Unimolecular and Collision-Induced Reactions of Doubly Charged Porphyrins

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Results from a tandem mass spectrometry (MS/MS) study, obtained with a reverse-geometry mass spectrometer, of the unimolecular and collision-induced reactions of doubly charged free-base and metal containing alkyl-substituted porphyrins formed by electron ionization are reported. These doubly charged porphyrin ions dissociate to yield both singly and doubly charged product ions via a number of reactions. This article classifies the major reactions observed, illustrating each with the appropriate spectra. Supplementary data from the same porphyrins, acquired with a tandem quadrupole MS/MS instrument, are also presented. The potential utility of some of these reactions as new methods for porphyrin analysis is discussed. (*J Am Soc Mass Spectrom 1992, 3, 235–242*)

D oubly charged ions are frequently observed in the electron ionization (EI) mass spectra of organic molecules, but their abundances rarely exceed a few percent of the total ion current [1]. In this regard porphyrins, which are extremely stable, macrocyclic tetrapyrroles (e.g., Structures 1 and 2), are exceptional. Electron ionization of a porphyrin usually forms, in addition to the singly charged molecular ion and singly charged fragment ions, an abundant doubly charged molecular ion and doubly charged fragment ions [2–5]. For example, the relative abundances of the doubly charged molecular ions in the EI mass spectra of short-chain alkyl-substituted porphyrins have been reported in many cases to approach 50% of the most abundant ion, which is usually the molecular ion [3]. Porphyrins with functionalized substituent groups or extended alkyl chain substituents tend to form less abundant molecular dications, owing to the fragility of the bonds in these substituents, but the doubly charged fragment ions in these spectra can be quite intense. Also, metalloporphyrins generally form a greater abundance of doubly charged ions than the corresponding free-base porphyrins [3].

A thorough analysis of porphyrin EI mass spectra over the past three decades has led to an empirical rationalization of the doubly charged ions that are observed. As noted above, it has been determined that the relative abundances of porphyrin doubly charged species depend on the nature of the substituent groups present on the porphyrin macrocycle,
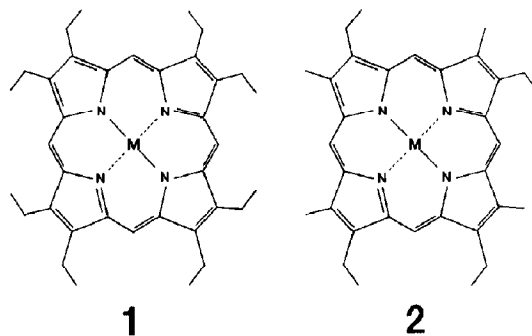
M = VO²⁺, Ni²⁺, or 2H (free-base)

Structures 1 and 2

on whether the porphyrin is a free-base or metal containing species, and, in the case of metalloporphyrins, on the type and valence state of the metal [2–5]. While benzylic-like or β-cleavage of the substituent groups from the macrocycle is the predominant fragmentation mechanism for singly charged ions, α-cleavage of the substituents has been found to account for a significant portion of the doubly charged fragment ions [5].

Further insight into the structure and chemistry of doubly charged ions formed from porphyrins by EI is accessible via tandem mass spectrometry (MS/MS) methods [6–8]. The propensity of porphyrins for dication formation makes this class of compounds a particularly strong candidate for a study of this type. Such information regarding porphyrin dications could prove useful, for example, in the development of new

mass spectrometric methods for porphyrin analysis. Little effort, however, has been expended toward applying MS/MS methods developed for dication analysis [9] to the analysis of doubly charged porphyrin cations. The only previous MS/MS study of doubly charged porphyrin ions formed by EI was carried out by Beato et al. [5] using a triple-quadrupole mass spectrometer. In that study, the low collision energy (< 100 eV laboratory) collision-induced dissociation (CID) spectra of the corresponding singly and doubly charged ions observed in the mass spectra of selected porphyrins were compared. Beato et al. [5] reported that the doubly charged ions fragmented almost exclusively to doubly charged product ions. Singly charged product ions from doubly charged parent ions were formed with very low abundances and with poor reproducibility. It was suggested that this was a result of the ability of the aromatic porphyrin macrocycle to stabilize the doubly charged product ion by charge separation and/or resonance.

We have been studying doubly charged porphyrin cations with a reverse-geometry sector mass spectrometer (BE, B = magnetic sector, E = electric sector), which allows for kinetic energy/charge analysis of the product ions formed from decomposition of metastable porphyrin dications or product ions formed from porphyrin dications induced to react via kiloelectronvolt collisions with a target gas. During the course of this work we have found that porphyrin dications *do* form abundant singly charged product ions, in addition to doubly charged product ions, both from metastable dications and from dications that have been activated by kiloelectronvolt energy collisions [10]. This article summarizes and categorizes the reaction phenomenology of porphyrin dications formed by EI as they occur in conjunction with kiloelectronvolt collisions and under collision-free conditions in a reverse-geometry sector mass spectrometer. Each reaction type is illustrated with data acquired from selected free-base and metal containing alkyl-substituted porphyrin standards. Supplementary data from the same porphyrins, acquired with a tandem quadrupole MS/MS instrument, are also presented.

