

INFRARED SPECTROSCOPIC INVESTIGATION OF NITROPHENOL COMPLEXES

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Abstract : The sensitivity of the hydroxylic stretching frequency of a particular substance in different solvents in the presence of proton acceptors, viz. organic bases, has been analysed to understand the nature of the interaction between the two entities and the extent of complex formation¹. The type (s) of complexes formed by 4 – nitrophenol, 2,4 – dinitrophenol and picric acid with nitrogenous bases including the tertiary amines, viz. triethylamine, 1,4 – diazabicyclo [2.2.2] octane (DABCO), 1,5 – diazabicyclo [5.4.0] undec – 5 – ene (DBU) and 4 - (N,N – dimethyl amino) Pyridine (4 – DMAP) in non – hydroxylic solvents, such as chloroform, dichloromethane, acetone, acetonitrile and tetrahydro furan have been analysed in this present investigation.

IndexTerms - 4- Nitrophenol, 2,4- dinitrophenol, 2,4,6- trinitrophenol.

I. INTRODUCTION

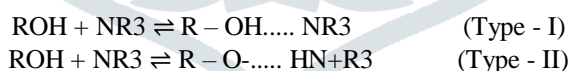
4–Nitrophenol (Riedel), 2,4–dinitrophenol (SISCO) and 2,4,6– Trinitrophenol (ALFA Biochom) were recrystallized from benzene and dried under reduced pressure. Triethyl amine (Glaxo) was freshly distilled before use. DABCO and DBU (both Aldrich) were used as such; 4 – DMAP (marck) was recrystallized from ether. Chloroform, dichloromethane, acetone, and tetrahydro furan were purified and dried as described in the literature.

II. THEORY

The equimolar mixtures of nitrophenols and amines were prepared by thoroughly mixing exactly their 0.4 M solutions in appropriate solvents. Infrared spectra were recorded on a Shimadzu IR – 435 spectro-photometer using sodium chloride liquid cell of slit width 0.072 cm for solutions

III. RESULTS AND DISCUSSIONS

The results are presented in Table 1. The stretching frequency for the free hydroxyl group of 4- nitrophenol appears as a sharp peak at 3580 cm⁻¹ in chloroform and dichloromethane solutions. Since the salvation through hydrogen bonding occurs, a shift in the peak position up to 3100 cm⁻¹ has been observed for the hydroxyl group in some solvents. When 4-nitrophenol is complexed with triethyl amine in chloroform or dichloromethane, a multiple absorption peak of medium intensity appears at 2400 cm⁻¹ which can be attributed to the presence of single hydrogen bonded complex of type -I, in the system². This system in acetone and acetonitrile gives an additional peak at 1900 cm⁻¹ indicating the formation of proton – transferred hydrogen bonded system of type –II, the proton of the nitrophenol is completely transferred to the base, but there is still hydrogen bonding interaction between the phenolate anion and the proton².



Due to the increase in polarity of the solvent, the formation of proton- transferred hydrogen bonded complex is favored. In Tetrahydro furan, however, no appreciable change in the spectrum of nitrophenol is observed in the presence of triethyl amine.

DABCO Forms Simple hydrogen bonded complex with nitrophenols as well as proton transferred hydrogen bonded complex in dichloro methane and acetonitrile to considerable extent, where as in tetrahydro furan, solid quaternary ammonium salt has separated out from the solution. It gives peaks at 2400 cm⁻¹, 3100 cm⁻¹ and 2000 – 1700 br cm⁻¹ due to N⁺H absorption³.

DBU-4-nitrophenol complexes are of both type – I and - II in all the solvents excepted in acetone where soluble quaternary ammonium salt results. The behaviors of 4–DMAP complexes with 4–nitrophenol also resembles that of DBU in all the solvents studied indicating the presence of equilibrium between type-I and II complexes. 2,4 – dinitrophenol gives OH stretching frequency at 3200 cm⁻¹ as a sharp peak accompanied by a broad peak at 3100 – 3400 cm⁻¹ in chloroform and in dichloromethane corresponding to U OH and U OH ... O (inter molecular) absorptions respectably. The same absorption occur at 3250 and 3100 – 2900 cm⁻¹ in the solvents viz. acetone, acetonitrile and tetrahydro furan. With triethyl amine, 2,4 – dinitrophenol forms simple hydrogen bonded complex in all the solvents used. The behavior of DABCO complexes of 2,4 – dinitrophenol is almost similar to that of triethyl amine. But, quaternary ammonia salt formation occurs in chloroform and acetone in addition to acetonitrile and THF. DBU is found to form both hydrogen bonded as well as soluble quaternary ammonium salt in chloroform and dichloro methane. 4–DMAP forms insoluble quaternary ammonium salt in chloroform and dichloro methane soluble quaternary ammonium salt in acetone and acetonitrile.

Table 1: I.R – Spectral Data for Nitrophenol – Amine Complexes in Various Solvents.

