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Negative Ions of Tetrapyrrole Compounds

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The mechanism of the formation of negative ions of phthalocyanine, porphyrins, and their metal derivatives is discussed, together with the effects of the tetrapyrrole ligand and the metal atom on the properties of the ions. The nature of the metal has a significant influence on the electronic structure of the negative ion, and thus on its properties, in particular its protonation, photoelimination of an electron from the ion, and its catalytic activity. Photodetachment of an electron combined with the spectral characteristics of the ions is considered as a method for investigating ionic forms. The Review concludes with a list of 132 references.

CONTENTS

I.	Introduction	281
II.	Photochemical detachment of an electron for the study of negative ions	282
III.	Electronic structure and the spectra of negative ions of metal phthalocyanines	283
IV.	Negative ions of porphyrins and metal porphyrins. Protonation of negative ions	285
V.	Photochemical generation of negative ions in solution	288
VI.	Complexes. Ionic association	289
VII.	Catalytic activity of negative ions of metal phthalocyanines	291

I. INTRODUCTION

Ideas on intermolecular charge transfer in organic systems and on the properties of ions of aromatic compounds developed in a comparatively orderly sequence: extensive experimental results fitted well into the framework of theoretical concepts, quantum-mechanical calculations consistent with observation were made for the simplest and most characteristic cases, and comprehensive reviews and monographs were written[1-13]. The structural features of porphin molecules—the presence of heteroatoms and a tetrapyrrole ring of conjugated bonds, high symmetry, the possibility of coordinating a metal atom into the molecular structure—combined with the well known role of certain naturally occurring members of the series in biochemical processes have invariably attracted the attention of research workers to charge-transfer phenomena involving porphin derivatives. However, it is these structural features, which are obviously responsible for the extraordinary variety of properties of porphin derivatives, that make their investigation difficult and prevent the application to them of the general ideas developed from the examination of ions of aromatic compounds. Without considering all aspects of the problem we shall make a preliminary summary of researches on the negative ions of some of the simplest porphyrins. We shall not make a systematic survey of all the relevant literature but shall reply predominantly on recent results, which are relatively free from the errors and discrepancies inevitable in the early work.

The negative molecular ion Por^{n-} is formed from the neutral molecule Por of a porphin derivative by the successive addition of electrons. These ions can be generated by the same methods as the anions of aromatic compounds [2,6,9]. A chemical method is most often adopted, by introducing into the solution as electron donor either an alkali metal or an anion formed by its interaction with an aromatic compound possessing a smaller electron affinity than the porphin molecule. Almost 100% yields of anions have been obtained by this method from phthalocyanine, several porphyrins, and their metal derivatives. Good results are obtained by the electrochemical method, equally applicable to the generation of negative and of positive molecular ions. The method is almost indispensable when alkali-metal ions must not be present.

The first experiments on negative ions of porphins were made by Shablya and Terenin, who measured the electronic absorption spectra of the monoanions formed when magnesium phthalocyanine was treated with sodium in oxolan [14,15]. Almost simultaneously Watt and Dawes [16] examined by X-ray diffraction the products formed by copper phthalocyanine with potassium in liquid ammonia. These workers said nothing about the ionic character of the products, although now, of course, this is not open to doubt. The investigations were subsequently extended to anions of other metal phthalocyanines, and also to metal tetraphenylporphins and metal aetioporphyrins. In spite of several correct observations and conclusions in the early papers, the latter were often contradictory, which can be attributed to unavoidable errors due to the absence of reliable criteria of the purely ionic character of the reduction products of tetrapyrrole compounds, criteria of their purity, and reliable methods for identifying them. A difficulty in identifying and investigating tetrapyrrole anions was that electron spin resonance—one of the main methods for investigating ions of aromatic compounds—provided relatively little information. The e.s.r. spectra of tetrapyrrole anions are usually narrow singlet lines devoid of hyperfine structure [17-21]. In the few cases in which structural e.s.r. spectra were obtained [22-24] their interpretation gave rise to difficulties. Nevertheless, detection of a structureless e.s.r. signal is useful as proof of the radical (though not necessarily ionic) nature of the product, and is regarded as evidence of delocalisation of the electron in the conjugated system of the tetrapyrrole ligand [18]. Many uncertainties and contradictions were removed by a series of investigations in which spectral examination of negative tetrapyrrole ions *during their formation* were immediately followed by experiments on the photochemical detachment of an electron from the resulting ions [20,21,25,26].

II. PHOTOCHEMICAL DETACHMENT OF AN ELECTRON FOR THE STUDY OF NEGATIVE IONS

Like anions of aromatic compounds [27] those of tetrapyrrole derivatives are able to eliminate electrons photochemically [25]:

$$Por^{n-} \xrightarrow{h\nu} Por^{(n-1)-} + e^{-} .$$

This process converts a molecular anion either into an anion of smaller charge or (when $n = 1$) into a neutral molecule. For example, ultraviolet exposure of a solution of magnesium phthalocyanine monoanions in a mixture of oxolan and diethyl ether at −196°C (this mixture freezes as a transparent, vitreous mass) converts them into neutral molecules, which can easily be followed from the variation in the absorption spectra: disappearance of the bands due to the monoanion and the appearance of those due to the neutral molecule are accompanied by the appearance of a characteristic broad band with its maximum at 1240 nm, corresponding to electrons detached from the monoanions and stabilised in intermolecular potential traps in the matrix [28].

Photoelimination of an electron from an anion is reversible: when the frozen solution melts, the stabilised electrons escape from the traps and charge the molecules to the original level. The reverse reaction can also be achieved photochemically by illuminating the frozen specimen in the region of absorption by the stabilised electron ($\lambda > 700$ nm). Such exposure results in complete disappearance of the band due to the stabilised electron, but only a proportion of the electrons liberated from the traps add to magnesium phthalocyanine molecules. Some of the electrons probably fall into deeper traps, in which they do not exhibit their own absorption bands (at least in the experimentally accessible spectral region). Electrons captured in such traps also escape when the specimen melts, add to magnesium phthalocyanine molecules, and charge the latter to the original level.

Photoelimination of the first electron from a multicharged ion usually requires a smaller light quantum than does photoelimination from a monoanion. However, complete discharge of the magnesium phthalocyanine dianion to the neutral molecule is far more difficult than discharge of the monoanion. Detachment of the first electron obviously results in a net positive charge in the matrix cell formed by the molecular anion, the positive gegenions interacting with it, and the solvate sheath surrounding them, and it is now considerably more difficult to remove a second electron. Tetra-anions of certain metal phthalocyanines split off the first electron even under the influence of visible light, ultraviolet exposure gives dianions, but no further photoelimination of electrons is observed. These experiments indicate that the matrix potential traps in which the photoeliminated electron is located lie outside the ionic association complex comprising the anion, positive gegenions, and the solvate sheath surrounding them.

Photorelease of an electron has been observed also in other vitreous matrices, e.g. in an equimolecular mixture of oxolan and dimethylformamide. Here the photodischarge of ions was not accompanied by the appearance of a band due to the stabilised electron, and the reverse reaction occurred only when the specimen was thawed [26]. The liberated electrons may be localised in intramolecular traps due to the presence of vacant molecular orbitals in the dimethylformamide molecules.

Photodetachment of an electron, similar to that described above for multicharged magnesium phthalocyanine anions, has been observed also with negative ions of several other metal phthalocyanines and metal porphyrins [20,21,25,26].

The appearance of stabilised electrons in the matrix accompanied by formation of neutral magnesium phthalocyanine molecules when monoanions are irradiated is sufficient proof that these monoanions are a purely ionic species, differing from the neutral molecules only in the presence of an additional electron. The purely ionic structure of multicharged magnesium phthalocyanine ions is proved by a comparison of the absorption and e.s.r. spectra of products of successive stages of one-electron reduction and their photochemical discharge.

More detailed investigations have established several special features of the photodetachment of an electron [26]. The longer-wavelength threshold of photodetachment

differs markedly with ions of different compounds. Impurities can be distinguished and sometimes identified from the absence of synchrony in the variation of absorption bands on photoelimination of an electron. Thus this phenomenon will give the missing proof of the ionic character of products of the reduction of tetrapyrrole compounds by alkali metals, and will yield reliable spectral characteristics for their identification and analysis.

