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Acid–Base Behaviour of Phthalocyanine

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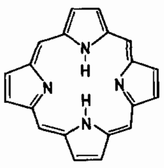
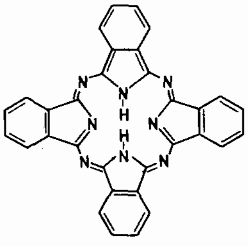
In the presence of strong bases, solutions of phthalocyanine display the previously reported anomalous spectrum similar to that of a metal phthalocyanine. Addition of acid to this solution produces the normal spectrum, and these changes are attributed to reversible deprotonation of the central imino groups. Electrical conductivity of solutions of phthalocyanine and its copper derivative in chlorosulphuric acid show that in both cases only four chlorosulphate ions are produced per phthalocyanine molecule, suggesting that in this acidic solvent only the bridging aza nitrogen atoms are protonated.

Introduction

Phthalocyanines are structurally related to the naturally occurring porphyrins. Both have a conjugated inner ring of 18 π-electrons with the phthalocyanines having aza nitrogen atoms rather than methine groups bridging the pyrrole units. Like porphin (*1*), phthalocyanine (*2*) is potentially amphoteric:


(1)


(2)

it could lose the two inner imino protons to form the dianion Pc^{2-}, while possible protonation sites are the inner basic nitrogen atoms and the four bridging nitrogen atoms. Although metal phthalocyanines are formally salts of the parent tetradentate ligand, nothing is known about the acidity of phthalocyanine itself. The possible protonation of the inner nitrogen atoms is of particular interest, since protonation of these atoms in some porphyrins is known to produce dramatic sterochemical changes[3], presumably as a result of steric crowding or electrostatic repulsion. We have investigated reactions of phthalocyanine with some strong acids and bases using conductometric and spectrophotometric techniques and report our results here.

Experimental

Phthalocyanine was prepared from phthalonitrile using methylnaphthalene as previously described[4]. Copper phthalocyanine was a commercial sample and was used as received. Chlorosulphuric acid (BDH), having a specific conductance of 6×10^{-4} ohm^{-1} cm^{-1} at 25° C, and other solvents were used as received. They were generally reagent grade (BDH), although AnalaR quality was used whenever possible. Conductivity cells and the procedure for obtaining electrical conductivities of chlorosulphuric acid solutions at 25.0 ± .003° C have been described by Robinson and Ciruna[5]. Visible spectra were recorded on Perkin-Elmer 402 and Pye Unicam SP800 spectrophotometers using 4 cm quartz cells.

Results and Discussion

Although phthalocyanine only dissolves in most common organic solvents to the extent of 10^{-5}–10^{-4} *M*, its high extinction coefficients in the visible region of the spectrum enable its reactions to be monitored. The most intense band ($\pi \rightarrow \pi^*$) in the visible spectrum of metal phthalocyanines is normally between 600 and 700 nm, whereas the parent base, phthalocyanine, has two approximately equally intense bands in this region. This splitting has been interpreted[6] in terms of deviations from D_{4h} symmetry caused by the presence of the two central hydrogen atoms. Phthalocyanine and its metal derivatives are therefore easily distinguished by their characteristic spectra in the 600–700 nm region.

In a variety of pure solvents, phthalocyanine ($\approx 10^{-6}$ *M*) displays its characteristic two band spectrum (Table I). The position of these bands and associated

TABLE I. Electronic Spectra.

Solvent	Absorption Maxima (nm)			
	Initial Spectrum		After Addition of Base[a]	
	Main Bands	Weak Bands	Main Band	Weak Band
Nitrobenzene	698, 663	644, 636, 602	677	611
Chlorobenzene	696, 658	641, 632, 598	672	608
Benzene	694, 657	639, 630, 597	670	607
p-xylene	694, 656	639, 629, 595	669	607
Pyridine	694, 659	640, 630, 602	670	596
a,a,a-trichlorotoluene	692, 655	638, 628, 595	669	605
Ethanol	too insoluble to measure		668	604
1,4-dioxane	688, 653	635, 627, 596	665	

[a] 2% KOH in ethanol. Positions reproducible to ± 2 nm.

