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The Use of Benesi-Hildebrand Equation in Molecular Complex Formation of *o*-Nitrophenol with Some Hydrazine Derivatives through Electronic Spectra

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The electronic spectra of the molecular complex formation of *o*-nitrophenol and some hydrazine derivatives have been recorded, with the help of Shimadzu 160A model (Japan) UV spectrophotometer at room temperature. With the Benesi-Hildebrand equation in original form it has been found that it is difficult to determine the stability constant K_{AD} and molar extinction coefficient ε_{AD} of the possible molecular complexes formed in solution.

Further we have seen that the K_{AD} of molecular complexes formed with this acceptor (*o*-nitrophenol) in methanol solvent is always far less than unity explaining the weaker acceptor capability of *o*-nitrophenol in comparison to other nitro-substituted phenols as already studied earlier.

Key Words: Benesi-Hildebrand equation, Molecular complex, *o*-Nitrophenol, Hydrazine, Electronic spectra.

INTRODUCTION

Studies on charge transfer complex formation have been reported by a no. of workers. A large number of chemists like Mullikan[1], Pfeffer[2], Briegleb[3], Benesi-Hildebrand[4], Ketelaar[5], Foster[6] and Rose Drage[7] have contributed much in this field. Among some of the relevant equations.[8, 9] for determination of K_{AD} and ε_{AD}, we have tested Benesi Hildebrand equation which seems to be fit for the determination of molecular complex parameters in our system. The Benesi-Hildebrand equation has been based at least initially on the assumption that a simple complex species with a definite stoichiometry is formed.

$$K_{AD}^{10} = \frac{[AD]}{\{[D_0] - [AD]\} - [AD]}$$

The principle behind the calculation of K_{AD} of the complex in the solution involves the absorption spectrum of a solution containing a donor acceptor complex, is markedly different from the composite spectra of the free donor and the acceptor on the formation of complex is accompanied by a shift in the absorption maxim a of either the donor or the acceptor or both. In this method for evaluating K_{AD} and ε_{AD}, it is studied under the situation in which the concentration of one of the other components, usually the donor, is in large excess of the other component, *i.e.*, acceptor whose concentration is kept fixed at low value. The concentration of [D] which is kept ≫ [A] is varied. Under this experimental condition the above equation can be used as

$$K_{AD} = \frac{[AD]}{\{[A_D] - [AD]\} - [D_0]}.$$

This equation is valid for [D] ≫ [A] and neither A nor D absorbs in the region of the CT band. This equation demands that a plot of $[A_0]/d$ *vs.* $1/[D_0]$ should be linear with slope $1/K_{AD}$ and intercept $1/\varepsilon_{AD}$. This equation is the most suitable and popular method of evaluating K_{AD} and ε_{AD} of CT complexes from spectroscopic data.

But in the system in which we are interested, the B-H equation seems to be fit with slight modification[11] because of the involvement of much weaker acceptor and that is

$$\frac{n}{n+1}\frac{[A_0]}{A}=\frac{1}{\varepsilon_{Ad}}+\frac{1}{\varepsilon_{Ad}}\frac{1}{K_{AD}}\frac{1}{A_0(n+1)}$$

where [A] is initial concentration of acceptor and $n/(n+1)$ the mole fraction of acceptor.

EXPERIMENTAL

All chemicals, *o*-nitrophenol, 2,4-dinitrophenyl hydazine and benzhydrazide, were purified by crystallization from alcohol and their m.p.s were checked carefully. Hydrazine and phenyl hydrazine (E. Merck) were used as such after checking their b.p. Methanol which was used as solvent was from E. Merck.

Stock solutions of acceptors and donors were prepared in methanol by measurement after appropriate dilution. All absorption measurements were recorded in well matched 5 mL silica cells through schimadzu 160 A model UV spectrophotometer (Japan).

RESULTS AND DISCUSSION

The CT spectra of *o*-nitrophenol with hydrazine, phenyl hydrazine, 2,4-dinitrophenyl hydrazine and benzhydrazide have been recorded. In this system four suitable wavelengths, *i.e.*, 345, 350, 355 and 360 nm have been selected for the determination of K_{AD} and ε_{AD} values. The calculations for K_{AD} and ε_{AD} at each wavelength have been carried out which have been tabulated in Tables 1 and 2. The plots were also drawn and they are linear, as reported earlier[12]. The values of K_{AD} and ε_{Ad} are still lower with respect to the two nitrophenols as reported earlier. But the order of these values with respect to selected donors is somewhat Different and is as follows:

2,4-Dinitrophenyl hydrazine > Phenyl hydrazine > Hydrazine < Benzhydrazide

As far as the intensity of the bonds and the stability of the complexes are concerned, we find both are poor in this system from which we assume that *o*-nitrophenol is not strong an acceptor as dinitro and trinitrophenol. The decrease of nitro group in phenol increases the donor property and decreases the acceptor property. Hence *o*-nitrophenol seems to be the weakest acceptor with respect to other nitro phenols.