A method of photoinduced dichroism is based on the photoelimination of an electron. It enables both the relative positions of the molecular oscillators in the anion (polarisation of electron transitions) and their distribution relative to those of the neutral molecule to be determined [29-33]. Such results are important for interpreting the electronic absorption spectra of the anions.

The essence of photoinduced dichroism is that, if a photochemical reaction (in the present case photoelimination of an electron from negative ions in a frozen solution) takes place in an isotropic solid medium under the influence of plane-polarised light, the medium becomes dichroic, since molecules (ions) appropriately oriented relative to the electric vector of the plane-polarised light are preferentially subject to photoconversion. Photoinduced dichroism lasts for a fairly long time in a frozen matrix, and it becomes possible to determine the spectral dependence of its characteristic parameter $\Delta D = D_{\parallel} - D_{\perp}$, where $D_{\parallel}$ and $D_{\perp}$ are the optical densities of the specimen measured in light polarised respectively parallel and perpendicular to the direction of polarisation of the light causing the photoreaction. If only three mutually perpendicular directions of polarisation of electronic transitions are possible owing to symmetry in the molecules (ions) (as occurs with porphyrins, phthalocyanine, and their metal derivatives), the direction of polarisation of transitions corresponding to absorption bands both of the starting material and of the photoreaction product can be determined in a coordinate system coincident with the molecular axes of symmetry. For this it is usually sufficient to determine the sign of ΔD in the given absorption band. This method has been used to determine the orientation of the dipole moments of electronic transitions in the monoanions of disodium complexes of chlorin and tetraphenylbacteriochlorin with respect to transitions of the neutral molecules (in a coordinate system unique to the molecule and the ion) [32,33].

III. ELECTRONIC STRUCTURE AND THE SPECTRA OF NEGATIVE IONS OF METAL PHTHALOCYANINES

The most detailed investigations have been made on the negative ions of metal phthalocyanines. Kholmogorov and Shablya [18] were the first to measure the e.s.r. spectrum of magnesium phthalocyanine monoanions and, from the form of the structureless narrow signal, suggested that the extra electron was delocalised over the cyclic conjugated-bond system of the tetrapyrrole ligand. Taube and his coworkers showed [34-41] that a metal phthalocyanine molecule may add successively 1–4 electrons on reaction with an alkali metal or with a benzophenone anion. They measured the magnetic susceptibility of the ions, made an elementary analysis of them, undertook LCAO-MO calculations to determine the electronic configurations of the metal phthalocyanine monoanions, and also studied the Mössbauer spectra of iron phthalocyanine anions. Unfortunately, none of their papers gives either optical or e.s.r. spectra. This omission makes it difficult either to compare the results with those of other workers or to reproduce them. Use of such a simple method as molecular orbitals for theoretical calculations of electronic configurations of complicated species containing transition-metal atoms is open to sceptism. In almost every individual case the calculations must be confirmed by experiment, which larely deprives the calculations of their predictive value. A recent attempt [42] to interpret the spectra of the mono-, tri-, and tetra-anions of magnesium phthalocyanine on the basis of calculations by the Pariser–Parr–Pople method, allowing for limited configuration interaction, omitted calculation of the intensities of the electronic transitions. Furthermore, agreement between calculated and experimental spectra of the mono- and trianions was obtained only on the hypothesis that the band of longest wavelength does not correspond to the transition of lowest energy among those predicted as allowed. There are no experimental grounds for such a hypothesis. Therefore the interpretation of the electronic spectra of the ions given by these workers cannot be accepted as reliable. Thus at the present stage theory plays only an ancillary part in relation to tetrapyrrole ions, and all the main conclusions, being based on a comparison of experimental results, are predominantly qualitative in character.

The problem in the electronic structure of metal phthalocyanine ions is essentially the location of the added electrons, since the nuclear configurations of ions and neutral molecules can be regarded to a first approximation as the same. The excess charge of the anion can in principle be located either on the central atom M or on the tetrapyrrole ligand, or shared between them in certain proportions. The hypothesis that the charge of the magnesium phthalocyanine monoanion is located on the ligand, which was based on e.s.r. data [18], has since found direct experimental confirmation in the close similarity between the electronic absorption spectra of the monoanions of magnesium and of metal-free phthalocyanines [43-45]. Comparison of the results of absorption spectroscopy, e.s.r. spectroscopy, and theoretical calculations shows that the electron is also located on the ligand in the monoanions of zinc, copper, and nickel phthalocyanines [19,22,23,37,43-48]. The monoanion of cobalt phthalocyanine has a different structure: although it is diamagnetic and therefore inaccessible to e.s.r. investigation, the close similarity of the electronic absorption spectra of the complex and its monoanion is sufficient to suggest that the electron is located on the cobalt atom in the latter [44,48,49]. The energy states of the principal chromophore of the molecule—the tetrapyrrole ligand—show little change, and the spectrum of the monoanion retains the main features of the neutral molecule. (Addition of an electron to the magnesium, copper, and nickel phthalocyanine molecules leads to significant spectral changes.) Taube's calculations [37] support the postulated location of the electron in the monoanion of cobalt phthalocyanine based on spectral data.

The absorption spectra of the dianions of metalfree, magnesium, nickel, and copper phthalocyanines, like those of the monoanions, depend little on the nature or even the presence of the metal atom in the molecule. This means that both electrons in the dianions are located in the tetrapyrrole system of the ligand [44-46,48]. The absorption spectra of cobalt phthalocyanine dianions are closer to those of the monoanions than those of phthalocyanine dianions (and the analogous metal phthalocyanine dianions). It may be assumed, in agreement with calculation, that one electron is located on the cobalt atom, and the other on the ligand.

The electronic structure of the monoanion of iron phthalocyanine may be considered separately. According

to Taube [37] the location of the extra electron in a metal phthalocyanine anion depends on the electronegativity of the metal atom. Thus nickel is the most electronegative of the iron-group metals, and in conformity with this its atom remains unchanged when its phthalocyanine complex is converted into a mono- or a di-anion, since both electrons are located on the ligand. Cobalt is intermediate in electronegativity, so that on reduction of its phthalocyanine complex the first electron goes to the cobalt atom, and the second to the ligand. Since the iron atom is the least electronegative, both electrons should be located on the iron atom when the phthalocyanine complex is reduced. However, the properties of a metal atom, including its electronegativity, may obviously change on coordination into the tetrapyrrole molecule. The absorption spectra of iron phthalocyanine anions show [49] that their electronic structure does not fit a simplified theoretical scheme: the spectrum of the monoanion in oxolan alone or mixed with diethyl ether differs both from that of the cobalt monoanion with its electron on the metal atom and from that of the nickel monoanion with a negatively charged ligand. It was suggested that the negative charge is shared between the iron atom and the ligand. In quantum-mechanical terms this may imply e.g. that the electron is located on a d-level of the iron atom, which is strongly mixed with a vacant π-electron level of the ligand as a result of their proximity. This suggestion has found experimental support, including aspects of the photodetachment of electrons from monoanions of various metal phthalocyanines. Ultraviolet exposure easily detaches the electron from the nickel phthalocyanine monoanion, in which it is situated on the ligand. Detachment of the electron does not occur with the complex cobalt monoanion. Iron phthalocyanine monoanion occupies an intermediate position: although photoelimination occurs, far more work is required than with the complex nickel anion.