Experimental

Porphyrin samples were acquired from commercial suppliers (Aldrich Chemicals, Milwaukee, WI or Strem Chemicals, Newburyport, MA) and used without further purification. The porphyrins studied were 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine (octaethylporphyrin, 1), 2,7,12,18-tetramethyl-3,8,13,17-tetraethyl-21H,23H-porphine (etioporphyrin-III, 2) and their vanadyl [VO(II)] and nickel [Ni(II)] derivatives, respectively. The majority of the data presented in this article was acquired by using a VG Instruments (Manchester, UK) ZAB mass spectrometer equipped with a syringe needle collision cell [11] in the second

field-free region (reaction region) of the instrument. A heated direct insertion probe was used to introduce the samples into the ion source which was maintained at temperatures in the range of 473–523 K. Porphyrins were ionized by using 70-eV electrons and an emission current of ~ 0.3 mA. To obtain metastable ion spectra, the ion source voltage (4.5 keV) and the magnetic field were fixed to allow doubly charged parent ions (M_p^{2+}) of the desired momentum-to-charge ratio to pass into the reaction region. The electric sector voltage was then scanned from 0 to $2E$ (where E is the electric sector voltage that passes the doubly charged parent ion formed in the ion source) so as to detect both singly (M_{pd}^{+}) and doubly charged (M_{pd}^{2+}) products formed from metastable ion decompositions in this region. To obtain spectra from collision-induced reactions, a collision gas was admitted into the reaction region via the syringe needle. Unless otherwise noted, the pressure of the collision gas was adjusted to obtain a beam attenuation of approximately 15–25%. The electric sector was then scanned as before to record the collision-induced reaction products, both singly and doubly charged, formed in this region. $2E$ mass spectra [9] were acquired by first setting the electric sector voltage to maximize the intensity of the singly charged reaction products formed from the parent dication by the reaction, $M_p^{2+} \xrightarrow{N} M_{pd}^{+}$, where N is the target gas, and then scanning the magnet.

Supplementary data were acquired by using a Finnigan-MAT (San Jose, CA) TSQ 700 tandem quadrupole mass spectrometer. This instrument contains a center rf-only octapole collision region rather than the normal rf-only quadrupole (i.e., quadrupole-octapole-quadrupole). A heated solids probe was used to introduce samples into the ion source which was maintained at a temperature of 523 K. Ionization was carried out by using 70-eV electrons with an emission current of 0.2 mA. Product ion spectra resulting from unimolecular decomposition were obtained by selecting the parent ion with the first quadrupole and scanning the second quadrupole to detect product ions formed from unimolecular decomposition of the parent ions in the center rf-only octapole. CID spectra were acquired in a similar manner except that argon was admitted as a collision gas into the rf-only octapole. It was found that products from the reactions of interest were maximized using a target gas pressure of ~ 1 mtorr with the parent ions entering the collision region with a nominal kinetic energy of 8 eV.

Results and Discussion

The EI mass spectra of alkyl-substituted porphyrins are characterized by two distinct regions of peaks as demonstrated by the EI mass spectrum of vanadyl octaethylporphyrin (vanadyl OEP, 1) shown in Figure 1. The molecular ion (M^+; m/z 599) and singly
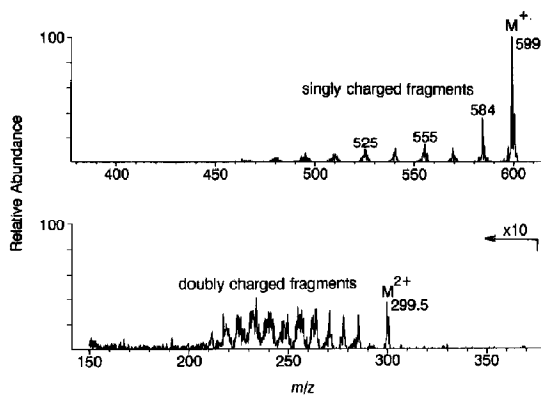
Figure 1. EI mass spectrum of vanadyl OEP obtained using the tandem quadrupole mass spectrometer.