Such apparent deviation which we observe here has been explained by Mulliken and Orgel[13] who suggested that there are two types of charge transfer complexes which satisfy mass action law and other with D-A pairs which happen to be together just through collisions. This was contradicted by Cartar Murell and

Rosch[14] and according to them this cannot be thermodynamically justified. However, we feel that in case of weak complex formation in our system, the solvent is also competing with the donor for the site around the donor, a belief that has been experimentally substantiated by the observation that K_{AD} depends on the solvents also. If the competition between complexing and solvation is allowed for, in theory, then in our opinion there is no need to invoke the concept of two kinds of complexes—real and contact, and the behaviour of weak complexes can be fitted into the same theory as that of strong complex. At this stage the solvent has been viewed as a competitor for either or both the donor and the acceptor. Further details require tedious computational investigations which seems difficult in the present situation.

Using various values of $[D]_0$ we have plotted the function and got a straight line. From the slope and intercepts we have determined the stability constant K_{AD} and molar extinction coefficient ε_{AD} of the various hydrazine derivatives of *o*-nitrophenol complexes. Although the values were verified using more other equations also but the Benesi-Hildebrand method gave more reliable values in view of the fact that there was appreciable absorbance by the acceptor solution at the wavelength where the complex AD absorbed.

Stability constants and order of basicity of donors and acidity of acceptors

The stability constant of complexes of o^{-}-nitro phenol with hydrazine derivatives can be seen in Table-1. The order may be comparable to that of Bronsted basicity of the aromatic NO_2 group is known to reduce the electron density at the nitrogen of the hydrazine derivatives. Thus stability constant of complexes may be taken as a measure of the Lewis basicity of the donor molecules. This order runs parallel to the π M.O. energies of respective amines. In case of o^{-}-nitrophenol, although the π orbital extends over the nitrogen atom but is not localized on it. Also the Lewis acid (nitro-substituted phenols) which it attracts may involve stereochemical factor in their interactions with some hydrazines, a factor which may be absent in the case of other interactions. This may hinder the Lewis acidity of the acceptors.

TABLE-1

DIFFERENT MOLECULAR PARAMETERS OF CT COMPLEXES AT SELECTED WAVELENGTH

Acceptor *o*-Nitro phenol (ONP)

	Donor											
max (nm)	Hydrazine			2,4-D.N.P.			Benzhydrazide			Phenyl hydrazine		
	ε_{AD} ($\times 10^5$)	K_{AD}	$\varepsilon_{AD}K_{AD}$ ($\times 10^5$)	ε_{AD} ($\times 10^5$)	K_{AD}	$\varepsilon_{AD}K_{AD}$ ($\times 10^5$)	ε_{AD} ($\times 10^5$)	K_{AD}	$\varepsilon_{AD}K_{AD}$ ($\times 10^5$)	ε_{AD} ($\times 10^5$)	K_{AD}	$\varepsilon_{AD}K_{AD}$ ($\times 10^5$)
345	.01	.04	.0004	.09	.12	.01	.07	.02	.001	.03	.05	.001
350	.01	.03	.0003	.08	.10	.008	.06	.02	.001	.02	.05	.001
355	.01	.03	.0003	.09	.12	.01	.06	.02	.001	.02	.05	.001
360	.01	.03	.0003	.09	.12	.01	.06	.02	.001	.02	.05	.001

TABLE-2

max (nm)	[D]	[A] *o*-Nitrophenol	Absorbance			
			Hydrazine	Phenyl hydrazine	2,4-D.N.P.	Benzhydrazide
345	1.00×10^{-3} M	1.00×10^{-2} M	0.90			
		2.00×10^{-3} M	0.10			
	1.25×10^{-4} M	2.00×10^{-3} M	0.25	1.55	1.90	1.70
		1.00×10^{-3} M	0.80	1.10	1.30	0.80
		2.50×10^{-4} M	1.50	0.20	0.65	0.25
		1.25×10^{-4} M	1.95	0.20	0.50	0.15
350	1.00×10^{-3} M	1.00×10^{-2} M	0.60			
		2.00×10^{-3} M	0.10			
	1.25×10^{-4} M	2.00×10^{-3} M	0.20	1.40	1.70	1.60
		1.00×10^{-3} M	0.50	1.00	1.30	0.70
		2.50×10^{-4} M	0.60	0.15	0.65	0.20
		1.25×10^{-4} M	0.70	0.10	0.50	0.10
355	1.00×10^{-3} M	1.00×10^{-2} M	0.80			
		2.00×10^{-3} M	0.20			
	1.25×10^{-4} M	2.00×10^{-3} M	0.25	1.50	1.60	1.50
		1.00×10^{-3} M	0.30	0.90	1.10	0.60
		2.50×10^{-4} M	1.00	0.10	0.60	0.10
360	1.00×10^{-3} M	1.00×10^{-2} M	1.00			
		2.00×10^{-3} M	0.90			
	1.25×10^{-4} M	2.00×10^{-3} M	0.30	1.30	1.50	1.10
		1.00×10^{-3} M	1.00	0.70	0.90	0.50
		2.50×10^{-4} M	1.50	0.10	0.50	0.10
		1.25×10^{-4} M	1.80	0.10	0.40	0.10