Convincing evidence for the suggested location of charge in the iron phthalocyanine monoanion is given by the phenomenon of thermochromism which we have discovered with these ions [26,49]. In solution at temperatures close to -196°C these ions are able to form unstable complexes with molecules of organic bases (pyridine, N-methylpiperidine, diethylamine, triethylamine), which decompose with rise in temperature and are re-formed on subsequent cooling. The changes in temperature are accompanied by changes in colour—blue at -196°C, but red at -100°C and above (thermochromism). The absorption spectrum of the red solution is identical with that of iron phthalocyanine monoanion in the absence of bases. However, the spectrum of the blue solution, in which the ions are present as complexes with the molecules of bases, become similar in detail to that of the monoanion of nickel phthalocyanine, in which the negative charge is located on the ligand, as already stated. The molecules of the base, being oriented with their dipoles directed towards the iron atom on formation of the complex with iron phthalocyanine monoanion, obviously make complete localisation of the extra electron at the π-electron level of the ligand energetically favourable. Such a phenomenon would hardly have been possible if the electron were located on the metal atom; in any case, the presence of bases in solution produces no spectral changes in cobalt phthalocyanine ions involving localisation of the electron on the metal atom. As was to be expected, the iron phthalocyanine monoanion in the complex with a molecule of a base, while having the extra electron on the ligand, eliminates it on exposure just as easily as does the monoanion of nickel phthalocyanine.

A recent investigation of the Mössbauer spectra of the singly and doubly charged anions of iron phthalocyanine also indicates some distribution of negative charge between ligand and metal atom in these ions. These results were explained in terms of mixing of the d-orbitals of the iron atom with the π-orbitals of the ligand [40,41].

A point in connection with terminology and the nature of the problem is that it was supposed in some of the early publications [16,35] that the reduction of a metal phthalocyanine (MPhth) involves a change in valency ("state of oxidation") of the central metal atom. This was represented by such notation as

$$Co^{II}\ Phth \xrightarrow{e^-} Co^{I}\text{-}Phth;$$

$$Fe^{II}\text{-}Phth \xrightarrow{e^-} Fe^{I}\text{-}Phth \xrightarrow{e^-} Fe^{0}\text{-}Phth.$$

Watt and Dawes supposed [16] that the initial product of the reduction of copper phthalocyanine CuPhth by potassium is $Cu^{I}Phth$, followed by $Cu^{0}Phth$, the copper atom in the latter being coordinated with the ligand, not combined covalently. The results discussed above show that in actual fact the copper atom in the phthalocyanine complex plays no decisive part in the addition of electrons. Even when the electron is actually located on the metal atom, as in the formation of $[CoPhth]^-$, there are no grounds for assuming that this involves a change in the valency of the cobalt atom or the nature of its bond with the ligand. It would therefore be logical to cease denoting the primary reduced form of cobalt phthalocyanine by the formula $Co^{I}Phth$, as is done even now in certain papers, and to use the formula $[CoPhth]^-$ or even, when the location of the charge is to be emphasised, the formula $[Co]^-Phth$. Analogous notation should be used also for negative ions of all other tetrapyrrole compounds.

The problem of the electronic structure of multicharged metal phthalocyanine ions has been solved only in general outline. Absorption spectroscopy, e.s.r. spectroscopy, and electron photoelimination have shown that the molecules of most metal phthalocyanines are able to add successively up to four electrons with the production of purely ionic forms [25,26]. The possibility of adding such a number of electrons is attributed to the doubly degenerate lowest vacant π-orbital in the metal phthalocyanine molecule [47]. The presence of the central metal atom with a more or less independent system of energy levels also permits the addition of extra electrons. It is assumed, for example, that an additional vacancy on the cobalt atom makes it possible for cobalt phthalocyanine to exist in five negatively charged ionic forms [37,48]. We have previously cast doubt [44] on the existence of the fifth ionic form. Recently we have been able to obtain a fifth reduced form of this compound, having the same absorption spectrum as given by Clack and Yandle [48]. In contrast to most other $[MPhth]^{n-}$ ions investigated, including tri- and tetra-anions of cobalt phthalocyanine, however, this fifth reduced form was incapable of photoelimination of an electron, which gave serious grounds for doubting whether it actually had a purely ionic structure.

Calculations by the LCAO-MO method showed [36-41,47,50] that the third and fourth electrons added to a metal phthalocyanine molecule to form tri- and tetra-anions should be located in a doubly degenerate π-electron level of the ligand. However, experimental studies of the Mössbauer spectra [40,41] and electronic absorption spectra [44] suggest that the charge in multicharged metal phthalocyanine ions is distributed between the metal atom and the ligand. The close similarity of the absorption spectra of tetra-anions of different metal phthalocyanines (magnesium, nickel,

cobalt, iron) shows that the charge distribution in them is little affected by the nature of the metal.

Clack and Yandle assume that the presence of paramagnetism in trebly charged magnesium phthalocyanine anions indicates that all three extra electrons are located on the ligand. The corresponding cobalt complex anion has similar electronic absorption spectra and hence the same electronic configuration[48]. Thus these workers conclude that, on passing from the doubly to the trebly charged cobalt phthalocyanine anion, not only does the third electron add to the ligand, but the electron located on the metal in the singly and doubly charged anions also passes to the ligand. Such a phenomenon can actually result from change in the relative positions of the π-orbitals of the ligand and the d-orbitals of the metal atom when an electron is added to the system, where the raising of the d-orbitals should exceed that of the π-orbitals. As yet, however, such a change in the relative positions of the orbitals has neither a theoretical nor an experimental basis. It is more reasonable to postulate that the π-orbitals undergo a greater rise than do the d-orbitals on addition of an electron, and that localisation of the electron in the d-orbitals will become possible at some stage. Such a process can be assumed in the formation of trebly charged anions of magnesium and similar metal phthalocyanines, and it is then easy to explain the spectral similarity of the trianions of magnesium and cobalt phthalocyanines: they have the same electronic configurations, with (the larger) part of their charge located on the ligand, and the other part on the metal atom.

Without analysis of the structure of the e.s.r. spectra neither the presence nor the absence of paramagnetism will give any information on the location of the charge in an anion. For example, the unpaired electron in the paramagnetic copper phthalocyanine molecule is located on the copper atom, and the extra electron of the singly charged anion on the ligand, but, despite such spatial separation of the electrons, the monoanion as a whole is diamagnetic. The trebly charged magnesium phthalocyanine anion must be assumed to be paramagnetic independently of the location of the extra electrons, since they are distributed within a single system of energy levels.

Peculiarities may be noted in the behaviour of certain metal phthalocyanines on conversion into negative ions. The metal-free compound reacts with sodium to give a disodium complex, which can be reduced to ionic forms analogous in spectra and structure to those of the magnesium and zinc complexes[47]. Singly and double charged phthalocyanine anions could be obtained and examined spectroscopically during the photochemical reduction of phthalocyanine by hydrazine[43]. Copper in its phthalocyanine complex has a tendency to be replaced by sodium on reaction with the latter, but substitution occurs when the molecule adds a third electron. The optical and e.s.r. spectra of singly and doubly charged copper phthalocyanine anions indicate that their electronic structures are similar to those of the corresponding complex magnesium and zinc anions[46,47]. The replacement of copper by sodium at the third stage of reduction is indirect confirmation of the hypothesis that localisation of the charge on the metal atom takes place at this stage[44].

Manganese phthalocyanine, like the cobalt complex, yields five reduced forms on interaction with an alkali metal in oxolan[51]. The metal atoms in manganese and chromium phthalocyanines are able to change their valency easily and reversibly by adding various out-of-plane groups or molecules (hydroxyl, cyano, acetate, pyridine, etc.)[52]. This greatly complicates investigation of their ionic forms[26]. It was observed in particular that the reduction of chromium phthalocyanine by sodium in oxolan gives a paramagnetic product whose e.s.r. spectrum contains nine lines, which means that the unpaired electron interacts with the four inner nitrogen atoms. When the complex is reduced in hexamethylphosphoramide, a signal comprising seventeen lines is observed, which corresponds to interaction of the unpaired electron with the eight nitrogen atoms[23,53]. Such behaviour of chromium phthalocyanine is obviously due to a different distribution of electron density in the resulting ion, which depends on the out-of-plane ligand, as in the interaction of iron phthalocyanine monoanions with bases[49].

