

Infrared Spectroscopic Investigation of Nitrophenol-Amine Complexes

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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*-dimethylamino)pyridine (4-DMAP) in non-hydroxylic solvents, such as chloroform, dichloromethane, acetone, acetonitrile and tetrahydrofuran have been analysed in this present investigation.

Experimental

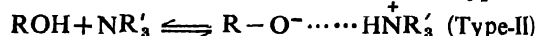
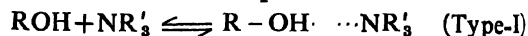
4-Nitrophenol (Riedel), 2,4-dinitrophenol (SISCO) and picric acid (ALFA Biochem) were recrystallised from benzene and dried under reduced pressure. Triethylamine (Glaxo) was freshly distilled before use. DABCO and DBU (both Aldrich) were used as such; 4-DMAP (Merck) was recrystallised from ether. Chloroform, dichloromethane, acetone and tetrahydrofuran were purified and dried as described in the literature.

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 spectrophotometer using sodium chloride liquid cell of slit width 0.072 cm for solutions.

Results and Discussion

The results are presented in Table I. The stretching frequency for the free hydroxyl group of 4-nitrophenol appears as a sharp peak at 3 580 cm⁻¹ in chloroform and dichloromethane solutions. Since the solvation through hydrogen bonding occurs, a shift in the peak position upto 3 100 cm⁻¹ has been observed for the hydroxyl group in some solvents. When 4-nitrophenol is complexed with triethylamine in chloroform or dichloromethane, a multiple absorption peak of medium intensity appears at 2 400 cm⁻¹ which can be attributed to the presence of simple hydrogen bonded complex of type-I in the system². This system in acetone and acetonitrile gives an additional peak at 1 900 cm⁻¹ indicating the formation of proton-transferred hydrogen bonded system of type-II along with simple hydrogen bonded complex I. In 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 favoured. In tetrahydrofuran, however, no appreciable change in the spectrum of nitrophenol is observed in the presence of triethylamine.

DABCO forms simple hydrogen bonded complex with nitrophenols as well as proton-transferred hydrogen bonded complex in dichloromethane and acetonitrile to considerable extent, whereas in tetrahydrofuran this complex is formed in small amount. In chloroform, solid quaternary ammonium salt has separated out from the solution. It gives peaks at 2 400, 3 100 cm⁻¹ and 2 000–1 700br cm⁻¹ due to NH^+ absorption³.

DBU–4-nitrophenol complexes are of both type-I and -II in all the solvents except in acetone where soluble quaternary ammonium salt results. The behaviour 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 3 200 cm⁻¹ as a sharp peak accompanied by a broad peak at 3 100–3 400 cm⁻¹ in chloroform and in dichloromethane corresponding to ν_{OH} and $\nu_{\text{OH} \cdots \text{O}}$ (intermolecular) absorptions respectively. The same absorptions occur at 3 250 and 3 100–2 900 cm⁻¹ in the solvents viz. acetone, acetonitrile and tetrahydrofuran. With triethylamine, 2,4-dinitrophenol forms simple hydrogen bonded complex in all the solvents used. The behaviour of DABCO complexes of 2,4-dinitrophenol is almost similar to that of triethylamine. But, quaternary ammonium 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 dichloromethane. 4-DMAP forms insoluble quaternary ammonium salt in chloroform and dichloromethane and soluble quaternary ammonium salt in acetone and acetonitrile.

Picric acid gives fairly sharp peak at 3 100 cm⁻¹ (OH) in chloroform and dichloromethane. In acetone and acetonitrile a broad peak appears at 3 200–2 900 cm⁻¹ (O–H \cdots O), and the same appears at 3 100–2 800 cm⁻¹ in tetrahydrofuran. Triethylamine forms simple hydrogen bonded complex in chloroform and dichloromethane and soluble quaternary ammonium salt in acetone, acetonitrile and THF. DABCO forms 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

NOTES

TABLE 1—IR SPECTRAL DATA FOR NITROPHENOL-AMINE COMPLEXES IN VARIOUS SOLVENTS

Phenol	Base	Solvent	ν_{\max} cm ⁻¹	Assignment
4-Nitrophenol	Triethylamine	CHCl ₃ , CH ₂ Cl ₂ , acetone, acetonitrile	2 400m	OH...N ⁺
		Acetone	3 500w	NH ⁺
		Acetonitrile	1 900w	O ⁻ ...HN ⁺
	DABCO	CH ₂ Cl ₂ , acetone, acetonitrile, THF	2 400m	OH...N ⁺
		CHCl ₃ ^a	3 100s, 2 400m, 2 000–1 700s	NH ⁺
		CH ₂ Cl ₂ , acetonitrile, THF	1 800m	O ⁻ ...HN ⁺
	DBU	Acetone	3 500s	NH ⁺
		CHCl ₃ , CH ₂ Cl ₂ , acetone, acetonitrile, THF	2 400m	OH...N
		CHCl ₃ , CH ₂ Cl ₂ , acetonitrile, THF	1 900m	O ⁻ ...HN ⁺
	4-DMAP	Acetone	3 500m	NH ⁺
		CHCl ₃ , CH ₂ Cl ₂ , acetone	2 400m,	OH...N ⁺
		acetonitrile	1 900w	O ⁻ ...HN ⁺
2,4-Dinitrophenol	Triethylamine	CHCl ₃ , CH ₂ Cl ₂ , acetone, acetonitrile, THF	2 400m	OH...N
		Acetonitrile	3 500m	NH ⁺
		THF	1 950m	O ⁻ ...HN ⁺
	DABCO	CHCl ₃ , CH ₂ Cl ₂ , acetone, acetonitrile	2 400m	OH...N ⁺
		CHCl ₃ , acetone, acetonitrile, THF	3 500m	NH ⁺
		THF	1 920m	O ⁻ ...HN ⁺
	DBU	CHCl ₃ , CH ₂ Cl ₂ , acetone, acetonitrile	2 400m	OH...N
		Acetone	3 500m	NH ⁺
		Acetonitrile	1 900m	O ⁻ ...HN ⁺
	4-DMAP	CHCl ₃ ^a , CH ₂ Cl ₂ ^a	3 100s, 2 600s, 2 050s, 1 950s	NH ⁺ N ⁺ NH
		Acetonitrile	3 500w, 2 400m	OH...N
Picric acid	Triethylamine	CHCl ₃ , CH ₂ Cl ₂ , acetone, acetonitrile, THF	2 400m	OH...N
		Acetone, acetonitrile	3 500m	NH ⁺
				NH ⁺
	DABCO	CHCl ₃ ^a , CH ₂ Cl ₂ ^a , THF ^a , acetonitrile	3 400s, 3 100s, 2 800m	NH ⁺
		Acetone	3 500m	NH ⁺
			2 400m	OH...N ⁺
	DBU		1 900m	O ⁻ ...HN ⁺
		CHCl ₃ , CH ₂ Cl ₂ , acetone, acetonitrile, THF	2 950m	OH...N ⁺ OH...N ⁺
		Acetone	1 900m	NH ⁺
	4-DMAP	CHCl ₃	2 950m	OH...N ⁺
		CH ₂ Cl ₂ ^a , acetone ^a , acetonitrile ^a	3 200m	NH ⁺
			1 900m	

^aSpectra of the thrown out solid taken in KBr wafer.

picric acid undergoes no significant change in the presence of DBU in chloroform, dichloromethane, 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 of the 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 to quaternary ammonium cation and phenoxide ion is facilitated.

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