charged fragment ions appear at the high mass end of the spectrum and the molecular dication (M^{2+}, m/z 299.5) and doubly charged fragment ions appear at the low mass end of the spectrum with the remainder of the spectrum relatively free of peaks. In the mass spectrum of vanadyl OEP, the base peak is the molecular ion. Singly charged fragment ions (e.g., m/z 584 and 569) result primarily from successive benzylic-like cleavages (i.e., β-cleavage) of the ethyl substituent groups from the porphyrin macrocycle. The doubly charged molecular dication and doubly charged fragments are of lower abundance. It is interesting to note, however, that the abundances of the doubly charged fragment ions relative to that of the molecular dication are as great or greater than the abundances of the singly charged fragment ions relative to the molecular ion abundance. $[M-29]^{2+}$ (m/z 285), which most likely results from α-cleavage of an ethyl group, is one of the more abundant of the doubly charged fragments. Doubly charged fragment ions resulting from β-cleavages, for example $[M-15]^{2+}$ at m/z 292, are also observed but at low intensity. A more de-

tailed comparison of the fragment ions observed from singly and doubly charged alkyl-substituted porphyrins, and the effect of the chelated metal on this fragmentation, can be found elsewhere [2–5].

In the present work, the metastable ion and collision-induced reactions of the doubly charged molecular ion of vanadyl OEP and molecular dications of similar porphyrins were investigated by using MS/MS. The types of reactions observed are listed in Scheme I and illustrated by the spectra in Figures 2 and 3 obtained during the study of the molecular dication (M_p^{2+}) formed from vanadyl OEP. Metastable porphyrin dications were observed to undergo unimolecular dissociation either by (1) loss of neutral substituent group units to form doubly charged product ions (i.e., metastable ion dissociation with charge retention, Figure 2a) or (2) via charge separation to form singly charged product ions (Figure 2b). Collision-induced reactions were observed in which (1) the dications dissociated to form doubly charged product ions via loss of neutral substitutent group units (i.e., CID with charge retention, Figure 3a), (2) the dications charge separated (i.e., collision-induced charge separation, Figure 3b), (3) the dications captured an electron from the collision gas forming the corresponding singly charged ion (Figure 3c), and (4) the dications, after charge exchange with the collision gas to form the singly charged ion, fragmented forming singly charged product ions (i.e., electron-capture-induced dissociation [ECID] [12], Figure 3c). The multiplication factors on these spectra indicate the abundances of these product ions relative to the attenuated abundance of the doubly charged parent ion. These spectra and other examples of the reactions observed, and their potential analytical utility, are discussed in more detail below. It should be pointed out that the mass resolution of the product ion spectra obtained on the BE instrument is limited due to the kinetic energy release associated with the reactions that give rise to the observed products. Therefore, the mass

Scheme I
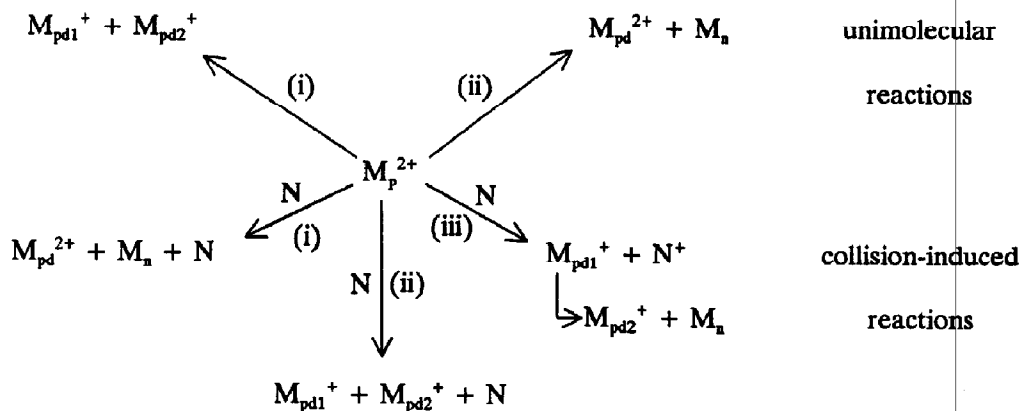
assignments on the peaks in the spectra shown have an uncertainty of at least one mass unit and a single peak may include a range of ions.

Metastable Ion Reactions

Metastable ion dissociation with charge retention. Metastable ion dissociation with charge retention refers here to unimolecular decomposition reactions of a doubly charged porphyrin (M_p^{2+}) that result in formation of a doubly charged product ion (M_{pd}^{2+}) and a neutral species (M_n) as described by eq 1.
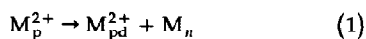
$$M_p^{2+} \rightarrow M_{pd}^{2+} + M_n \qquad (1)$$

Figure 2a shows the metastable ion spectrum obtained from the doubly charged molecular ion of vanadyl

