

UV Spectral Studies in Protonation of Cu-Phthalocyanine and Phthalocyanine in Sulphuric Acid-Solvent

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Our studies in protonation of phthalocyanine (H_2Pc) with sulphuric acid remove the controversy concerning its degree of protonation. The absorption spectra of phthalocyanine (H_2Pc) and Cu-phthalocyanine (CuPc) have been used to illustrate the effect of electronic nature of coordinated metal, its protonation depth and position of bands in sulphuric acid medium. The CuPc and its ligand H_2Pc absorb 786 nm and 754 nm respectively in sulphuric acid. The position of bands of H_2Pc and CuPc in electronic absorption spectra do not seem to depend upon the sulphuric acid concentration and remain the same even in 100% H_2SO_4 . This obviously indicates that CuPc and H_2Pc both yield a single protonated form in sulphuric acid. The spectral changes during the protonation are almost the same. This is clear indication of the same type of proton attachment and the same site of its localization.

INTRODUCTION

The ultraviolet spectra of copper phthalocyanine and its ligand phthalocyanine in organic solvents have been known for some time^{1,2}. But the interpretation of observed bands as well as of changed colour of the solution in different dilutions of sulphuric acid has not been clear so far. Available literature shows that in aqueous solution of the ligand molecule in sulphuric acid beginning with 8 N concentration only protonation is observed irrespective of the acid concentration and temperature³. Gurinovich⁴ *et al.* have given a detailed analysis of all contemporary spectroscopic approaches to solve the problem of the type of protonated phthalocyanine. Some authors^{5,6} using polarised luminescences have also tried to establish that protonation of phthalocyanine and its copper complex with sulphuric acid takes place at the periphery of H_2Pc molecule. The nature of formation of such particle ions has been established from the quantitative studies of the solubility equilibrium of H_2Pc ligand in protonating media⁷⁻¹⁰.

The solubility of H_2Pc and CuPc has been examined¹¹ in the broad region of sulphuric acid in the range of temperature 293–343 K. A rectilinear relationship between solubility and the concentration of sulphuric acid permitting reaction between them is excluded¹². The salt-like compound's solutions of concentrated

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aqueous sulphuric acid are completely ionized which is perhaps due to the extremely high dielectric constants¹³ of these solutions.

Because of this situation we have tried to study in detail the behaviour of sulphuric acid medium not only towards the CuPc complex but its ligand H₂Pc also.

EXPERIMENTAL

Only sulphuric acid of different dilutions has been selected for the study of the protonation of CuPc as it is hardly soluble in common solvents and even in dilute H₂SO₄ (< 4N). α -Chloronaphthalene is also a somewhat fit solvent for this complex. So this was also selected for this study. The solutions of known concentrations were prepared by weighing proper amount of CuPc on a chemical balance and dissolving it in the appropriate amount of sulphuric acid with higher concentration.

A Shimadzu-UV-vis (160 A Japan) double beam spectrophotometer with automatic recording device was used and the spectra scanned through 200–1100 nm with an accuracy of 0.1 nm. They were run at room temperature using silica cells. The spectra as usual were obtained in the shape of broad bands— a plot of transmittance against wavelength from which the positions of maximum absorption (λ_{max}) were estimated from the centre of symmetry of the graph. In case the graphs were beyond the scale, the solutions were diluted such that the peak position may fall within the desired range.

RESULTS AND DISCUSSION

A list of bands of CuPc and its ligand H₂Pc in two different solvents is given in Table-1.

TABLE-1

Solvents used	Strength	H ₂ Pc	CuPc	Absorbance
H ₂ SO ₄	36 N	754	786	1.74
		230	300	1.60
H ₂ SO ₄	18 N	700	720	
H ₂ SO ₄	12 N	714	772	
H ₂ SO ₄	8 N	684	798	
H ₂ SO ₄	6 N	608		
α -Chloronaphthalene	—	692	726	
		292	323	
		293		

The corresponding absorption spectra have been shown in Fig. 1.

The absorptions of H₂Pc and CuPc seem to remain almost the same as we go from α -chloronaphthalene to H₂SO₄ as shown in Fig. 1.