Phenol	Base	Solvents	γ_{\max} Cm^{-1}	Assignment
4- Nitrophenol	Triethyl amine	$\text{CHCl}_3, \text{CH}_2\text{Cl}_2$ acetone	2400 m	HO ...N
		acetonitrile Aceto nitrile Acetone	3500 w 1900 w	N ⁺ H O ⁻ ...N ⁺ H
	DABCO	CH_2Cl_2 , acetone, acetonitrile, THF CHCl_3^a	2400 m 3100s, 2400 m	HO...N N ⁺ H
		CH_2Cl_2 , acetonnitrile, THF Acetone	1900 m 3500 s	O ⁻ ...N ⁺ H N ⁺ H
DBU	$\text{CHCl}_3, \text{CH}_2\text{Cl}_2$ acetone, acetonitrile, THF $\text{CHCl}_3, \text{CH}_2\text{Cl}_2$, acetonitrile, THF Acetone	2400 m	HO...N	
		1900 m 3500 m	O ⁻ ...N ⁺ H N ⁺ H	
4 -DMAP	$\text{CHCl}_3, \text{CH}_2\text{Cl}_2$ acetone Acetonitrile	2400 m 1900 w	HO...N O ⁻ ...N ⁺ H	
2,4- Dinitrophenol	Triethyl amine	$\text{CHCl}_3, \text{CH}_2\text{Cl}_2$ acetone, acetonitrile, THF Acetonitrile THF	2400 m 3500 m 1900 m	HO...N N ⁺ H O ⁻ ...N ⁺ H
		$\text{CHCl}_3, \text{CH}_2\text{Cl}_2$ acetone, acetonitrile, CHCl_3 , acetone, acetonitrile THF THF	2400 m 3500 m 1920 m	HO...N N ⁺ H O ⁻ ...N ⁺ H
	DBU	$\text{CHCl}_3, \text{CH}_2\text{Cl}_2$ acetone, acetonitrile Acetone Acetonitrile	2400 m	HO...N
			3500 m 1900 m	N ⁺ H O ⁻ ...N ⁺ H
4 – DMAP	$\text{CHCl}_3^a, \text{CH}_2\text{Cl}_2^a$ Acetonitrile	3100 s 2600 s 2050 s 1900 s 3500 w, 2400 m	N ⁺ H N ⁺ H HO...N	
2,4,6 Trinitrophenol (Picric acid)	Triethyl amine	$\text{CHCl}_3, \text{CH}_2\text{Cl}_2$ acetone, acetonitrile, THF Acetone Acetonitrile	2400 m	HO...N
			3500 m	N ⁺ H
	DABCO	$\text{CHCl}_3^a, \text{CH}_2\text{Cl}_2^a$, THF ^a , acetonitrile Acetone	3400 s 3100 s 2800 m 3500 m	N ⁺ H N ⁺ H
			2900 m 1900 m	HO...N HO...N N ⁺ H
DBU	$\text{CHCl}_3, \text{CH}_2\text{Cl}_2$, acetone, Acetonitrile, THF Acetone	2900 m	HO...N	
		1900 m	HO...N N ⁺ H	
4 – DMAP	CHCl_3 CH_2Cl_2^a , acetone ^a , Acetonitrile ^a	2950 m 3200 m 1900 m	HO...N N ⁺ H	

'a' spectra of the thrown out side taken in KBr wafer.

2,4,6 – Trinitrophenol (Picric acid) gives fairly sharp peak at 3100 cm^{-1} (OH) in chloroform and dichloromethane. In acetone and acetonitrile a broad peak appears at $3200\text{ -}2900\text{ cm}^{-1}$ (O-HO), and the same appears at $3100\text{ -}2800\text{ cm}^{-1}$ in tetrahydro furan. Tri ethylamine forms simple hydrogen bonded complex in chloroform and dichloro methane and soluble quaternary ammonium salt in acetone, acetonitrile and THF. DABCO form insoluble quaternary ammonium salt in all the solvents except in acetone whereas the quaternary ammonium salt is soluble. In addition, presence of simple as well as proton – transferred hydrogen bonded complex was also noticed in acetone establishing equilibrium among all the three types of complexes. The spectrum of (picric acid) 2,4,6 – trinitrophenol under goes no significant change in the presence of DBU in chloroform, dichloro methane, acetonitrile and THF. 4 – DMAP forms simple hydrogen bonded complex in chloroform and insoluble quaternary ammonium salt in all the other solvents.

From the analysis above data it is concluded that nitrophenol – amine system forms simple hydrogen bonded complex in the solvents of low dielectric constant and proton – transferred hydrogen bonded complex in solvents of high dielectric constants. When the basicity of the amine is high (as in 4 - DMAP) and the solvent is polar (as acetone) dissociation of the complex is quaternary ammonium cation and phenoxide ion is facilitated

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