv C$) 2220 cm^{-1} [b] ν ($C\equiv C$) 2225 cm^{-1} [c] ν ($C\equiv C$) 2230 cm^{-1}

Preparation of the Ligands. — Phenylpropiolic acid was synthesized by bromination of cinnamic acid in boiling carbon tetrachloride followed by dehydrohalogenation with methanolic potassium hydroxide. The melting point of the once crystallized product was 136 °C (reported 136 °C)[22].

Acetylmandelic acid was synthesized by the acetylation of mandelic acid with acetyl chloride at a low temperature[23].

The other carboxylic acids were available commercially. Acid chlorides were prepared by the action of thionyl chloride on corresponding carboxylic acid[24].

N-Arylhydroxylamine was prepared by the reduction of corresponding nitrobenzene with zinc dust and ammonium chloride from aqueous and aqueous ethanolic solution and crystallized from the mixture of benzene and petroleum ether[1,25].

The hydroxamic acids were prepared by the method of Priyadarshini and Tandon[18], by the condensation of acid chloride and the desired *N*-arylhydroxylamine at a low temperature in diethylether medium made alkaline with a suspension of sodium bicarbonate. All the hydroxamic acids were recrystallized from the mixture of benzene and petroleum ether at least twice. The crystals were obtained after keeping the solution in ice overnight in the case of phenylphenylpropiolohydroxamic acid. Elemental analyses were made and the melting point, and infrared spectra of the synthesized hydroxamic acids have been determined for their characterization. Infrared spectra were taken in Nujol as mull.

Reagents. — 0.1% (w/v) hydroxamic acid solutions in ethanol-free chloroform were used for all extraction works.

Ammonium metavanadate. — A stock solution was prepared by dissolving analytical grade ammonium metavanadate in glass distilled water and oxidized by potassium permanganate solution in sulphuric acid medium, to keep vanadium in the pentavalent state. The vanadium content was determined by standard methods.

Diverse ions. — The solutions of diverse ions were prepared from reagent grade salts using the procedure of West[26].

Colour reaction. — The chloroform solution of N-arylhydroxamic acids reacts with vanadium(V) giving extracts the colour of which depends on hydrochloric acid concentration. The molar absorptivities of the coloured complexes were determined at their respective wavelength of maximal absorption by the method described earlier[16,20]. Many organic solvents, such as chloroform, benzene, carbonatetrachloride, 1:2-dichlorobenzene, ethyl acetate and diethyl ether could be used for the extraction of coloured complexes. Chloroform was found to be the most suitable solvent.

Absorption spectra. — The absorption spectra of the coloured chloroform extracts were determined in the visible region. The hydrochloric acid concentration of the aqueous phase was adjusted to 4 molar, except in the case of compounds No. 3—5, 9 and 11, where hydrochloric acid concentration was adjusted to 6 molar, which was their optimum acidity range.

The results of the studies are given in Table I. *N*-phenylphenylpropiolohydroxamic acid was found to be the most sensitive reagent for vanadium(V), hence it was studied in detail.

Spectrophotometric Determination of Vanadium(V) with N-*Phenylphenylpropiolohydroxamic Acid*

Reagent Solution. — A 0.1% (w/v) solution of *N*-phenylphenylpropiolohydroxamic acid in ethanol free chloroform was used for all extractions. The reagent blank is negligible at 560 mμ.

Procedure. — Transfer an aliquot of the sample solution containing 0.02 to 0.15 mg of vanadium (all in the pentavalent state) into a separatory funnel. Adjust the volume of the solution to about 25 ml and the acidity to 4.0—8.0 mol/dm^3 using concentrated hydrochloric acid. Add 10 ml of 0.1% chloroform solution of *N*-phenylphenylpropiolohydroxamic acid and shake the funnel vigorously. Allow the phase to separate for 2 minutes, and proceed as described earlier[16,20]. Measure the absorbance against chloroform as blank at 560 mμ and calculate the amount of vanadium(V) corresponding to the absorbance with reference to a calibration curve.

RESULTS AND DISCUSSIONS

In aqueous media which are 2—10 mol/dm^3 in hydrochloric acid, *N*-phenylphenylpropiolohydroxamic acid reacts with vanadium(V) to form a bluish violet complex, extractable in many organic solvents.

This extract has a broad absorption band arround 560 mμ, with a molar absorptivity of 5900 + 50 l mol^{-1} cm^{-1} (calculated on the basis of vanadium(V)).

