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Electron Ionization Mass Spectrometric Analysis of 5-Nitro Octaethylprophyrin: Evidence for Scission of the Porphyrin Macrocycle

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Analysis of the electron ionization mass spectrum (EIMS) of 5-nitro octaethylporphyrin reveals that the molecular ion *m/z* 579 undergoes novel fragmentations. The typical fragmentation pathway of β-cleavage of peripheral substituents is suppressed. Furthermore, the presence of the fragment ion *m/z* 375 provides strong evidence for a fragmentation pathway that involves cleavage of the porphyrin macrocycle. Such a fragmentation pathway has not been reported previously for porphyrins bearing β-pyrrolic substituents. Subsequent EIMS and electron ionization tandem mass spectrometric analyses, both of the 5-nitro octaethylporphyrin and of its analogs isotopically labeled at the *meso* (bridge) position (^{13}C) or at the pyrrolic nitrogens (^{15}N) or at the nitro group (^{15}N), confirmed the ring scission process. The elemental composition of the significant fragment ions was confirmed by high-resolution EIMS. The anomalous behavior may be attributed to macrocyclic distortion and/or the electron-withdrawing effect of the nitro group. © **1997 by John Wiley & Sons, Ltd.**

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INTRODUCTION

Porphyrins are of considerable importance in many areas of chemistry and biology. For example, heme, the prosthetic group in hemoglobin and most cytochromes, plays a crucial role in biological transportation of oxygen and electrons respectively. Perhaps the most important property of porphyrin macrocycles is their ability to chelate with virtually all the metallic elements.

Porphyrins have been of interest in mass spectrometry as they have proved useful in investigating various phenomena. The high relative abundance of doubly charged ions occurring in electron ionization mass spectrometry (EIMS) of porphyrins and their fragmentation pathways was studied by Beato *et al.*[1] In chemical ionization mass spectrometry (CIMS), surface-assisted decomposition of porphyrins into mono-, di- and tripyrrolic units has been observed.[2–6] Recently, Van Berkel *et al.*[7] reported that Ni(II) porphyrins undergo electrochemical reactions in the electrospray needle in electrospray mass spectrometry (ESMS).

There have been only limited reports on the detailed EIMS analysis of *meso* (bridge) substituted porphyrins.[8,9] In general, it was believed that the *meso* substituent did not modify the fragmentation pathway significantly. However, Clezy *et al.*[8] determined that the presence of a nitro group at one of the bridge carbons modified the EIMS spectrum substantially, because the normally encountered *β*-cleavage of pyrrolic alkyl substituents[5,8–11] was suppressed. Investigation of such a novel fragmentation by electron ionization tandem mass spectrometry (EIMS/MS) would be of fundamental interest to mass spectrometrists and porphyrin chemists alike. Moreover, recent studies on nitro octaalkyl porphyrins have indicated that the compounds are of considerable value as model compounds for investigating the properties of non-planar porphyrins in biological systems such as cytochrome *c*.[12–14]

In this paper we present the results of EIMS, EIMS/MS and electron ionization high-resolution mass spectrometric (EIHRMS) analyses of 5-nitro octaethylporphyrin. We present a novel fragmentation involving the scission of the porphyrin macrocycle and discuss the implications. This is the first of a series of investigations into the mass spectra of nitrated porphyrins and their metal derivatives.

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EXPERIMENTAL

Chemicals

5-Nitro octaethylporphyrin (5-nitro OEP) was prepared by the method of Bonnett and Stephenson.[15] Octaethylporphyrin (OEP) labeled with ^{15}N at all four nitrogens was prepared by the method of Callot and co-workers[16,17] using ^{15}N ammonium chloride (Cambridge Isotopic Laboratories) as the initial source of nitrogen. Octaethylporphyrin labeled with ^{13}C at each of the four bridge positions was also prepared by the method of Callot and co-workers.[16,17] Each of these two isotopically labeled compounds was nitrated by the method of Bonnett and Stephenson.[15] 5-Nitro octaethylporphyrin isotopically labeled with ^{15}N at the nitro position was prepared using ^{15}N nitrogen dioxide by the method of Gong and Dolphin.[18]