weaker transitions is slightly solvent dependent, but their relative positions remain constant within experimental error. Addition of *ca.* 0.05 ml of a 2% solution of KOH (or NaOH) in ethanol to these solutions (*ca.* 4 ml) caused an immediate change in the visible spectrum to a single intense band at *ca.* 670 nm (see Table I) resembling the spectrum of a metal phthalocyanine. This reverted to the original two band spectrum after the addition of sulphuric acid or hydrogen chloride dissolved in the appropriate solvent (for typical spectra, see Figure 1). Further addition of acid produced spectra characteristic[7] of protonated cationic phthalocyanines (see below). In each case, addition of ethanol alone had no effect. At concentrations considerably higher than those used here, phthalocyanines are known to dimerise[8]. However, by comparison with the spectrum of dimeric sulphonated phthalocyanine[9], the spectrum produced by the addition of a very small volume of KOH/EtOH solution to one of phthalocyanine is clearly not due to dimerisation. The type of spectrum is quite different, and further on dimerisation *observed* bands in the visible spectra of phthalocyanines are about half as intense as those of the original monomer solution[8] (*i.e., molar* extinction coefficients of both species are similar, but the molar concentration is halved on dimerisation). The single band formed by the addition of strong base to PcH_2 is as intense as the original bands of the monomer. Therefore, these changes cannot be due to conversion from monomer to dimer, but are best interpreted in terms of replacement of the inner imino hydrogen atoms by the alkali metal concerned[10]:

$$PcH_2 + MOH/EtOH \xrightarrow{\text{solvent}} PcM_2 + H_2O$$

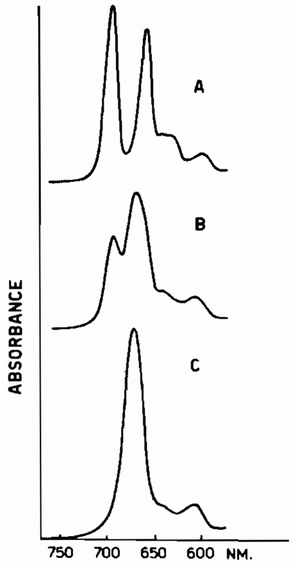


Figure 1. Typical spectral changes in the 600–750 nm region caused by the addition of alcoholic sodium hydroxide to a solution of phthalocyanine. A: phthalocyanine in $PhCCl_3$ (*ca.* 15 ml); B: after addition of 0.01 ml of NaOH/EtOH solution; C: after addition of *ca.* 0.1 ml of NaOH/EtOH.

Related observations have been reported[11] for the reaction between porphyrins and methoxide ion in pyridine, and these were similarly interpreted as being due to metalloporphyrin formation. However, it appears that the alkali metalloporphyrins are more sensitive towards hydrolysis than are the phthalocyanine derivatives, but addition of excess acid does result in the reformation of PcH_2. Presumably as a result of the enhanced solubility of $PcLi_2$ in ethanol compared with the other alkali metal phthalocyanines[12], considerable quantities of phthalocyanine can be dissolved in ethanol containing lithium hydroxide. This could provide a useful synthetic route to some metal phthalocyanines because the lithium can be readily exchanged for other metals, and phthalocyanine itself is readily available[4].

Anomalous Phthalocyanine Spectra

There are several reports in the literature concerning anomalous visible spectra of phthalocyanine. Linstead and his co-workers[13] commented on the fact that in 1-chloronaphthalene they did not observe a band at 675 nm as found by Stern and Pruckner[14] who used quinoline. Russian workers[15] observed anomalous spectra in dioxane, and using fluorescence techniques, they showed that two species were present, one having an absorption at 670 nm, the other at 693 and 657 nm. Their conclusions, that these originate from monomeric and dimeric species, are questionable in the light of our results. Edwards and Gouterman[16] found that phthalocyanine in dimethylsulphoxide and hexamethylphosphoramide has a normal spectrum together with a superimposed "metal type spectrum". Although no absorption maxima were given for the "metal type spectrum", it seems likely that it could have resulted from reaction with basic impurities in these solvents.

