

A Spectroscopic Study of N-p-Tolyhydroxamic Acids

Chemistry

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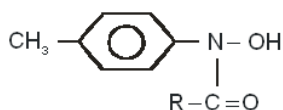
ABSTRACT

The ultraviolet and infrared spectra of several N-p-tolyl substituted hydroxamic acids, $\text{CH}_3\text{C}_6\text{H}_4\text{N}(\text{OH})\text{COR}$, have been determined and interpreted. These hydroxamic acids are involved in intramolecular hydrogen bonding. The absorption bands due to $-\text{OH}$, $=\text{CO}$, and $-\text{NO}$ occur at 3250-3110, 1640-1610 and around 940 cm^{-1} , respectively. In ultraviolet region the benzenoid absorption predominates. The band positions, shapes and intensities are strongly influenced by the nature of solvents. Spectra in concentrated sulphuric acid throw a light on the protonation behaviour of these hydroxamic acids. These compounds were prepared by coupling N-p-tolyhydroxylamine with acid chloride in weakly alkaline media and characterized by elemental analyses and melting points.

KEYWORDS:

INTRODUCTION:

Hydroxamic acids are becoming increasingly important class of compounds because of their applications in analytical chemistry (1-7) and biological science (8-12). Lesser systematic studies have been made to interpret the spectra of hydroxamic acids. In present communication IR and UV spectra of N-p-tolyhydroxamic acids, represented by general formula I, are described.



I

R = chloromethyl, cinnamo, hydrocinnamo, 2-furyl or substituted phenyl group.

EXPERIMENTAL:

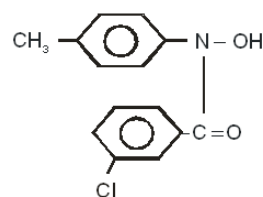
Apparatus and Materials- A Perkin-Elmer Model 377 double beam recording spectrophotometer, equipped with potassium bromide disks and cells of 0.2 mm path length, was used for determining infra-red spectra of hydroxamic acids. The spectrophotometer was calibrated by standard method using polystyrene film. The hydroxamic acids were dried in vacuum over P_2O_5 for several hours. The spectra of all the hydroxamic acids were determined from suspension in nujol. The spectra of hydroxamic acid no. 1 and 2 were determined in carbontetrachloride also.

A Carl Zeiss UV VIS Specord recording spectrophotometer, with 10 mm matched silica cells, was used for determining ultraviolet absorption spectra. An Electronic Corporation of India, Model G.S. 865, and spectrophotometer was used for absorption measurements at fixed wavelengths for calculation of molar absorptivity. The molar absorptivity, ϵ , is expressed in units of litre . Molar absorptivity at the wavelength of maximum absorption was determined in 95% ethanol, dioxane, water, 0.1 N HCl (GR. S. Merck) and 0.1 N KOH (Analar, BDH). In concentrated H_2SO_4 (G.R. BDH about 36N) the position of absorption band only was determined. The shift in absorption band with time was also studied.

95% ethyl alcohol and dioxane were purified by standard methods (13). Glass distilled water was used throughout. The aqueous, acidic and alkaline solutions of hydroxamic acid were prepared fresh and spectra were scanned within two minutes. This was done to avoid complications due to the possible acid or base catalysed hydrolysis of hydroxamic acids. The alkaline solutions of hydroxamic acids are unstable and even in dilute solutions (0.1 N KOH) turn green or bluish-green in about two to three hours.

Preparation of Hydroxamic Acids- The method for preparing the

typical compound N-p-tolyl-m-chlorobenzohydroxamic acid is described below :

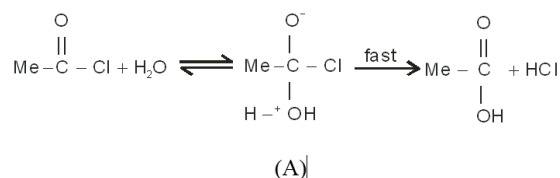


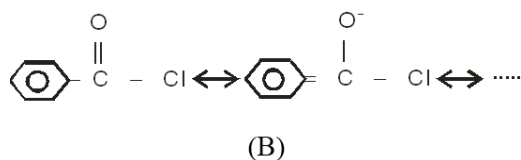
All other hydroxamic acids reported here were prepared similarly.