Electron Ionization Mass Spectrometric Analyses

All electron ionization (EI) mass spectra presented here were obtained with a Finnigan MAT TSQ45 triple-quadrupole mass spectrometer. Porphyrin samples were dissolved in dichloromethane and 1 μl aliquots of the solution were deposited onto a direct exposure probe (DEP) filament. The DEP was heated from 100–600 °C at 600 °C min^{-1}. The rapid rate of heating was found to reduce the amount of thermal elimination of NO_2 observed in EIMS. The EI emission current was maintained at 0.3 mA and the electron energy was 70 eV for all experiments. For the initial EIMS experiments, quadrupole 1 (Q1) was scanned from m/z 50–800 in 0.8 s with Q2 and Q3 passing all masses.

Electron Ionization Tandem Mass Spectrometric Analyses

Tuning for MS/MS was achieved with Co(II) OEP in a capped aluminum solids probe vial heated to 275 °C. The MS/MS experiments were performed with a collision gas pressure of 1.6 mTorr argon and a collision energy of 24.8 eV.

High-Resolution Electron Ionization Mass Spectrometric Analyses

A Finnigan MAT 95 high-resolution mass spectrometer was used for determination of exact masses for EI fragment ions. The MAT 95 was tuned for a resolution of 7000. The high-resolution data were used as an aid in determining the elemental composition of key fragment ions.

RESULTS AND DISCUSSION

EIMS Analysis

Octaethylporphyrin was analyzed using EIMS conditions identical with those employed for 5-nitro OEP and its isotopically labeled analogs. The singly charged fragment ions of OEP arose primarily from a sequence of β-cleavages of the peripheral ethyl groups [Fig. 1(a)] as has been observed many times before.[5,8–11] The porphyrin macrocycle remains intact; doubly charged ions are present in high relative abundance as would be expected.[5,8–11] Thus, any variations in the fragmentation pathway of the 5-nitro OEP cannot be attributed to the conditions under which the spectra were obtained.

The EIMS analysis of 5-nitro OEP is not easy to perform, because the nitro group may be thermally eliminated on the solids (or direct exposure) probe in the ion source with intermolecular hydrogen abstraction to form OEP.[8] This problem can be minimized by heating the sample rapidly. Therefore, the use of a direct exposure probe is recommended. The EIMS of 5-nitro OEP, using the DEP, is shown in Fig. 1(b). The spectrum is broadly similar to that reported by Clezy *et al.*[8] In the present study there was little contamination due to thermal decomposition of the 5-nitro OEP, as evidenced by the very low abundance of the molecular ion of OEP (m/z 534). The singly charged region of the molecule is complex and is substantially different from that of OEP. The presence of the m/z 564 ion $[M - 15]^+$ as a minor component in the EIMS spectrum and in the EIMS/MS daughter ion spectrum of the $M^{\cdot +}$ ion, as discussed below, confirmed that the β-cleavage fragmentation pathway is suppressed in 5-nitro OEP. The 10 most abundant fragment ions observed appear in Table 1. It was not obvious which of these ions were produced directly from the molecular ion; thus, it was necessary to carry out EIMS/MS analyses.

EIMS/MS Analysis

The EIMS/MS daughter ion spectrum of the $M^{\cdot +}$ ion (m/z 579) of 5-nitro OEP is shown in Fig. 1(c). The 14 most abundant daughter ions are listed in Table 2. The origin of each of these ions will be discussed in turn.