We have not hitherto specified how the charge is actually distributed in the tetrapyrrole system of the ligand. Yet this distribution determines the chemical properties of the ion. Unfortunately, theoretical and experimental information is at present insufficient to solve this problem. Published data can be found permitting comparison of the distribution of π-electron density in certain molecules and their ionic forms. For example, theoretical calculations showed that, on formation of the negative ion of tetracyanoquinodimethane, the π-electron density increased most strongly on those atoms on which it was highest even in the neutral molecule (on the cyano-nitrogen atom and on the carbon atom linking the cyano-group with the quinoid ring). In neutral molecules the π-electron density has its minimum value on the cyano-carbon atom. Subsequently it diminishes still more strongly (though slightly) on conversion of the molecule into the singly and doubly charged anions[54,55]. In just the same way the increase in charge density on a carbon atom accompanying formation of radical-anions of polyacenes is greater the higher the π-electron density on the atom in the neutral molecule[56,57]. The physical reason for such a charge distribution in a negative molecular ion is obviously that the added electron, merging with the π-electrons of the neutral molecule, obeys the same distribution laws as do the latter in the force field of the given atomic configuration, which changes little on transformation of the molecule into an ion.

It may be supposed as working hypothesis, by analogy with polyacenes and tetracyanoquinodimethane, that the charge of an electron added to a metal phthalocyanine molecule is distributed (if it is located on the ligand) mainly between both inner and outer nitrogen atoms, which in the neutral molecule bear a considerable excess charge relative to the carbon atoms of the benzene rings[58-61].

IV. NEGATIVE IONS OF PORPHYRINS AND METAL PORPHYRINS. PROTONATION OF NEGATIVE IONS

The structural features distinguishing metal porphyrins from metal phthalocyanines are responsible for the distinctive physicochemical properties both of their neutral molecules and of their ions. Negative ions could be obtained by the same methods as those of the latter, but significant differences between them were immediately discovered: metal porphyrins form only singly and doubly charged anions, although their lowest vacant π-orbital is doubly degenerate, as in metal phthalocyanines, and the addition of four electrons is formally possible[50]. Reports of the formation of more highly charged ionic forms[17,22,62-64] have since been disputed. Experiments on the photodetachment of an electron and on the protonation of ions have shown[20,25,26,65,66] that partly protonated multicharged anions had erroneously been

regarded as purely ionic forms. It is not yet clear why metal porphyrins do not form multicharged ions.

As with metal phthalocyanines, the formation of negative ions of metal porphyrins and their structure depend significantly on the presence and on the nature of the central metal atom. Porphyrins and their copper derivatives resemble phthalocyanine and copper phthalocyanine in being converted into disodium complexes at the first stage of interaction with alkali metals or with negative anthracene ions, and these complexes yield ionic forms at later stages [46,64]. This transformation slows down with fall in temperature, and both monoanions and dianions could be obtained by running together solutions of a porphyrin (aetioporphyrin or tetraphenylporphin) and singly charged anthracene anions at −70°C. [26,64,67] An electrochemical method can also be used to obtain and investigate negative ions of metal-free porphyrins [68-70].

Zinc and magnesium combined with porphyrins are not replaced by alkali metals, and their valency is not changed by redox reactions, so that the first successful experiments on the preparation and spectral investigation of ions of metal porphyrins were made with zinc tetraphenylporphin by Closs's method [17,62]. Later experiments [20,26] with photodetachment of an electron from anions of this complex confirmed the correctness of the spectral characteristics predicted for these anions.

The close similarity of the electronic absorption spectra of the singly charged anions of tetraphenylporphin and its zinc complex, which contain comparatively few bands and, it may be said, are unique [67-70], demonstrate, when combined with e.s.r. measurements [17,19,20,22] and theoretical conclusions [50], that the extra electron is delocalised in the cyclic bond system of the tetrapyrrole ligand. Charge is similarly distributed in the singly charged anions of metal-free, zinc, magnesium, and disodium aetioporphyrins and of metal-free, copper, tin, magnesium, and disodium tetraphenylporphins. The second electron in the doubly charged anions of aetioporphyrin, tetraphenylporphin, and their zinc, magnesium, and copper derivatives is probably also located on the ligand, although the only evidence is a comparison of the absorption spectra of the doubly charged anions of porphyrins and of their metal derivatives. Cobalt and iron atoms introduce a significant anomaly into the charge distribution in the ions of metal porphyrins. Many experimental results indicate that the negative charge in the monoanion of cobalt tetraphenylporphin is located on the cobalt atom [19,71,72]. Information is lacking on products of the further reduction of cobalt porphyrins. Hush and Woolsey report [73] that, when an analogue of cobalamin is reduced with sodium, the first electron is located on the cobalt atom, but on addition of the second electron the whole of the excess charge shifts to the ligand. On formation of singly and doubly charged anions of the corresponding nickel complex both electrons are localised on the ligand. These conclusions were based on a comparison of the absorption spectra of ionic forms and the neutral molecules of the compounds.

Iron porphyrins occupy a special position among other metal porphyrins by virtue of their exceptional capacity for complex formation with out-of-plane ligand molecules and the readiness with which the state of the iron atom changes between bivalent and tervalent. The metal atom in iron(III) porphyrins binds outside the plane of the tetrapyrrole ring with CN, OH, Cl, etc. This ability of iron derivatives of the porphin series, which is responsible for the important part played by individual representatives in biological processes and on which numerous publications have appeared, greatly complicates investigation of their ionic forms. According to spectral data the first stage of interaction between ClFe^{III}AeP and negative pyridine ions is reduction of the central iron atom to the bivalent state [64]. Subsequent stages of this interaction are dissimilar in spectral characteristics from the changes undergone by other metal aetioporphyrins under the same conditions, and no data are yet available on the structure of the ionic forms of iron aetioporphyrin. Three reduction products have been characterised spectroscopically when oxybis[iron(III) tetraphenylporphin] (two molecules of the iron complex bound by an oxygen atom between the iron atoms) is treated with sodium amalgam in oxolan. The first stage is assumed to involve formation of a singly charged iron tetraphenylporphin anion with localisation of the charge on the metal [72].

Singly charged anions and cations of many metal derivatives of octaethylporphin have been obtained by electrochemical reduction. The potentials at which addition or removal of an electron takes place have been measured. Comparison of the absorption spectra of ionic forms and neutral molecules indicated whether the ionic charge was located on the metal atom or on the ligand [74]. Metals which are not involved in redox reactions when present in octaethylporphin complexes (the whole of the ionic charge is localised on the ligand) include alkali and alkaline-earth metals, the bivalent metals palladium, copper, zinc, and cadmium, tervalent antimony, scandium, aluminium, gallium, indium, and thallium, quadrivalent silicon, germanium, and tin, and also the metals present in vanadyl and titanyl. Among metals which change their valency under these conditions are—(*a*: I ⇌ II) cobalt; (*b*: II ⇌ III) manganese, iron, cobalt, chromium, and silver; (*c*: II ⇌ IV) lead; (*d*: III ⇌ IV) chromium and iron; and (*e*: IV ⇌ V) molybdenyl—where a metal atom undergoes a real change in valency only when a redox reaction involves a change in the number of atoms with which it forms valency bonds. If this number remains unchanged [as in the interconversion of cobalt(I) and cobalt(II) porphyrins], it is preferable to regard this as a change not in valency but in the population of the orbitals of the metal atom.

An interesting distinction between the ions of metal porphyrins and those of metal phthalocyanines is the enhanced tendency of the former to protonation. Slight contamination with proton-donating impurities (alcohols, weak acids) may result in conversion of the ionic forms of a metal porphyrin into partly or completely protonated ionic forms [17,20,25,26,66,68,69,75]. The protonation of doubly charged anions is represented by the scheme

$$Por^{2-} \xrightleftharpoons{H^+} PorH^- \xrightleftharpoons{H^+} PorH_2$$

(where Por represents a molecule of a neutral tetrapyrrole compound).

Products of the protonation of zinc tetraphenylporphin ions obtained by this method [20] were identical in absorption spectra and other properties with products of the photochemical reduction of the complex by hydrazine [76]. Protonation of doubly charged zinc aetioporphyrin anions follows by removal of zinc atoms from the protonated ions yielded reduced products spectrally identical with products of the photochemical or dark reduction of metal-free porphyrins to the corresponding dihydro-derivatives [77]. This gave independent confirmation of the structure of the photoreduced forms of porphyrins and their metal derivatives, while the reduction of a metal porphyrin to its hydrogenated form was separated experimentally into two stages: primary addition of an electron was followed by protonation of the resulting negative molecular ion.