It should be noted that there is no reaction between vanadium(IV) and *N*-phenylphenylpropiolohydroxamic acid.

The optimal hydrochloric acid concentration range in the aqueous phase is 4—8 mol/dm^3. The absorbance decreases by 5% in 3 mol/dm^3 hydrochloric acid and by 10% in 9 mol/dm^3 hydrochloric acid. Only hydrochloric acid is suitable for adjusting the acidity.

Colour is extracted into the chloroform layer within 2 minutes and remains stable for 24 hours.

Absorbance increases rapidly as the mole ratio of the reagent to vanadium(V) increases from 1 : 1 to 8 : 1, then it remains constant up to 100 : 1. In practice, for each milligram of vanadium(V) 60—70 mg of the reagent were used. The order of mixing of the reagent is not critical.

Beer's law is obeyed in the concentration range 21.5—175 μg. of vanadium(V) per 25 ml, hence the practical range for the determination of vanadium is computed to be 1.75—6.05 p. p. m.

The procedure for the effect of diverse ions was the same as described earlier[20]. The results obtained in some typical determinations of vanadium(V) are given in Table II. The following ions do not interfere: Al(III), Ag(I), Ba(II),

TABLE II

Effect of Diverse Ions (Vanadium(V) concentration = 127.56 μg/25 ml.)

Ion	Added as	Amount added/mg	Absorbance at 560 mμ
None	—	—	0.605
Ag^+	$Ag(NO_3)$	30	0.605
Al^{+3}	$Al(NO_3)_3$	30	0.605
Ba^{+2}	$BaCl_2$	30	0.600
Ca^{+2}	$Ca(NO_3)_2$	30	0.605
Cd^{+2}	$CdCl_2$	30	0.610
Ce^{+4}	$(NH_4)_2Ce(NO_3)_6$	20	0.600
Co^{+2}	$Co(NO_3)_2$	30	0.605
Cu^{+2}	$Cu(NO_3)_2$	30	0.605
Fe^{+3}	$Fe(NO_3)_3$	30	0.605
K^+	KCl	20	0.600
Mn^{+2}	$Mn(NO_3)_2$	30	0.610
MoO_4^{-2}	$(NH_4)_2MoO_4$	5	0.385
NH_4^+	NH_4NO_3	30	0.605
Ni^{+2}	$Ni(NO_3)_2$	30	0.610
Sr^{+2}	$SrCl_2$	20	0.600
Sulfate	H_2SO_4	30	0.605
UO_2^{+2}	$UO_2(NO_3)_2$	30	0.605
WO_4^{-2}	Na_2WO_4	5	0.465
Zr^{+4}	$Zr(NO_3)_4$	10	0.605
Oxalate	$H_2C_2O_4$	30	0.605

Ca(II), Cd(II), Ce(IV), Co(II), Cu(II), Fe(III), K(I), Mn(II), Ni(II), Sr(II), U(VI), Zr(IV), ammonium, nitrate, oxalate, and sulphate. Mo(VI) and W(VI) interfere. Zr(IV), which interferes in the determination of vanadium(V) with PBHA, does not interfere in this determination.

The absorption bands due to O—H, C=O, and N—O stretching vibrations are assigned to regions 3290—3140 cm^{-1}, 1650—1610 cm^{-1}, and 950—895 cm^{-1}, respectively.

These bands are in agreement with the reported value[27-29]. In the region 2230—2220 cm^{-1}, C≡C stretching vibration bands were obtained, which are in agreement with the reported value[27].

Contrary to our anticipation that hydroxamic acids with triple bond may be more sensitive to vanadium(V) and more selective reagents for metal ions, it has been observed that their sensitivity to the vanadium(V) reaction is nearly the same or even less than that of hydroxamic acid containing double bonds in the side chain. The effects of the other substituent were similar to those observed earlier[16]. The reactions of the synthesized hydroxamic acids with other metal ions are now under investigation to develop analytical reagents.

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SAŽETAK

Priprava i svojstva *N*-arilhidroksamskih kiselina. Spektrofotometrijsko određivanje vanadij(V) s *N*-fenilfenilpropiolohidroksamskom kiselinom

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Pripravljeno je i opisano dvadeset *N*-arilhidroksamskih kiselina. Sve kiseline tvore komplekse s vanadij(V) i mogu se ekstrahirati s kloroformom u jako kiselom mediju. Tri kiseline sadrže trostruku vezu u pokrajnom lancu. *N*-fenilfenilpropiolohidroksamska kiselina je opisana kao reagens za vanadij(V).

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