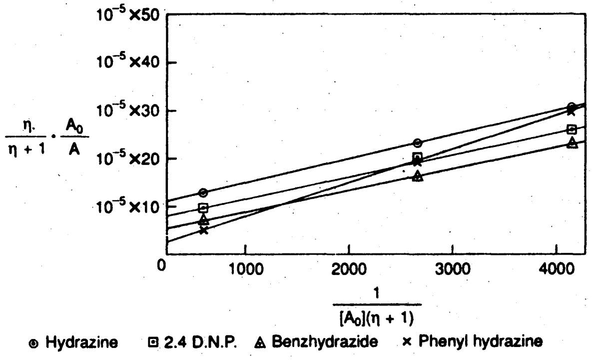


Fig. 1. B.H plot of *o*-nitrophenol *vs.* different donors (λ_{max} = 345 nm)

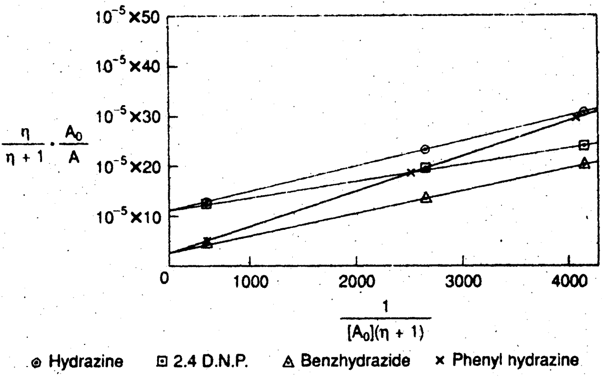
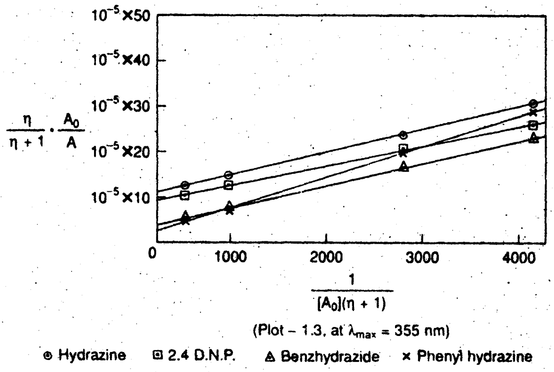
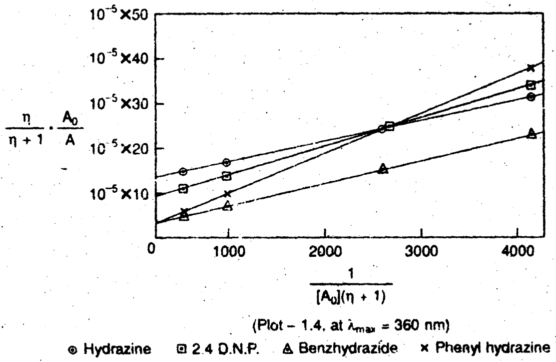


Fig. 2. B.H plot of *o*-nitrophenol *vs.* different donors (λ_{max} = 350 nm)



(Plot – 1.3, at λ_{max} = 355 nm)

Fig. 3. B.H plot of *o*-nitrophenol *vs.* different donors (λ_{max} = 355 nm)



(Plot – 1.4, at λ_{max} = 360 nm)

Fig. 4. B.H plot of *o*-nitrophenol *vs.* different donors (λ_{max} = 360 nm)

The acceptors like trinitrophenol (TNP), dinitrophenol (DNP) and nitrophenol (NP) in their interaction with four different hydrazines show the following order in each case with respect to their values K_{AD}.

TNP > DNP > NP

This is the expected order of the Lewis acidities. As we increase the NO_2 groups in the molecule, the NO_2 group being strong electron withdrawing group, the electron density of the lowest unoccupied M.O. will increase. Accordingly, *o*-nitrophenol will have the sufficient electron density with respect to trinitro phenol in the lowest unoccupied M.O. and hence it should behave as the moderate Lewis acid in the multi-substituted phenols due to the presence of phenolic group in benzene ring.

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