The form $PorH^-$ can be obtained in an oxolan solution of zinc aetioporphyrin anions by reaction of Por^- or Por^{2-} with a comparatively weak proton donor, e.g. methanol. The monoanion Por^- is converted into $PorH^-$ by disproportionation:

$$2\,Por^- + H^+ = PorH^- + Por\ .$$

Interaction with a strong proton donor—acetic acid—yields the dihydro-derivative[66]. Protonation of the anions of metal porphyrins leads, of course, to significant changes in their spectral characteristics: the electron delocalised in the tetrapyrrole system of the ion becomes localised near the added proton, forming a valency bond with it. If the proton adds to a methine bridge, as is assumed to occur, the cyclic conjugation in the tetrapyrrole system will break down, and the whole system of energy levels will change. Addition of a second proton will lead to further spectral changes[20,66].

It proved impossible to effect photoelimination of an electron from the forms $PorH^-$ and $PorH_2$. Nor were attempts to obtain neutral radicals PorH· by the protonation of monoanions successful.

Partly protonated ionic forms $PorH^-$ of zinc and magnesium aetioporphyrins and tetraphenylporphins, like the neutral molecules, are able to add electrons on reaction with sodium, with the successive formation of $PorH^{2-}$ and $PorH^{3-}$. The first of these forms is paramagnetic and capable of photoelimination of an electron with regeneration of $PorH^-$, which is proof of its structure $[PorH^{2-}]$. In the presence of methanol the form $PorH^{3-}$, which can be termed a partly protonated trianion, is converted via a disproportionation stage into diamagnetic protonated tetra-anions, which exist in two spectroscopically distinguishable forms containing different numbers of excess protons[26,66].

The form $PorH_2$ is easily converted by loss of a proton into $PorH^-$, a reversible change governed by the acid–base equilibrium conditions. For example, a critical review, in the light of later results, of earlier work[76] on the photoreduction of zinc tetraphenylporphin shows that the presence of ammonia or hydrazine in pyridine solution leads to conversion of the dihydro-derivatives into the form $PorH^-$. Evaporation of the solution and dissolving the precipitate in pure pyridine again yields the $PorH_2$ form. In frozen solutions in organic bases a proton can be detached photochemically from the dihydro-derivative of zinc aetioporphyrin. The resulting $PorH^-$ form is again converted into $PorH_2$ when the solution melts[78].

Parly protonated anions and hydro-derivatives of metal porphyrins were repeatedly observed earlier in experiments on the dark and photochemical reduction of these compounds[76,79–84]. Successful attempts have recently been made to determine the structure of the products by nuclear magnetic resonance. Thus the added hydrogen atoms in the dihydro-form were shown to be situated on two opposite methine bridges, and in $PorH_3^-$ (or $PorH_4$) three of the four methine bridges were hydrogenated[84,85]. The form $PorH^-$ was regarded by the Closs's[17] on the basis of n.m.r. data as a metal phlorin, in full agreement with spectroscopic results.

In an optically excited state the capacity of negative ions of metal porphyrins for protonation is considerably increased, as is indicated by the possibility of accomplishing the photochemical protonation of metal aetioporphyrin ions in the presence of negative ions of pyridine. Here the pyridine ions act as proton donors, being converted into bipyridyl during the reaction[75].

Negative ions of metal-free porphyrins can also be converted into protonated forms. Experiments on the electrochemical reduction of tetraphenylporphin, the dimethyl ester of deuteroporphyrin, and the dimethyl ether of mesoporphyrin yielded not only singly and doubly charged anions but also the form $PorH^-$ having a phlorin structure, protonated tetra-anions $PorH_n^{(4-n)-}$ with a porphomethene structure, and protonated hexa-anions $PorH_n^{(6-n)-}$ with a porphyrinogen structure. The exact number of protons n in these forms was not determined[68,69]. Highly reduced colourless products formed from zinc aetioporphyrin by interaction with sodium had been observed earlier[63,64], probably containing six extra electrons and an unknown number ($n \leq 6$) of protons.

The protonated ions of porphyrins and of their metal derivatives exhibited closely similar absorption spectra at the same state of reduction. This similarity provides hints for determining the structure of the reduction products of porphyrins, in particular the location of hydrogen atoms added to the molecule.

Like porphyrins, their hydrogenated derivatives—chlorins and bacteriochlorins—are able to form singly and doubly charged anions. Negative ions of tetraphenylchlorin and tetraphenylbacteriochlorin have been obtained electrochemically and investigated by means of their absorption spectra[69]. In the presence of proton donors tetraphenylchlorin ions are converted into protonated forms: partly protonated dianions and protonated tetra-anions with an unknown number of protons have been recorded spectroscopically, but protonated hexa-anions are not formed by tetraphenylchlorin. In general the same final reduction product, porphyrinogen, is obtained from the tetraphenyl derivatives of porphin, chlorin and bacteriochlorin[65,69]. The bacteriochlorin molecule requires only two electrons and two protons for conversion into porphyrinogen, and the chlorin and porphyrin molecules require respectively four and six electrons and protons each. Partly protonated ions are intermediate stages in the reduction of these molecules to porphyrinogens.

Singly charged anions of disodium complexes of tetraphenylchlorin and tetraphenylbacteriochlorin have been obtained by the action of sodium on the metal-free compounds in dimethylformamide. They were proved to possess a purely ionic structure by photoelimination of an electron[32,33]. Singly charged anions of bacteriochlorophyll and of zinc tetraphenylbacteriochlorin were obtained by an electrochemical method[86]. The absorption spectra of the latter are similar to those of mono-anions of the corresponding disodium derivatives[33], which indicates that the extra electron is located on the ligand.

The effects of the central metal atom and of the charge distribution on protonation of the anion have not been investigated, although the charge distribution in the tetrapyrrole system of the ligand probably determines both the capacity of the ion for conversion into a protonated form and the structure of the latter (location of added protons). In support of the suggested role of the distribution of negative charge in an ion on its protonation we can consider the photochemical reduction of various metal phthalocyanines, involving as initial stage formation of a negative ion and a subsequent protonation stage. The ability of these complexes to form photoreduced varieties is substantially dependent on the nature of the metal. Magnesium and zinc phthalocyanines are converted into dihydro-derivatives when their pyridine solutions are exposed in the presence of hydrazine[87], whereas all cases investigated[44] of the photoreduction of cobalt phthalocyanine led merely to the formation of singly charged

anions $[CoPhth]^-$. Photoreduction of iron phthalocyanine has not yet been achieved[88]. These differences can be explained in terms of the electronic structures of the singly charged anions. In the magnesium complex ion the electron is located on the ligand, and a proton readily interacts with this ion to give a hydro-derivative, forming a valency bond with one of the outer nitrogen atoms. (It is on these atoms that the excess charge of magnesium phthalocyanine anions is presumably located.) A proton interacting with the complex cobalt anion is located near the cobalt atom, on which almost all the negative charge of the ion is situated; the conjugated system of the ligand remains unchanged, and the proton forms a purely ionic bond with the singly charged anion. The inability of iron phthalocyanine to be photoreduced can also be explained by peculiarities of the charge distribution in its monoanion (see above). We have recently been able to achieve the photoreduction of this complex in *N*-methylpiperidine by exposure to ultraviolet radiation at a low temperature, with formation of a photoproduct spectrally similar to the product of the photoreduction of magnesium phthalocyanine, and obviously also a dihydro-derivative. A possible explanation of the photoreduction of iron phthalocyanine is that the singly charged anion formed in the first stage of the photoreaction acquires in this medium an electronic structure with the charge localised on the ligand in virtue of the above redistribution of charge in the ion on formation of a complex with a molecule of a base.