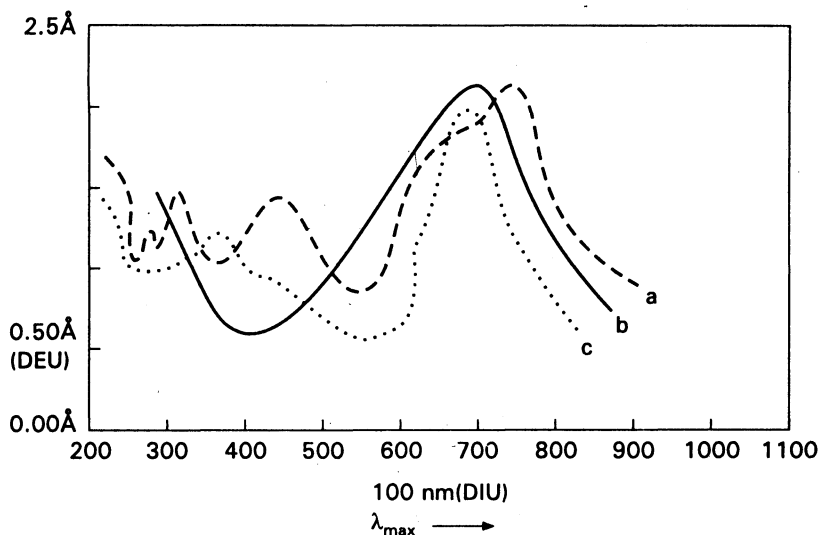
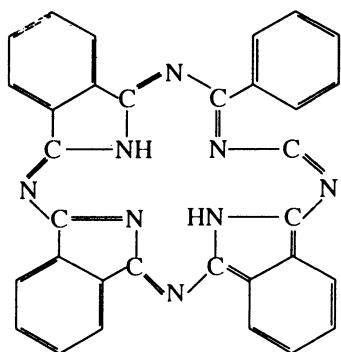
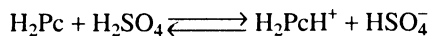
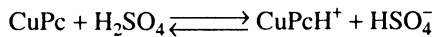


Fig. 1. Absorption Spectra of CuPc (a & c) and H₂Pc (b) in α -chloronaphthalene (b & c) and 18 N H₂SO₄ (a)

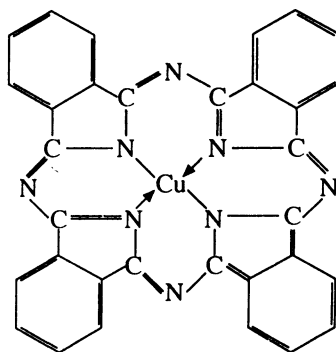
A strong red shift (10–75 nm) of all bands occurs except for one at a wavelength of 220–230 nm.

As regards the protonation of H₂Pc and its complex CuPc, a wealth of thermodynamic data has been shown in literature^{14–16}. These data combined with the spectroscopy and knowledge of the electronic structure of molecules provide a clear picture of the process.

The spectra of CuPc in H₂SO₄ remaining unchanged on long storage suggest that slow reactions like sulphonation or oxidation take place in solutions. The electronic spectra of CuPc and its ligand H₂Pc in sulphuric acid and its dissolution result from an acid-base interaction that can be expressed as follows:



[Structure of H₂Pc]



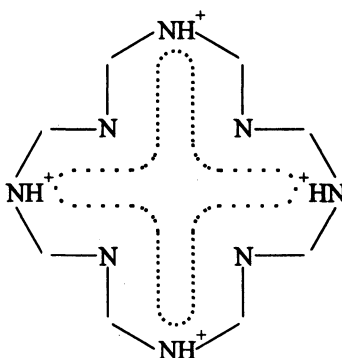
[Structure of CuPc]

The changes in spectra during protonation are absolutely the same for CuPc and other metal phthalocyanines. This clearly shows the same type of proton attachment and the same sites of its localization.

The structures of H₂Pc and CuPc shown prove the above facts.

The absence of electron donor centres in the CuPc molecule on the intracyclic N-atoms and the strong bathochromic shift in H₂SO₄ leave no doubt that H⁺ is attached to the external, so called extracyclic, N-atoms of CuPc.

Thus, the manner in which spectral change occurs in H₂Pc is sufficient proof that in the H₂Pc ligand protons are attached not to the centre of the molecule but to its periphery. The attachment of H⁺ to the periphery of the macroaring molecule (as shown in the figure) strongly polarizes the phthalocyanine molecule. The resulting dipole decreases the energy of all electronic transitions associated with the macroaring.



[Structure of macroaring H₂Pc Molecule]

Thus, the protonation of the ligand of CuPc at the periphery rather than at the centre of the molecule is one of the arguments in favour of the internal ionization of the two imino H-atoms of the ligand. The position of the bands in the electronic absorption spectra of CuPc with Cu²⁺ ion does not depend on the concentration (8–36 N) of H₂SO₄ and remains practically the same even in 100% H₂SO₄ which gives the clue that CuPc yields only a protonated form.

The electron distribution pattern in case of CuPc in any concentration (8–36 N) of H₂SO₄ depends on the strength of the σ - and π -bonds formed between Cu-metal atom and ligand.

Thus, experimentally, it is established that the formation and strengthening of the σ -bond, accumulation of the positive charge on the metal atom in CuPc and the steric ligand coplanarity disturbance factor give rise to hypsochromic shift of the first absorption band in the spectrum of CuPc. The formation and strengthening of the back dative π -bond and the increasing coplanarity of the ligand, on the contrary, cause bathochromic shift of the first absorption band in the ligand H₂Pc.

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