2.5 g (0.02 mole) of freshly prepared and purified N-p-tolyhydroxylamine (obtained by the reduction of p-nitrotoluene with Zn dust and NH_4Cl) dissolved in 35 ml. Diethyl ether and a suspension of about 4g sodium bicarbonate in 5.0 ml water, were mixed together and stirred mechanically. External cooling was done to bring the temperature of 0°C or lower. A solution of 3.5 g (0.02 mole) m-chlorobenzoylchloride in 40 ml of diethyl ether was added from a dropping funnel during the course of about 60-90 minutes. It was then triturated in a mortar with 25 ml of saturated solution of sodium bicarbonate for removing the acidic impurities. The solution was filtered and the solid was washed with water and dried. The product was crystallized from a mixture of benzene and petroleum ether two times. The yield of once crystallized product was 4.2 g (80%).

RESULTS AND DISCUSSION:

Preparation : All of the hydroxamic acids are obtained as crystalline solids, the yield ranging from 60 – 90%. The preparations confirm the observation of earlier workers that the use of stoichiometric proportions of N-substituted hydroxylamine and acid chloride was most satisfactory for obtaining a pure product. With excess of acid chloride dimerivative was formed and with excess of hydroxylamine the product was impure due to the decomposition products such as azobenzene, azoxybenzene, nitrosobenzene and aniline (14 – 16). Low temperature and longer period of addition helped in improving the yield and minimizing side reactions involving n-acylation. The hydrolysis of acid chlorides, particularly of alkyl acid chlorides, is also minimized at low temperature. The rate of hydrolysis of acetyl chloride is much faster (A) than those of aroyl chlorides. In benzoyl chloride (B) the electrophilic character of carbon atom of carbonyl group is much less than





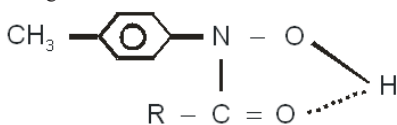
in Me-CO-Cl and so its reaction with water (the nucleophile) is very much slower than of acetyl chloride.

Properties : The properties of hydroxamic acids are summarized in Table I. Except cinnamic acid derivative which in light yellow all are white compounds. These are stable towards heat, light and air and can be stored indefinitely in tightly stoppered bottles. Their aqueous, alcoholic, chloroform, dioxane solutions, too are stable and can be kept for several weeks, if stored in amber bottles. The solutions in alkaline and acidic media are unstable due to hydrolysis. The alkaline solutions turn green or bluish-green within two-three hours. All the hydroxamic acids described here are sparingly soluble in water but are soluble in organic solvents such as benzene, diethyl ether, chloroform, o-dichlorobenzene, ethanol, dioxane etc. and also in ammonia and caustic alkali solutions.

All hydroxamic acids gave the characteristic purple colour test with ferric chloride. The chloroform solutions of all hydroxamic acids give violet coloured extracts when these are shaken with ammonium metavanadate solution in 4N HCl.

Infrared Spectra. The changes in electron density around the characteristic group due to substitution in the molecule bring about displacements in the positions of absorption bands. The mesomeric (M) and inductive (I) effects, steric inhibition of resonance, intra and intermolecular interactions, physical state etc. alter the positions of absorption band in infrared region.

O-H band – The O-H stretching band is assigned in the region of 3255-3110 cm^{-1} (Table -1). The position and shape of the band depends upon the extent of hydrogen bonding. As the strength of hydrogen bonding increases the band becomes more broad and moves to lower frequency. All the hydroxamic acids are involved in strong intramolecular hydrogen bonding.