Ions of metal phthalocyanines are not so sensitive as those of metal porphyrins to contamination with proton-donating impurities, and are protonated only at comparatively high concentrations of protons. Singly and doubly charged magnesium phthalocyanine anions are converted into the dihydro-derivative on treatment with acetic acid, as are the corresponding ions of metal porphyrins, but they probably retain their ionic structure in the presence of methanol, which leads merely to a change in the solvate sheath of the ions and to replacement of positive alkali-metal gegenions by protons, as is indicated by the comparatively small spectral differences. Nor can the possible formation of complexes between the metal phthalocyanine anion and the alcohol molecule be excluded. Such complexes have recently been discovered in experiments with fluorenyl anions[89]. Protonation of quadruply charged magnesium phthalocyanine anions by methanol or acetic acid yields new products, not yet identified, which may include both tetrahydro-derivatives and partly protonated tetra-anions[21].

V. PHOTOCHEMICAL GENERATION OF NEGATIVE IONS IN SOLUTION

The photochemical generation of ions not only supplements existing methods (chemical and electrochemical) but also gives indications of the reasons for the photochemical activity of molecules and the mechanism of the photo-transfer of an electron, the primary act in any redox reaction. Attempts were made long ago to obtain photochemically ionic forms of tetrapyrrole compounds, especially chlorophyll and its analogues, but only recently have positive results been obtained in isolated cases thanks to the development of methods for the spectroscopic identification of ions and to the selection of appropriate experimental conditions. The problem of the photogeneration and stabilisation of negative ions of porphyrins and their metal derivatives in liquid solutions is complicated by the high proton-accepting activity of these ions. When this property was established, the requirements of the medium in which they could exist became obvious—absence of those proton-donating and electron-accepting impurities causing oxidation of the ions and their discharge to neutral molecules, as well as adequate solvating power to stabilise the ionic forms.

One of the most suitable solvents for the photogeneration and stabilisation of anions of tetrapyrrole compounds was dimethylformamide with hydrazine added as reductant, provided that the reagents had been reliably freed from the above impurities. Almost complete conversion of magnesium phthalocyanine into stable singly charged anions could be achieved in this medium by exposure to visible light at $-50°C$.[43,90] Absorption and e.s.r. spectra showed that the photogenerated monoanions were identical with those obtained by interaction with alkali metals. Similar transformation on illumination occurred in this medium also with metal-free phthalocyanine. Ultraviolet irradiation of solutions of monoanions of phthalocyanine or its magnesium complex led to their further reduction to dianions[43].

Singly charged anions of magnesium phthalocyanines can be obtained in almost 100% yield also by exposing solutions of this complex in piperidine, which acts also as an electron donor. Radical-cations of piperidine could not be detected in the e.s.r. spectrum, probably owing to dimerisation of the cations or some other process leading to their neutralisation. In combination with the good solvating properties of piperidine as a solvent this ensures relatively high stability of the radical-anion of magnesium phthalocyanine in the liquid solution[91]. The presence of a proton donor—ascorbic acid—in a piperidine solution of the complex leads to the formation on exposure, not of monoanions, but of a dihydro-derivative which has been observed many times in previous work on the photoreduction of magnesium phthalocyanine[87]. Nevertheless, there are no grounds for doubting that monoanions are formed at the initial stage even in this case, subsequently add a proton, and pass through a stage of disproportionation with conversion into the dihydro-derivative.

N-Methylpiperidine in dimethylformamide can also be used as reductant for the photochemical production of singly charged anions of magnesium phthalocyanine. In this system illumination with visible light at $-60°C$ gives initially monoanions, then a dihydro-derivative with an absorption band at 560 nm, and finally a new product with a band at 780 nm.[26] This latter spectrum was identical with that of a protonated form of tetra-anions of the complex[21], and the product was probably a tetrahydro-derivative.

Monoanions of several other metal phthalocyanines can be obtained in dimethylformamide with hydrazine or *N*-methylpiperidine as reducing agent[26]. Those of the lead and cadmium complexes obtained in this way were spectroscopically indistinguishable from singly charged phthalocyanine anions. These compounds probably lose their metal atoms immediately after addition of an electron: i.e. a phenomenon takes place analogous to the photophaeophytinisation of chlorophyll on reduction[92]. Copper and nickel phthalocyanines on exposure form monoanions with the typical absorption spectrum characteristic of localisation of the added electron on the ligand. Cobalt phthalocyanine is reduced to a monoanion with localisation of the charge on the cobalt atom. In the presence of *N*-methylpiperidine in dimethylformamide alone or in an equimolecular mixture with oxolan at $-60°C$ iron phthalocyanine is reduced photochemically to monoanions having an absorption spectrum indicating a distribution of charge between the ligand and the iron atom, as in

the reduction of the metal complex by an alkali metal. Cooling a solution of monoanions of iron phthalocyanine to −196°C changes the spectrum, and the charge shifts to the ligand (thermochromism—see above).

Application of this method for the photogeneration of ions in liquid solutions to tetraphenylporphin and its zinc derivative [67,93] also yielded monoanions at −60°C, although their yield was only 60%. This may have been due to the photoinduced reverse reaction. When heated to 20°C these monoanions are converted partly into a dihydro-derivative and partly into the original compound. Protonation was not observed with ions of phthalocyanine and metal phthalocyanines, probably owing to their greater stability towards protonation.

The ionic character and the magnitude of the charges on the products of the above photoprocesses have been confirmed by e.s.r. measurements [91] and by photoelimination of an electron leading to regeneration of neutral molecules of the original tetrapyrrole compound (or its monoanion if the electron has been detached from the dianion) [43,67].

Sufficient data are not yet available to settle the mechanism of the photogeneration of molecular ions, and only certain general considerations can be expressed. The act of electron transfer occurs between a photoexcited molecule of the tetrapyrrole compound Por* and an electron-donating molecule Don:

$$Por^* + Don \rightarrow Por^- + Don^+ .$$

The electron donor may be either a solvent molecule (as occurred in the reduction of magnesium phthalocyanine by piperidine) or an added reactant molecule (hydrazine in dimethylformamide); these cases may differ significantly in reaction kinetics. The excited molecule Por* is most often present in the lowest triplet state, but activity in the charge transfer may be exhibited both by a singlet state and by excited states due to the presence of the d-shell of the central metal atom [94]. A special case is the photogeneration of iron phthalocyanine monoanions and also of dianions of phthalocyanine and the magnesium complex. These reactions do not occur on exposure in the region of long-wavelength absorption bands but require short-wavelength bands, which suggests that higher excited states are involved in these photoreactions. Since the lifetimes of such states are usually brief, diffusion processes must play an insignificant part, and the electron donors must be either solvent molecules from the solvate sheath or out-of-plane added molecules present in a complex with the Por* molecule.

The stability of photogenerated negative ions of tetrapyrrole compounds in liquid solutions is determined firstly by the solvating properties of the solvent and secondly by the ability of the positive gegenions Don^+ formed in the photoreaction to be deactivated in time to prevent electron transfer in the opposite direction. The actual occurrence of such deactivation is confirmed by the absence from the e.s.r. spectra of signals due to radical-cations. The most probable mechanism of deactivation is interaction with solvent molecules or with neutral molecules of the donor.

In solid solutions (predominantly solutions frozen at −196°C, but polymerised matrices can in principle be used) the general mechanism of the phototransfer of an electron is the same as in liquid solutions, but conditions for stabilisation of the ions differ considerably. Molecular diffusion is slowed down, and the presence of proton-donating and electron-accepting impurities does not affect the stability of negative ions provided that these impurities do not form complexes with molecules of the tetrapyrrole compound and do not enter their solvate sheaths.

Krasnovskii and his coworkers [95] reported the possibility of the photochemical generation and stabilisation of radical-ion forms of porphin in acidified alcoholic solutions at −196°C. Gribova detected radical-ions on irradiating frozen alcoholic solutions of magnesium aetioporphyrin [96]. The hypothesis that these radical-ions were monoanions of the complex was not supported by later work: exposure of frozen solutions of zinc and magnesium aetioporphyrins in mixtures of diethyl ether with ethanol or with oxolan results in detachment of an electron from the molecules of these compounds and formation of their monocations. Negative ions may also be formed in subsequent stages of the reaction as a result of migration of the freed electrons [97,98]. Magnesium phthalocyanine, in contrast to magnesium aetioporphyrin, is converted into monoanions on exposure in a frozen ethereal oxolan matrix [90]. The porphyrin ring is obviously a better electron donor than is the phthalocyanine ring. Monoanions of zinc tetraphenylporphin may be photogenerated in frozen pyridine, and were recorded in photoconductivity experiments [99].