The daughter ion m/z 564 $[M - 15]^+$, which is of fairly low relative abundance (Table 2), is formed by the classic β-cleavage of ethyl groups. Loss of a hydroxyl radical generates the more abundant daughter ion m/z 562 $[M - 17]^+$. Presumably, this ion is generated by a rearrangement such as that proposed by Clezy *et al.*[8] The m/z 550 $[M - 29]^+$ and 533 $[M - 46]^+$ ions are formed by α-cleavage of ethyl and nitro groups respectively. Similarly, the m/z 504 $[M - 75]^+$ ion is formed by α-cleavages of both ethyl and nitro groups. It is important to note that α-cleavage of ethyl groups is a minor process in the spectrum of OEP. The origins of the daughter ions m/z 535 $[M - 44]^+$, 523 $[M - 56]^+$, 522 $[M - 57]^+$, 521 $[M - 58]^+$, 520 $[M - 59]^+$, 508 $[M - 71]^+$, 494 $[M - 85]^+$ and 375 $[M - 204]^+$ could not be assigned with certainty from the EIMS/MS. In order to proceed with the elucidation, it was necessary to carry out EIHRMS analyses to determine the elemental composition of fragment ions and the neutrals lost (see below). Obviously, m/z 375 is an especially intriguing daughter ion. It has too large an m/z to be a multiply charged ion, but too small an m/z to be gener-

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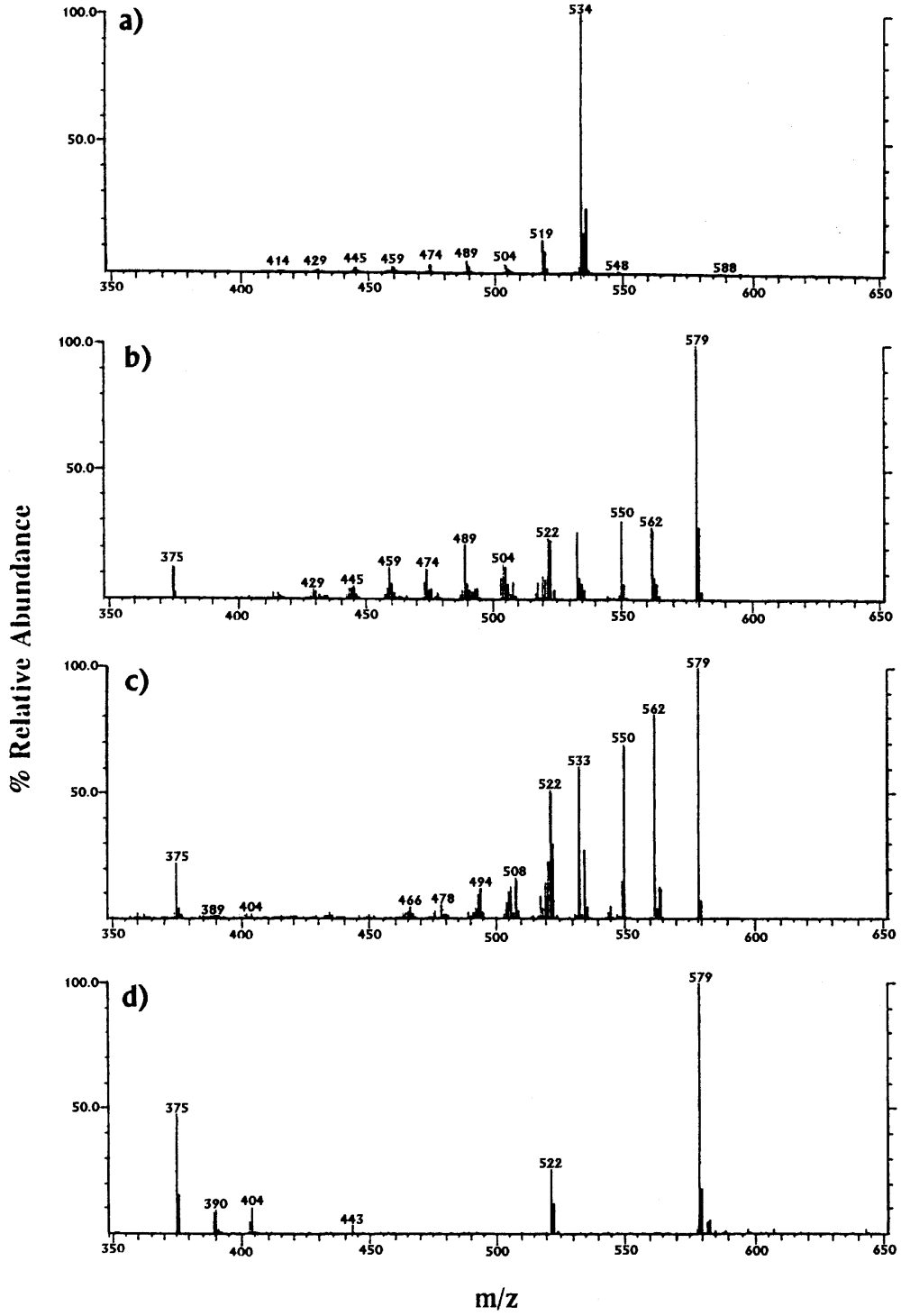