C=O band – This band appears in the region 1640-1608 (Table 1). The displacement of the band to lower frequencies further confirms the formation of intramolecular hydrogen band.

N-O band - In oximes, this band appears around 950 cm^{-1} . In N-arylhydroxylamines, this band appears around 928 cm^{-1} (15). In the hydroxamic acids examined here, the absorption due to N-O stretching vibration occurs in the range 924-960 cm^{-1} (Table 1).

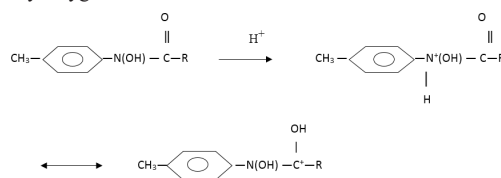
Ultraviolet spectra – All of the hydroxamic acids show strong absorptions in the region 270±20nm. The shape, position and magnitude of absorption of the band strongly confirm the benzenoid absorption. The substituent groups and the solvent used for examining the spectra

strongly influence the shape, position and the intensity of the band. In the parent compound, N-p-tolylbenzohydroxamic acid, the absorptions, band appears at 270 nm. In 3, 5 dimethoxy derivative (compound 4) this band shifts to 279 nm. The shift in band position to 285 nm is still more conspicuous in cinnamo derivative compound 8. At this stage no explanations for shift in band positions can be given quantitatively although qualitatively these shifts are in conformity with expected electronic and resonance effects. In 2-furo derivative (compound 5) the broadness of the absorption band is probably due to overlapping of absorptions bands of furyl and phenyl rings both. Though the band is not fairly resolved in ethanol, yet in dioxane presence of a shoulder at 257 nm in addition to absorption maximum at 285 nm indicates two distinct absorptions. In monochloroaceto derivative (compound 6) which has single substituted benzene ring, the overall electronic interaction is such as to cause the absorption at 255 nm.

With increasing polarity of solvents the spectra suffer a loss in vibrational fine structure because of strong solvent-solute interaction. In non polar solvent, dioxane (D=2.24) the bands are generally very sharp. In ethanol (D=25) too the bands are fairly well defined although these are relatively broad. In aqueous solution (D=78), however, either very broad bands or shoulders are observed. In several cases bands are altogether obliterated. Such behaviour indicates strong solute-solvent interaction in polar media.

The spectra of most of the hydroxamic acids in dilute hydrochloric acid (~0.1N) and water are super imposable within limits or experimental error. This shows that the molecular form is the absorbing species and protonated species is practically absent in dilute acids solutions. In alkali solutions (~0.1N KOH) the absorptions spectra are completely changed. These arise from the anionic species. An additional band around 300 nm appears in these spectra. This band is absent in ethanol, dioxane, water and hydrochloric acid spectra.

With the exception of N-p-tolyl-m-chloro and N-p-tolyl-m-fluorobenzohydroxamic acid (compounds 2, 1) all hydroxamic acids when dissolved in concentrated H_2SO_4 (~36 N) show a shift in absorption maxima towards longer wavelengths. In former compounds the band shifts to lower wavelengths. The marked change in the positions of absorption band indicates the formations of protonated species. The evidence for site of protonation, either at carbonyl oxygen

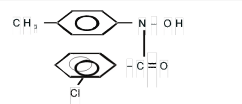
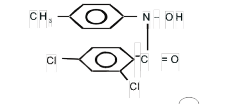
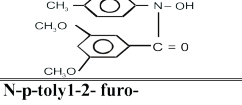
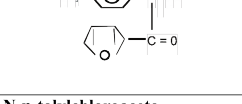
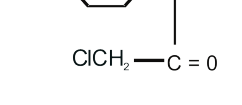
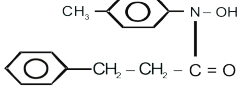
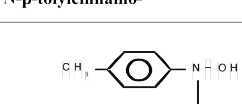


or hydroxylamino nitrogen, is to be adduced by more exhaustive studies especially by N. M. R. The effect of sulphuric acid concentration on the UV spectra is also being examined in more detail.