Whalley[17] found that extraction of phthalocyanine into pyridine in a Soxhlet apparatus produced a solution having a spectrum similar to a metal derivative, and this was attributed to pyridinium salt formation. The pyridinium salt of tetrazaporphin (characterised by i.r. spectroscopy) was isolated from an irradiated solution of tetrazaporphin in pyridine. We did not produce this spectrum by boiling phthalocyanine in pyridine, but the normal two band spectrum. However, a single absorption was observed after the addition of a little alkali.

Protonation of Phthalocyanine

When dissolved in dilute aqueous solutions of mineral acid, the two central basic nitrogen atoms of most porphyrins become protonated[18]. Steric, together with, perhaps, electrostatic factors, cause (in the solid state at least) the molecule to deviate markedly from planarity, the pyrrole rings being tilted alternately up and down[3]. Phthalocyanine, on the other hand, is only sparingly soluble in most common organic solvents and insoluble in dilute aqueous solutions of mineral acid. It is, however, moderately soluble in concentrated sulphuric and chlorosulphuric acids.

Infrared[19] and nmr[20] studies have demonstrated that the imino hydrogens of porphyrins may be deuterated, and that in trifluoroacetic acid, the diacid is formed[20]. The central hydrogen atoms of phthalocyanine have been exchanged for deuterium by "crystallisation" from D_2SO_4 (ref. 21). However, our preliminary attempts to detect the ^1H N–H nmr signal(s) of phthalocyanine dissolved in chlorosulphuric[22] acid were not successful, although the ^1H C–H signals were observed. It seems likely that the N–H protons are exchanging rapidly with the bulk solvent protons. We therefore used conductometric techniques[5] to determine the degree of protonation of phthalocyanine in chlorosulphuric acid at 25° C. Using KSO_3Cl as a standard, the conductivity data indicated that almost four (3.8) SO_3Cl^- ions were produced per phthalocyanine molecule in solution, suggesting that only the four outer bridging nitrogen atoms are protonated and *not* the inner ones. Experimental specific conductance values might be smaller than required for four SO_3Cl^- ions per phthalocyanine molecule because of the disruptive effect the large protonated macrocycle +4 ion has on the solvent. Conductivity data for copper phthalocyanine in chlorosulphuric acid at 25° C are identical to those for phthalocyanine (see Figure 2), and tend to suggest that the two *central* tertiary nitrogen atoms of phthalocyanine itself are *not* protonated, even in this highly acid medium. *A priori* there is no reason why the inner nitrogen atoms of phthalocyanine should appear considerably less basic than those of the porphyrins. Electronic effects resulting from protonation of the four bridging atoms could be significant, and a structure less flexible than that of the porphyrins would contribute to an apparent reduced basicity, since the molecule has to distort to accommodate the extra protons. Some porphyrins are known to be ruffled[23] in the solid, and N-methyl as well as N,N′-dimethyl porphyrin derivatives have been synthesised[24]. Phthalocyanine, on the other hand, is planar in the solid state[23], as are its metal derivatives, with only special exceptions[25]. It is, therefore, perhaps not surprising that attempts[26] to prepare N-methylated phthalocyanine were unsuccessful.

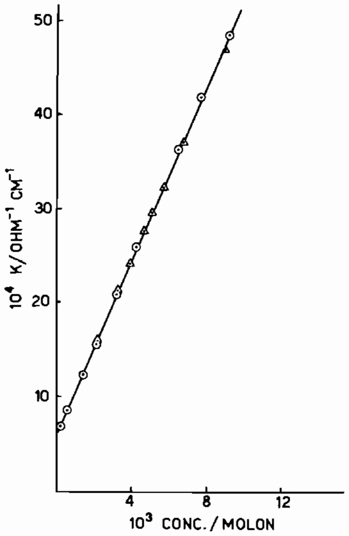


Figure 2. Specific conductance plotted against concentration (moles per kilogram of solution) for PcH_2 (○) and CuPc (⍋) in chlorosulphuric acid at 25.0° C under nitrogen.

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10 PcM_2 is in fact likely to exist as an ion-pair. It would be sterically difficult, if not impossible, to place the two alkali metals within the ring.

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Note added in proof:

The work of K. Bernauer and S. Fallab, *Helv. Chim. Acta, 45,* 2478 (1962), has just come to our attention. They interpreted pH dependent spectra of tetrasulphonated phthalocyanine in terms of dissociation of the inner N–H protons.