OEP (1). The spectra from free-base and nickel OEP, with the exception noted below, were qualitatively similar. The major ions observed in this product ion spectrum are $[M-15]^{2+}$ and $[M-29]^{2+}$, resulting from β-cleavage and α-cleavage of an ethyl group, respectively. Several other product ions of lesser abundance are also observed including those species centered at mass-to-charge ratio values corresponding to $[M-44]^{2+}$ and $[M-56]^{2+}$. The $[M-44]^{2+}$ peak (m/z 277.5) appears to be due to the combination of an α-cleavage (ethyl loss) and a β-cleavage (methyl loss). The origin of the $[M-56]^{2+}$ ion (m/z 271.5) might be due to the loss of two ethylene groups. Of particular interest in this spectrum is the peak at m/z 290.5, corresponding to $[M-18]^{2+}$, presumably due to the loss of H_2O. This ion was not observed in the spectra of the free-base porphyrins or the nickel porphyrins in this study. This is consistent with the fact that the vanadyl porphyrins are the only porphyrins studied that contain an oxygen atom.

As might be expected, the relative abundances of the different doubly charged product ions in the metastable ion spectra are dependent on the relative number of the particular substituent groups on the macrocycle. This is illustrated by comparing the metastable ion spectrum of vanadyl etioporphyrin-III (vanadyl etio-III, 2) shown in Figure 4 with the metastable ion spectrum of vanadyl OEP shown in Figure 2a. These two porphyrins have different numbers and types of substituent groups (OEP = eight ethyl groups; etio-III = four methyl and four ethyl groups). Similar product ions are observed in both spectra, including $[M-18]^{2+}$, which is characteristic of the vanadyl group. The relative abundances of the two major product ions in the spectrum of vanadyl OEP (viz. m/z 292 and 285) indicates that α-cleavage of an ethyl group (i.e., $[M-29]^{2+}$) is twice as probable as β-cleavage (i.e., $[M-15]^{2+}$). This may be due to the greater stability of $C_2H_5 \cdot$ formed by α-cleavage over the stability of $CH_3 \cdot$ formed by β-cleavage. Whereas β-cleavage of an ethyl group is the only source of $[M-15]^{2+}$ in the case of vanadyl OEP, both α-cleavage of a methyl group and β-cleavage of an ethyl group can give rise to this peak for vanadyl etio-III. This probably accounts for the near equal abundance of the $[M-15]^{2+}$ and $[M-29]^{2+}$ peaks in the spectrum in Figure 4. Assuming that α- and β-cleavage of an ethyl group have the same probability for vanadyl etio-III as for vanadyl OEP ($\sim$ 2:1), over 50% of the $[M-15]^{2+}$ ion intensity in the vanadyl etio-III spectrum should be due to α-cleavage of a methyl group.

Metastable ion charge separation. Metastable ion charge separation refers here to the unimolecular decomposition of a doubly charged porphyrin cation to form two singly charged product ions as described by equation 2.