Figure 1. Mass spectra of OEP and 5-nitro OEP: (a) EIMS of OEP; (b) EIMS of 5-nitro OEP; (c) EIMS/MS daughter ion spectrum of molecular ion (*m/z* 579) of 5-nitro OEP; (d) parent ion spectrum of *m/z* 375 ion of 5-nitro OEP.

ated by classic porphyrin fragmentations. The most straightforward way to account for the loss of 204 mass units was to propose that the porphyrin macrocycle had undergone ring scission. If this idea were correct, it would represent a novel fragmentation for the porphyrins.

In order to obtain more information on the fragmentation pathways to *m/z* 375, the parent ion spectrum of that ion was obtained [Fig. 1(d)]. The spectrum indicated that the molecular ion, *m/z* 579, was the major parent ion, but the ions *m/z* 522, 404 and 390 were also parents. The *m/z* 390 and 404 parents support the idea that an ethyl group from another pyrrolic ring is a part of the neutral that is lost in the formation of *m/z* 375. The *m/z* 522 ion may generate *m/z* 375 via the fragmentation pathway shown in Fig. 2 or an analogous route. In order to pursue further the identification of the fragmentation pathway, it was essential to carry out EIHRMS analyses so that elemental compositions of the key fragment ions were assigned.

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Table 1. EIMS and EIHRMS data for selected ions of 5-nitro OEP and isotopically labeled analogs

Compound[a]	Ion	% Rel. abund.	Accurate mass	Δ (mmu)	Ion composition	Neutral loss composition
5-NO_2 OEP	579	100	579.3600	−2.7	$C_{36}H_{45}N_5O_2$[b]	
	564	2	564.3384	−4.5	$C_{35}H_{42}N_5O_2$[b]	CH_3
	562	6	562.3505	4.1	$C_{36}H_{44}N_5O$[b]	OH
	550	5	550.3270	−8.8	$C_{34}H_{40}N_5O_2$	C_2H_5
	549	5	549.3505	8.8	$C_{36}H_{45}N_4O$[b]	NO
				−3.7	$C_{35}H_{43}N_5O$	CH_2O
	533	15	533.3621	2.3	$C_{36}H_{45}N_4$[b]	NO_2
	523	2	523.3250	6.1	$C_{33}H_{41}N_5O$[b]	C_3H_4O
	522	4	522.3218	1.5	$C_{33}H_{40}N_5O$[b]	C_3H_5O
	504	4	504.3222	3.1	$C_{34}H_{40}N_4$[b]	$C_2H_5 + NO_2$
	375	20	375.2291	2.0	$C_{24}H_{29}N_3O$[b]	$C_{12}H_{16}N_2O$
5-NO_2OEP $^{13}C_4$	583	100	583.3716	−0.7	$C_{32}H_{45}N_5O_2\,^{13}C_4$	
	526	5	526.3366	0.3	$C_{29}H_{40}N_5O\,^{13}C_4$	C_3H_5O
	378	1	378.2415	0.2	$C_{21}H_{29}N_3O\,^{13}C_3$	$C_{11}H_{16}N_2O\,^{13}C$
5-NO_2OEP $^{15}N_4$	583	100	583.3412	4.2	$C_{36}H_{45}NO_2\,^{15}N_4$	
	553	4	553.3425	4.9	$C_{36}H_{45}O\,^{15}N_4$	NO
	537	1	537.3467	5.8	$C_{36}H_{45}\,^{15}N_4$	NO_2
	526	15	526.3117	−0.3	$C_{33}H_{40}NO\,^{15}N_4$	C_3H_5O
	378	1	378.2210	1.1	$C_{24}H_{29}O\,^{15}N_3$	$C_{12}H_{16}NO\,^{15}N$
5-NO_2OEP $^{15}NO_2$	580	100	580.3554	−1.0	$C_{36}H_{45}N_4O_2\,^{15}N$	
	550	3	550.3463	−2.5	$C_{35}H_{43}N_4O\,^{15}N$	CH_2O
	549	5	549.3558	3.5	$C_{36}H_{45}N_4O$	^{15}NO
	533	14	533.3637	0.7	$C_{36}H_{45}N_4$	$^{15}NO_2$
	523	6	523.3134	6.9	$C_{33}H_{40}N_4O\,^{15}N$	C_3H_5O
	375	1	375.2320	−0.9	$C_{24}H_{29}N_3O$	$C_{12}H_{16}NO\,^{15}N$