An interesting case of electron phototransfer from negative pyridine ions to zinc aetioporphyrin molecules has been observed in a frozen mixture of oxolan and ether [75]. When solutions of these species are mixed, they form a complex which in the frozen state is highly photosensitive: brief exposure in any of the absorption bands of zinc aetioporphyrin converts it into monoanions, which with increase in exposure eliminate the extra electron and regenerate the neutral molecule. Magnesium, copper, nickel, and disodium aetioporphyrins do not form complexes with pyridine ions under similar conditions, and in frozen solutions possess no photosensitivity to visible light. Thus slight individual peculiarities of different tetrapyrrole compounds may be efficacious under certain conditions.

In acid medium two protons add to a molecule of a metal-free porphyrin, with formation of a porphyrin dication [100]. The presence of the positive charge enhances its electron affinity: the acid dicationic form of a porphyrin can be reduced not only in the presence of typical reducing agents but even by anions of mineral acids. Photochemical reduction of the acid cationic forms in frozen solutions may yield either ionic or hydrogenated forms. The photoprocesses can be directed towards either reduction or oxidation by varying the composition of the incident radiation by introducing typical oxidants or reductants into the solution [25,101,102].

Frozen solutions enable molecular ions to be generated by γ-radiolysis, which effects electron transfer between solvent and solute molecules. Depending on the properties of the solvent the solute molecules can be converted into either anionic or cationic forms. The advantage of this method is that the resulting ions do not interact with the gegenion. Though widely used for investigating ions of aromatic compounds, γ-radiolysis has hardly been applied at all to the generation of tetrapyrrole ions. Only one paper has been published, on the radiolysis of chlorophyll: irradiation in frozen methyloxolan gave monoanions, and exposure in isobutyl chloride yielded monocations [103].

VI. COMPLEXES. IONIC ASSOCIATION

The formation of molecular complexes (association) is a widespread phenomenon with neutral molecules, and has been investigated in detail. The presence of the excess

charge in a molecular ion, by introducing a specific character into its interaction with the medium, not only does not prevent but rather promotes such interaction. The specific character of a molecular ion governs the association of ions of opposite sign. In solution this phenomenon leads to the formation of ion-pairs (e.g. comprising a molecular anion and an alkali-metal cation) or larger aggregates. In the solid state ionic association leads to the formation of saltlike products. Another feature of interaction of a molecular ion with the medium is its enhanced capacity for solvation in solution. The excess charge of the ion ensures a more stable orientation of the molecular dipoles surrounding it and deeper potential wells formed by the solvating dipoles. This ability of ions to form stable solvates makes it possible to stabilise the ions in liquid solutions.

Furthermore, molecular ions can also be involved in the interactions usually observed between neutral molecules. For example, monocations of perylene and tetracene form dimers by donor–acceptor interaction [104]. We have discussed above complexes comprising a negative ion and a neutral molecule, which are probably weak charge-transfer complexes in which the negative ion obviously acts as electron donor. Such are the complexes between the iron phthalocyanine monoanion and a neutral molecule of an organic base, whose formation leads to a redistribution of charge in the monoanion, and the complex between a negative ion of pyridine and a neutral molecule of zinc aetioporphyrin. The latter complex is not formed if the component solutions are mixed and kept at or below −100°C: complex formation takes place only around −60°C. The need to raise the temperature for complex formation to occur is obviously due to the necessity of rearrangement of the solvate sheaths surrounding the pyridine ions and the zinc aetioporphyrin molecules. The sheath around the pyridine ions, which bear an excess negative charge and therefore exert an enhanced orienting effect on the surrounding dipoles, exhibits especially great stability, which increases the lower the temperature. Once the complex has been formed at −60°C, of course, it does not decompose when the temperature is subsequently lowered [75]. Exposure entails electron transfer within the complex, with formation of the zinc aetioporphyrin monoanion—not dianions—so that the complex must be regarded as equimolecular.

Returning to the phenomenon of ionic association, we note that in general an equilibrium is established in solution between ion-pairs of various types (contact, separated) and dissociated ions [1-3,9,105]. The solvating properties of the solvent become stronger with fall in temperature, and the equilibrium shifts towards separated and dissociated ion-pairs. The position of equilibrium depends on the solvating power of the solvent, the dimensions of anion and cation, and the charge on the molecular ion: a multicharged ion retains gegenions more firmly than does a singly charged ion. In methyloxolan, in particular, the monolithium salts of anthracene, tetracene, and pentacene, both at 20 and especially at −196°C, are dissociated or form separated ion-pairs differing little in properties from dissociated ions. Monosodium and monopotassium salts of polyacenes exist in this solvent at 20°C predominantly as contact ion-pairs, which are converted into separated pairs or dissociated ions when the temperature is lowered. Dianions of polyacenes are associated with two positive ions at 20°C, but in most cases with one such ion at −196°C. [3,106,107]

No detailed investigations have been made on the association of negative ions of tetrapyrrole compounds. Preliminary data show that they obey the same laws as do the ions of aromatic compounds. Although it was suggested that ionic association was strengthened by lowering the temperature of solutions of singly charged magnesium phthalocyanine anions, the grounds for such a hypothesis were insufficient [21], and it must be abandoned in the light of later results. As in the general case, lowering the temperature of solutions of metal phthalocyanine anions probably displaces the equilibrium towards the dissociation of ion-pairs.

Comparison of the absorption spectra of negative ions of metal phthalocyanines at 20°C and at −196°C shows that in an ether–oxolan mixture all ions—from monoanions to tetra-anions—change their state of association with change in temperature. An exception is the cobalt phthalocyanine monoanion, in whose spectrum no change was observed over the above temperature range. An explanation of the absence of change is that the absorption bands of this anion are due to transitions between energy levels of a ligand not bearing a negative charge that, on interaction with the positive charge of a cation, might cause a displacement of levels and bands as occurs with anions of other metal phthalocyanines [44]. The absence of spectral changes with variation in temperature does not mean, of course, that the equilibrium between aggregates and dissociated ions does not shift.

Since an obvious difference is observed [21,44] between the absorption spectra of solutions of metal phthalocyanines at 20°C and at −196°C, it must be supposed that in the former case they are associated with alkali-metal cations, but in the latter case are present as separated ion-pairs or in a dissociated state. The state of association of monoanions of other tetrapyrrole compounds—zinc tetraphenylporphin [20,93], zinc aetioporphyrin [26], disodium chlorin [32]—changes similarly when the temperature is lowered.

On the basis of available experimental data it is difficult to say anything definite on the state of association of multicharged ions of tetrapyrrole compounds, other than that this state changes when the solutions freeze. Comparison with the properties of anions of aromatic compounds suggests that, in oxolan at 20°C, the multicharged ions form aggregates in which the number of alkali-metal cations is equal to the anionic charge. With fall in temperature these aggregates partly dissociate, eliminating one alkali-metal cation—or less probably two cations—as a consequence of the strengthening solvating power of the solvent. It is to be hoped that a detailed study of electron photoelimination from multicharged ions will enable the structure of aggregates in frozen solutions to be refined, since the spectral threshold of such photoelimination should depend significantly on the state of association of the ions: the more complete is dissociation, the more easily can photoelimination be accomplished right up to conversion of the multicharged anion into a neutral molecule.