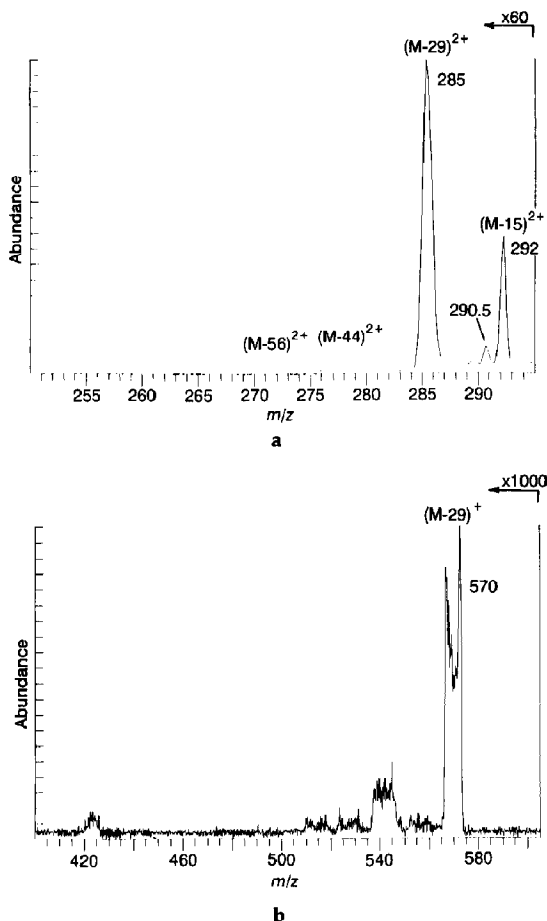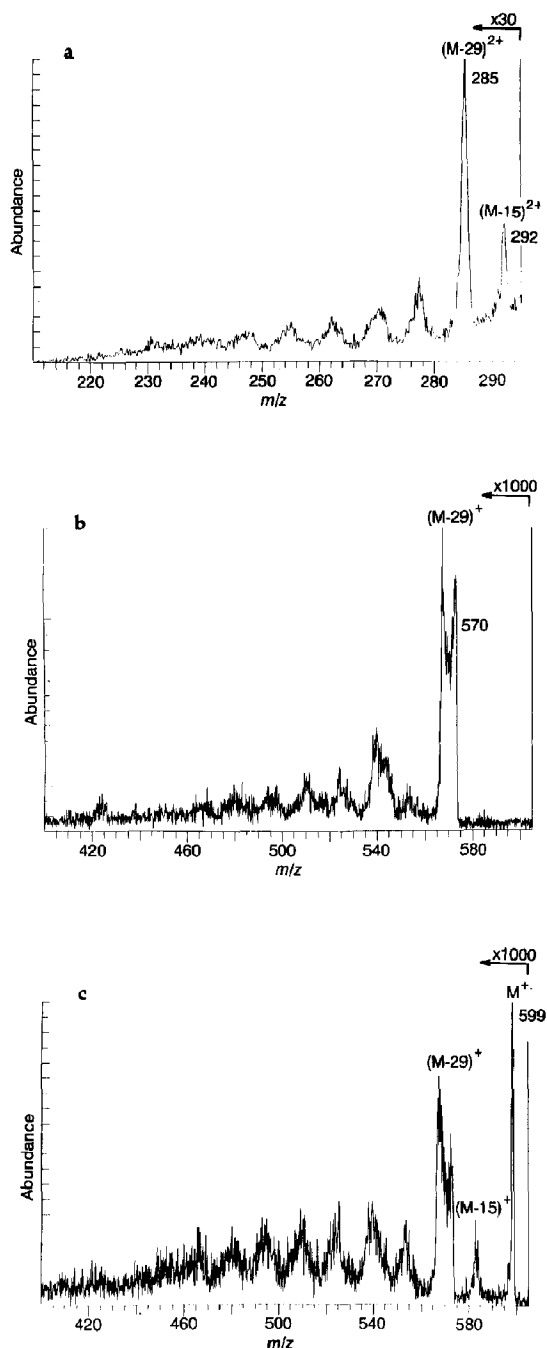$$M_p^{2+} \rightarrow M_{pd1}^+ + M_{pd2}^+ \qquad (2)$$

Figure 2. Product ion spectra of the doubly charged molecular ion of vanadyl OEP (1, MW = 599 u) obtained on the BE instrument illustrating the different metastable ion reactions observed. (a) Metastable ion decomposition with charge retention. (b) Metastable ion charge separation. Multiplication factors indicate abundance relative to the attenuated abundance of the doubly charged parent ion.

Figure 3. Product ion spectra of the doubly charged molecular ion of vanadyl OEP (1, MW = 599 u) obtained on the BE instrument illustrating the different collision-induced reactions observed. (a) Collision-induced decomposition with charge retention using He as the collision gas (20% beam attenuation). (b) Collision-induced charge separation using He as the collision gas (20% beam attenuation). (c) Charge exchange and ECID using ammonia as the collision gas (50% beam attenuation). Multiplication factors indicate abundance relative to the attenuated abundance of the doubly charged parent ion.

Figure 2b shows the charge separation spectrum acquired from vanadyl OEP, the major product ion being that formed from the reaction $M_p^{2+} \rightarrow$ [M-29]$^+$ + 29$^+$. As observed in this spectrum, when charge separation occurs between analyzers in a BE instrument, and the electric sector is scanned to analyze the product ions formed, the peaks are broad and often dished. This is because the charge separation process results in a very large kinetic energy release, T, owing to the Coulombic repulsion of the two product ions formed. The flat-top or dished peaks recorded for reaction products of this type are due to the well-known z-discrimination introduced by finite slit height [9]. It should be noted that the complementary singly charged low mass ions associated with this reaction were not observed on the same scale as the higher mass ions. This is not unexpected, however, given the discrimination of the detector against ions of low kinetic energy (i.e., the low mass product ions) and the more acute z-axis discrimination associated with the low mass product ions in BE type instruments.

The spectrum in Figure 5 shows the three most abundant charge separation peaks, centered at mass-to-charge ratio values that correspond to [M-29]$^+$, [M-43]$^+$, and [M-56]$^+$, observed from the molecular dication of free-base OEP. The presence of several dished peaks in this spectrum, as well as in the spectrum in Figure 2b, indicates that several different charge separation reactions can occur with the OEP macrocycle. The only charge separation product that can be assigned with certainty is [M-29]$^+$, which most probably results from α-cleavage of a charge carrying ethyl substituent (i.e., $C_2H_5^+$) from the doubly charged macrocycle. The other charge separation peaks observed cannot, however, be explained by a single loss of a charge carrying substituent group since only ethyl groups (29 u) are present on the macrocycle. One possible explanation for these other peaks is loss of charge carrying groups that originate within the porphyrin macrocycle (e.g., $C_2H_5N^+ = 43$ u). Another possibility is the loss of a neutral moiety from the doubly charged ion followed by charge separation or vice versa.