The UV spectra in concentrated sulphuric acid (~36N) are not significantly changed with time. However the cinnamo derivative (compound 8) shows reversal of intensities of band at 336 and 228 nm with time. The spectra recorded after 21 and 62 hours show that the peak at 228 nm is more intense than that at 336 nm although with fresh solutions the latter peak is more intense.

Table – 1: SPECTRAL CHARACTERISTICS OF N-p-TOLYLHYDROXAMIC ACIDS

S. No	Hydroxamic Acid	Mol. Formula & Mol. Wt.	M.P. C	ULTRAVIOLET, λ_{max} (nm) ϵ^a						INFRA-RED (NUJOL) cm^{-1}		
				Ethanol	Dioxane	Water	0.1N HCl	0.1N KOH	36N H_2SO_4	ν (O-H)	ν (C=O)	ν (N-O)
1	N-p-tolyl-m-fluorobenzo-											
		$\text{C}_{14}\text{H}_{12}\text{O}_2\text{NF}$ 245	99	271 (6.4)	271 (12.7)	GA	GA	GA	254 (Fresh) 250 (21) 255 (63)	b 3248 ^c	1630 1627 ^c	940 -

2	N-p-tolyl-m-Chlorobenzo-												
		$C_{14}H_{12}O_2NCl$ 261.5	99	274 (6.5)	277 (8.0)	GA -	GA -	275 (4.2)	258 (Fresh) 258 (21) 259 (63)	b 3255 ^c	1632 1638 ^c	940 940 ^c	
3	N-p-tolyl-2, 4- dichlorobenzo-												
		$C_{14}H_{10}O_2NCl_2$ 296	161	256 (10.0)	262 (9.6)	GA	GA	GA	270 (Fresh) 276 (21) 280(63)	3110	1615	940	
4	N-p-tolyl-3, 5- dimethoxybenzo-												
		$C_{15}H_{17}O_4N$ 287	130	274 (9.2)	279 (904)	GA	GA	288 (6.7)	- - -	3195	1630	927	
5	N-p-tolyl-2- furo-												
		$C_{12}H_{11}O_3N$ 217	131 ^d	285 (13.8)	284 (11.8)	269 (13.1)	268 (13.3)	245 (10.3)	301 (Fresh) 296 (21) 296 (63)	3130	1608	926	
6	N-p-tolylchloroaceto -												
		$C_9H_{10}O_2NCl$ 199.5	123	255 (9.9)	258 (9.6)	240 (7.1)	244 (7.4)	284 (6.7)	GA (Fresh) 264 (21) 264 (63)	3190	1640	930	
7	n-p-tolyl-hydrocinnano												
		$C_{16}H_{17}O_2N$ 255	118	255 (11.3)	256 (11.6)	GA -	GA -	GA -	260 (Fresh) 260 (21) 261 (63)	3180	1630	924	
8	N-p-tolylcinnamo-												
		$C_{16}H_{15}O_2N$ 253	156 ^e	288 (21.0)	285 -	293 (20.7)	292 (22.5)	272 (15.2)	336 (Fresh) 288 (21) 228(63)	3110	1630	950	

Abbreviation:

- Molar Extinction Coefficient, ϵ , is given in parentheses (10^3 litre mole⁻¹ cm⁻¹).
- Shoulder around 3100 cm⁻¹
- Spectra in CCl₄
- Reported, 142^o C, Tandon S.G., Bhattacharya, S.C. J. Chem. Engg. Data 1, 553(1962).
- Reported, 159^o C, Tandon S.G., Bhattacharya, S.C. J. chem.. Engg. Data 1, 553 (1962).
- GA, General Absorption
- Time elapsed, in hours, is given in parentheses.

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