Electron photoelimination enables ionic aggregates of unusual composition to be obtained in a frozen solution. Thus in methyloxolan at −196°C monoanions of terphenyl and tetracene are usually present in the dissociated state. By detaching an electron from the dianion, which at this temperature is associated with one sodium cation, it was possible to obtain under these conditions associated monoanions clearly distinguishable by their absorption spectra from the dissociated monoanions [107]. Detachment of an electron from magnesium phthalocyanine dianion in a frozen ether–oxolan mixture gave a monoanion with a spectrum similar to that of the monoanion at room temperature [21]. Comparison of this experiment with those on the photodischarge of dianions of terphenyl and tetracene

indicates that the same phenomenon is observed even in this case, i.e. that magnesium phthalocyanine dianion is associated with one sodium cation in frozen solution. The photodetachment of one electron from the dianion gives the associated monoanion, which does not normally exist in frozen solution. Complete photodischarge of the dianion should result in formation of the neutral magnesium phthalocyanine molecule in direct contact with the alkali-metal cation. The photodischarge of tetra-anions may yield a metal phthalocyanine molecule surrounded by two or three cations, which opens up the possibility of investigating the properties of a molecule in the field of contiguous charged species.

VII. CATALYTIC ACTIVITY OF NEGATIVE IONS OF METAL PHTHALOCYANINES

Although molecular ions are involved as intermediate structures in most redox reactions, their use as reactants is still fairly limited. The ability of negative ions to transfer an electron to compounds of greater electron affinity makes possible their use for reductions, including the initiation of anionic polymerisation [108]. Anions of aromatic hydrocarbons, obtained on interaction with alkali metals, can be employed in metallations [109]. Use of the protonation of negative ions to obtain hydrogenated derivatives of the compounds is a promising possibility. It must be supposed that negative ions of tetrapyrrole compounds can be employed in the same reactions as ions of aromatic compounds. The existence of multicharged ions of metal phthalocyanines and the localisation of the negative charge either on the tetrapyrrole ligand or on the complexing metal atom may extend significantly the potential use of ions of metal phthalocyanines and porphyrins as selective reactants. Hitherto, however, hardly any investigations on these lines have been made on ions of tetrapyrrole compounds. Information is available only on a series of Japanese studies in which negative ions of tetrapyrrole compounds, mainly metal phthalocyanines, were used as catalysts.

Neutral metal phthalocyanines catalyse, for example, hydrogen exchange, the conversion of para- into ortho-hydrogen, the oxidation of cumene to its hydroperoxide, and the dehydrogenation and decomposition of formic acid [110,111]. In several cases the catalytic activity is determined by the nature of the central metal atom, but with heterogeneous catalysis the rate of reaction is significantly affected by the crystalline modification of the metal phthalocyanine, which indicates the part played by the π-conjugated system of the tetrapyrrole ligand [110]. Polymeric metal phthalocyanines, which have an extended π-electron system, exhibit catalytic activity towards reactions involving activation of hydrogen atoms that exceeds the activity of the monomeric complexes by an order of magnitude [111].

The negative ions of metal phthalocyanines, which are distinguished from the neutral molecules by a higher π-electron density in the tetrapyrrole ring, exhibit a significantly higher catalytic activity than the latter. In 1966 Ichikawa et al. discovered [112,113] that "donor–acceptor complexes" formed on contact between a sublimed film of a metal phthalocyanine and sodium vapour effectively catalyse hydrogen exchange between molecular hydrogen and deuterium, and between acetylene and deuteroacetylene. These "donor–acceptor complexes" were later identified with ionic salts of the metal phthalocyanines [114,115], and were found to catalyse several other chemical reactions, in particular the hydrogenation of alkenes in isomerisations, the synthesis of ammonia from hydrogen and nitrogen, and that of hydrocarbons from carbon monoxide and hydrogen [114,116,117]. It was found also that two central hydrogen atoms in sodium phthalocyanine were replaced by deuterium in the presence of molecular deuterium or deuteroacetylene. Negative ions of metal phthalocyanines also exchange their hydrogen for deuterium atoms [118,119]. This implies that hydrogen exchange takes place even in the benzene rings of metal phthalocyanine ions [113]. The excess negative charge of the ion, being distributed over the phthalocyanine ring, obviously covers the benzene rings also, whence the latter become more protophilic, which makes possible hydrogen exchange between magnesium phthalocyanine ions and deuterium molecules (or deuteroacetylene). This conclusion is supported directly by the increased rate of isotopic exchange between molecular deuterium and the metal phthalocyanine ion with increase in the ionic charge, but only slight variation with the nature of the central metal atom [115]. Exceptions are the monoanions of cobalt and iron phthalocyanines and the dianion of the latter, which do not exchange their hydrogen atoms for deuterium and catalyse neither exchange in a mixture of hydrogen and deuterium molecules nor the hydrogenation of alkenes by hydrogen [120,121]. The reason for such exceptions becomes clear from the electronic structure of these ions (see above): almost all the excess charge in the complex cobalt monoanion is concentrated on the cobalt atom, and a considerable proportion is localised on the iron atom in the complex iron monoanion. Multicharged ions of cobalt and iron phthalocyanines exhibit catalytic activity, as do the ions of other metal phthalocyanines.

The possibility of isotopic exchange between metal phthalocyanine ions and molecular deuterium of deuteroacetylene opens up a route for obtaining under laboratory conditions completely deuterated metal phthalocyanines, which are necessary for spectroscopic investigations on these compounds.

Whereas isotopic exchange between molecular deuterium and metal phthalocyanine ions is little affected by the nature of the metal atom, the hydrogen exchange between molecular hydrogen and deuterium catalysed by these ions depends significantly on the metal atom. The two reactions obviously have different mechanisms. Dissociative chemisorption of the hydrogen (deuterium) molecule in the vicinity of the central metal atom is assumed to be a stage in the latter reaction [115]. The mechanism of isotopic exchange in the benzene ring is obscure: it may be effected either by direct contact between the ring and a deuterium molecule or by contact with atomic deuterium formed by dissociative chemisorption on a neighbouring metal phthalocyanine ion.

The above series of papers on the catalytic action of negative metal phthalocyanine ions contain insufficient spectroscopic data, without which it is difficult, firstly, to monitor the identity of the ionic forms and their stability during an experiment, and secondly, to compare the results with those of other investigations on such ions made predominantly by spectral methods. An unsuccessful attempt was made to obtain infrared absorption spectra of negative ions of phthalocyanine: the spectrum of the initial phthalocyanine film remained unchanged after contact with sodium vapour. Hence it was concluded that formation of ions and catalysis take place only in the surface layer of the film [118,119]. This seems to us a dubious result, as the colour of metal phthalocyanine films was changed by con-

tact with sodium vapour [119]. Using the same method as the Japanese workers, we obtained without special difficulty the electronic and infrared absorption spectra of various ionic forms of magnesium phthalocyanine after films of the neutral complex had been kept in an alkali-metal vapour [122]. This means that the alkali-metal atoms are able to penetrate inside microcrystals of the metal phthalocyanine. Furthermore, comparatively thick films of a metal phthalocyanine are permeable to such small and even large molecules as water, ammonia, phenylhydrazine, aniline, diphenylamine, pyridine, indole, etc. [123,124] This implies that catalysis can occur not only on the surface of films of metal phthalocyanines and their ionic forms but also inside the layer.

Catalytic activity towards various chemical reactions is not an exceptional property peculiar to ions of metal phthalocyanines, as was to be expected. Such activity has been observed with negative ions of metal tetraphenylporphins [125-127], as well as with negative and positive ions of several other organic compounds—tetracyanopyrene [128], phenothiazine [129], polyacenes, quinones, nitriles, and several other aromatic compounds [114,116,120].

Detailed investigation (kinetic and spectroscopic) of the mechanism of the interaction of negative ions of anthracene with hydrogen showed that the product was an anthracene carbanion (the anion of 9-hydroanthracene) [116,130-132]. Carbanions of anthracene are probably formed also in hydrogen exchanges catalysed by anthracene ions and in the hydrogenation of alkenes. The kinetics of the sorption of hydrogen on metal phthalocyanine ions resembles that of the interaction of hydrogen with anthracene ions, but no changes were detected in the electronic absorption spectrum of a film of nickel phthalocyanine tetra-anions in the presence of molecular hydrogen, which was assumed [115] to exclude the suggested possibility of the formation of protonated anions of nickel phthalocyanine.

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