The most intriguing peak in the charge separation spectrum of free-base OEP is the double-dished peak centered at a mass-to-charge ratio value corresponding to [M-56]$^+$. This double-dished peak might originate from different charge separation reactions that generate singly charged product ions of the same mass, but the value of T associated with each reaction is different. Another possible origin for this peak pattern is different charge separation reactions that generate products of only slightly different mass and of near equal abundance with nearly equal T values. In such a case, the overlap of the peaks could generate the symmetrical peak shape observed. Support for this possibility comes from an experiment with the tandem quadrupole instrument which indicates that two charge separation products with mass-to-charge ratio values corresponding to [M-55]$^+$ and [M-57]$^+$
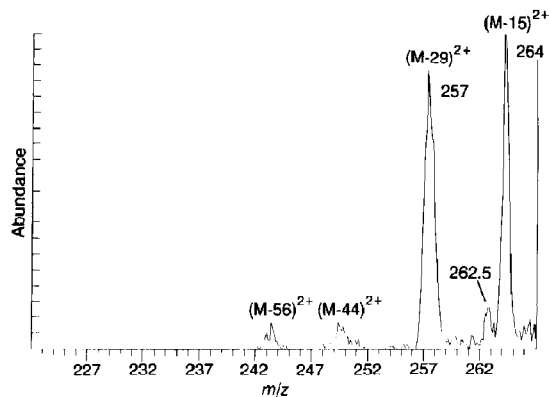
Figure 4. Product ion spectrum of the doubly charged molecular ion of vanadyl etio-III (2, MW = 543 u) obtained on the BE instrument showing the products of metastable ion decomposition with charge retention.

are produced. The molecular dication was selected with the first quadrupole and the product ions formed by unimolecular dissociation of the selected parent ions in the collision region (no collision gas) were mass analyzed using the final quadrupole.

The width of a charge separation peak reflects the kinetic energy spread of the ions making up the peak, which arises primarily from the kinetic energy release [9]. By far the major contribution to T for a charge separation reaction is expected to come from Coulombic repulsion of the two charged product ions. Charge separation, R, in the transition state ion, assuming no dielectric contribution from the molecule, can be estimated using eq 3 [9]

$$R(\mathring{A}) = 14.39/T_{FWHM} \ (eV) \qquad (3)$$

where T_{FWHM} is the kinetic energy release determined from the peak width at half height. T_{FWHM} is expected

to provide an estimate of the average T to within 20% [13]. Charge separation values determined in this manner have been used in some cases, for example, to distinguish among isomeric species [14, 15]. Since $[M-29]^+$ is a charge separation product common to each of the porphyrins studied, and its origin is relatively certain, we compare here the T_{FWHM} values determined from the kinetic energy release for this reaction for several of the porphyrins studied. These results, summarized in Table 1, reveal that the calculated intercharge separation based on eq 3 is similar for all the porphyrins studied, ranging from 8.1 to 9.6 $\mathring{A}$. Since the experimental error involved in these measurements of T amounts to several tenths of an electronvolt, the charge separation values in Table 1 are not significantly different. Given that the diameter of the porphyrin macrocycle is ~ 8 $\mathring{A}$, these intercharge separation values indicate that the charges on the transition state ion are located on opposite sides of the molecule. However, it should be recognized that because any dielectric contribution from the molecule, which effectively shields the charges from one another and allows their closer approach, is ignored in eq 3, these calculated R values are upper limits. In any case, it appears that the metal chelated does not have a major effect on the distance of charge separation in the transition state ion for these porphyrins, since free-base and metal containing porphyrins show very similar T_{FWHM} values.

Collision-induced Reactions

Collision induced dissociation with charge retention. Collision-induced dissociation with charge retention is used in this article to refer to those CIDs that result in formation of a doubly charged product ion and a neutral species as described by eq 4:

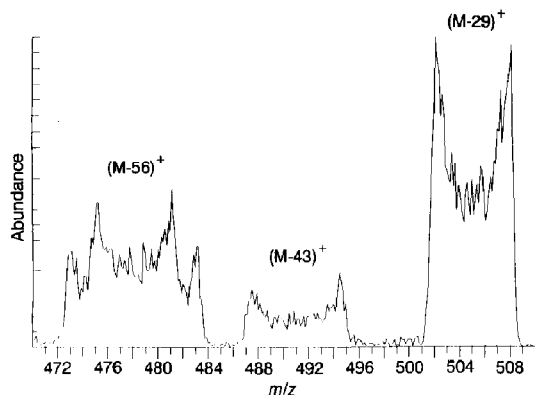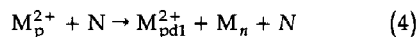$$M_p^{2+} + N \rightarrow M_{pd1}^{2+} + M_n + N \qquad (4)$$

Figure 5. Product ion spectrum of the doubly charged molecular ion of free-base OEP (1, MW = 534 u) obtained on the BE instrument showing the major products of metastable ion charge separation.

Table 1. Calculated kinetic energy release and transition state charge separation for the charge separation reaction $M^{2+} \rightarrow [M-29]^+ + 29^+$

| Porphyrins	Kinetic energy release (eV)	Charge separation (Å)
Etioporphyrin-III (etio-III)	1.50	9.6
Nickel etioporphyrin-III (etio-III)	1.77	8.1
Vanadyl etioporphyrin-III (etio-III)	1.64	8.8
Octaethylporphyrin (OEP)	1.62	8.9
Vanadyl octaethylporphyrin (OEP)	1.59	9.0

where N is the neutral target. This process is dealt with only briefly here since low collision energy CID of doubly charged porphyrins has been discussed in detail by Beato et al. [5] and the high energy CID results were found to be similar. Shown in Figure 3a is the CID spectrum of the doubly charged molecular ion of vanadyl OEP. The fragmentation noted in this CID spectrum is similar to that observed in the metastable ion spectrum (Figure 2a, but the absolute abundance of the peaks is increased, and additional product ions at lower mass are also observed. The peaks in the CID spectrum are also broader than those in the metastable ion spectrum. Several phenomena can contribute to the differing peak shapes observed in the CID spectrum relative to those observed in the metastable ion spectrum. These include, for example, additional product ions arising from CID, and a greater range of kinetic energy releases due both to the fact that higher internal energy parent ions are sampled in the CID experiment and that a wide range of kinetic energies are transferred to internal energies. This range in energy transferred is expressed as a spread in the kinetic energy loss experienced by the parent ions. All of these factors can contribute to the observed differences in the spectra, but the relative importance of each cannot be determined from these data.

Collision-induced charge separation. Collision of the doubly charged porphyrins with gaseous targets promoted collision-induced charge separation as described by eq 5:

$$M_p^{2+} + N \rightarrow M_{pd1}^+ + M_{pd2}^+ + N \qquad (5)$$
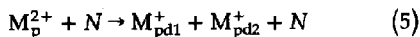
The spectrum in Figure 3b obtained from vanadyl OEP, using He as the target gas, is a combination of metastable ion charge separation products and collision-induced charge separation products. $[M-29]^+$ gives rise to the major peak in this spectrum as it does in the metastable ion charge separation spectrum for this compound (Figure 2b). The broad peaks at lower mass in the spectrum in Figure 3b, which are not present in the metastable ion charge separation spectrum (Figure 2b), are product ions formed by collision of the parent with the target gas. As can be noted from the multiplication factor on this spectrum, collision-induced charge separation is minor reaction pathway relative to the others that have been identified for doubly charged porphyrins.

Charge exchange. Charge exchange refers here to the reaction of the doubly charged porphyrin with a neutral target gas that results in formation of the singly charged porphyrin and presumably the singly charged target molecule as described by eq 6:

$$M_p^{2+} + N \rightarrow M_{pd}^+ + N^+ \qquad (6)$$
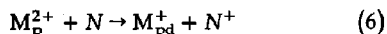
We found that charge exchange of the doubly charged porphyrins, with formation of the porphyrin molecular ion, did not occur to any detectable extent when using He, Ne, Ar, Kr, or Xe as the collision gas at laboratory collision energies of 9 keV (i.e., 4.5-keV accelerating potential). To observe the singly charged porphyrin via charge exchange it was necessary to use target gases with an ionization energy (IE) below that of Xe (IE = 12.1 eV [16]). Both isobutane (IE = 11.4-11.7 eV [16]) and ammonia (IE = 10.2 eV [16]), for example, were found to transfer an electron to doubly charged vanadyl OEP. Maximum intensity of the singly charged molecular ion was observed using ammonia as the collision gas and a beam attenuation of ~ 50% as illustrated by the spectrum in Figure 3c. Along with the charge separation and collision-induced charge separation products, the molecular ion, M^+, formed by charge exchange, and an ion at $[M-15]^+$ are observed. The $[M-15]^+$ species, corresponding to loss of $CH_3 \cdot$ from M^+, probably results from ECID [12], although CID of the singly charged molecular ion cannot be precluded at this beam attenuation. ECID, described in eq 7,

$$M_p^{2+} + N \rightarrow M_{pd1}^+ + N^+$$
$$\rightarrow M_{pd2}^+ + M_n \qquad (7)$$
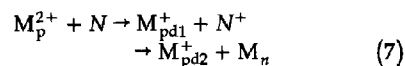
consists of two events: charge exchange of the doubly charged ion with a collision gas to form the singly charged ion in an excited state and fragmentation of the singly charged species forming singly charged product ions. $[M-15]^+$ is the only possible ECID product that is observed unobscured by charge separation products. It should be noted that $[M-15]^+$ is the most abundant fragment ion in the EI mass spectrum of vanadyl OEP.

The ability to form the singly charged molecular ion of a porphyrin from the dication formed in the ion source via charge exchange suggests that the so-called 2E mass spectrum [9] might be analytically useful for porphyrin analysis. The singly charged ions formed from doubly charged ions by charge exchange have a kinetic energy/charge ratio twice that of the singly charged ions formed in the ion source (i.e., 9 versus 4.5 keV). By using ammonia as the collision gas, setting the electric sector voltage at 2E (i.e., twice that necessary to pass the parent dications through the electric sector), and scanning the magnetic sector over the appropriate mass-to-charge ratio range, a 2E mass spectrum is obtained. Only the doubly charged species in the mass spectrum that undergo the reaction described by eq 6 (i.e., $M_p^{2+} \rightarrow M_{pd}^+$) are observed in the 2E mass spectrum. Shown in Figure 6a is the doubly charged region of the mass spectrum of vanadyl OEP, which also contains a peak from a singly charged ion of unknown origin. Figure 6b shows the 2E mass spectrum obtained over this same mass-to-charge ratio region. Although the mass resolution is poor in the 2E spectrum (mainly a function of the particular BE instrument used), all the doubly charged ions in
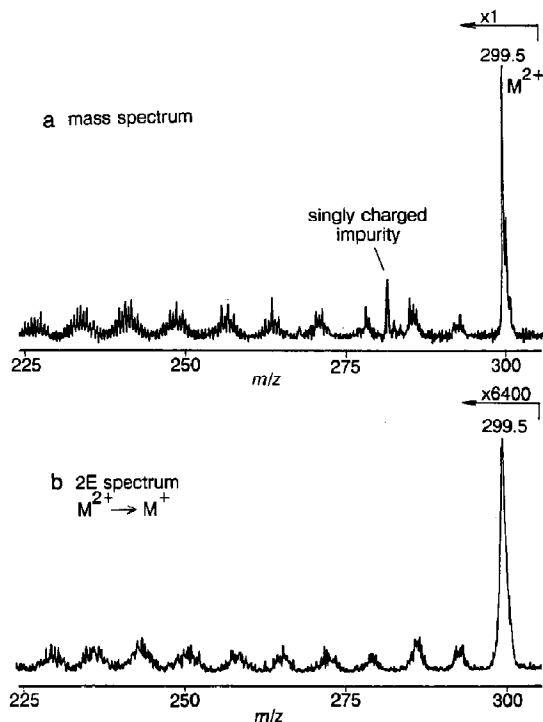
Figure 6. (a) Doubly charged ion region in the mass spectrum of vanadyl OEP (1, MW = 534 u). (b) The 2 E mass spectrum of vanadyl OEP acquired over the same mass range as the mass spectrum in (a). Both spectra were obtained on the BE instrument.

the spectrum in Figure 6a are observed in the 2 E spectrum. Note, however, that the 2 E scan excludes the singly charged impurity ion present in the doubly charged region of the normal mass spectrum. It should be mentioned that a 2 E type spectrum can also be obtained using tandem quadrupole instruments [17].

The 2 E mass spectrum has potential utility in the analysis of porphyrins. As an analytical screening method, the 2 E spectrum could be used, for example, when analyzing complex matrices for porphyrins. This would be particularly useful if the matrix consists mainly of compounds, such as aliphatic hydrocarbons, that do not form abundant doubly charged ions. However, the low overall cross section for charge exchange under the current conditions (note the abundance multiplication factors in Figure 6) limits its practical utility at present. The use of target species with lower IEs than those used in this study, such as metal atoms, might increase the cross section for this reaction to an analytically useful level.

Conclusions

By using a reverse-geometry (BE) sector mass spectrometer, we have found that doubly charged porphyrin cations, formed by EI, undergo unimolecular

and collision-induced reactions that produce *both* doubly charged and singly charged product ions. We also found (although not extensively discussed herein) that many of these doubly charged to singly charged ion reactions could be observed using a tandem quadrupole MS/MS instrument. A variety of reactions occur, as described here, some of which may have utility for the analysis of porphyrins by mass spectrometry. In particular, the charge exchange process shows potential analytical importance. Screening methods for the analysis of porphyrins in complex mixtures might be developed around a 2 E scan, which is sensitive only to those doubly charged ions formed in the ion source that can be converted to the singly charged molecular ion via charge exchange in an MS/MS experiment. Realization of this methodology requires that the cross section for the charge exchange process be increased, which might be expected given the appropriate target species.

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