[a] 5-NO_2OEP $^{13}C_4$, 5-NO_2 OEP labeled at each *meso* C with ^{13}C; 5-NO_2OEP $^{15}N_4$, 5-NO_2 OEP labeled at each pyrrolic N with ^{15}N; 5-NO_2OEP $^{15}NO_2$, 5-NO_2 OEP labeled at the nitro group with ^{15}N.
[b] Assignment also confirmed from EIHRMS of ^{13}C- and ^{15}N-labeled compounds ($\Delta \leqslant \pm 6$).

EIHRMS Analysis of 5-Nitro Octaethylporphyrin

Octaethylporphyrin was observed in the EIHRMS spectra of 5-nitro OEP and its isotopically labeled analogs because of the thermal elimination/intermolecular hydrogen abstraction process discussed earlier.[8] Fortunately, only two significant ions, *m/z* 535 and 520, were masked by this artifact. The ions *m/z* 508 and 494 were of too low an abundance to obtain valid EIHRMS data. The EIHRMS data for significant ions of 5-nitro OEP and its isotopically labeled analogs are summarized in Table 1. The EIHRMS analyses confirmed the findings of the EIMS and EIMS/MS analyses of structures of the *m/z* 562 and 533 daughter ions. It was surprisingly difficult to obtain meaningful data for the *m/z* 550 fragment ion, which was assumed to be due to α-cleavage of an ethyl group. In several of the EIHRMS analyses undertaken, the Δ-value for the *m/z* 550 ion was over 10 mmu from the expected value. The composition of the *m/z* 549 ion $[M - 30]^+$ also proved intriguing. The EIHRMS data were consistent with a loss of NO, which was not surprising because this is a common fragmentation process for aromatic nitro compounds.[19] However, subsequent EIHRMS studies using isotopically labeled porphyrins revealed that the ion could also be generated by loss of CH_2O (see below). The *m/z* 522 daughter ion was shown to be produced by loss of C_3H_5O from the molecular ion. Thus the *m/z* 522 daughter ion is generated without the loss of NO or NO_2 from the porphyrin macrocycle. To account for this ion, it is necessary to invoke a cleavage of a carbon from the macrocycle such as that shown in Fig. 2. A similar pathway may be used to explain the formation of the ions *m/z* 523 $[M - 56]^+$ and *m/z* 521 $[M - 58]^+$, in which the neutrals lost have elemental

Table 2. EIMS/MS data for selected daughter ions of $M^{\cdot+}$ ion of 5-nitro OEP[a]

Ion *m/z*	% Rel. abund.[b]	Mass of neutral loss (composition)[c]
579	100	
564	12	15 (CH_3)
562	81	17 (OH)
550	72	29 (C_2H_5)
549	14	30 (NO and CH_2O)
535	28	44
533	26	46 (NO_2)
523	30	56 (C_3H_4O)
522	50	57 (C_3H_5O)
521	15	58 (C_3H_6O)
520	12	59
508	16	71
504	10	75 ($C_2H_5NO_2$)
494	10	85
375	22	204 ($C_{12}H_{16}N_2O$)

[a] Ions with ⩾10% relative abundance are listed.
[b] Relative to *m/z* 579 ($M^{\cdot+}$ = 100.
[c] Elemental compositions as determined from EIHRMS (see Table 1).

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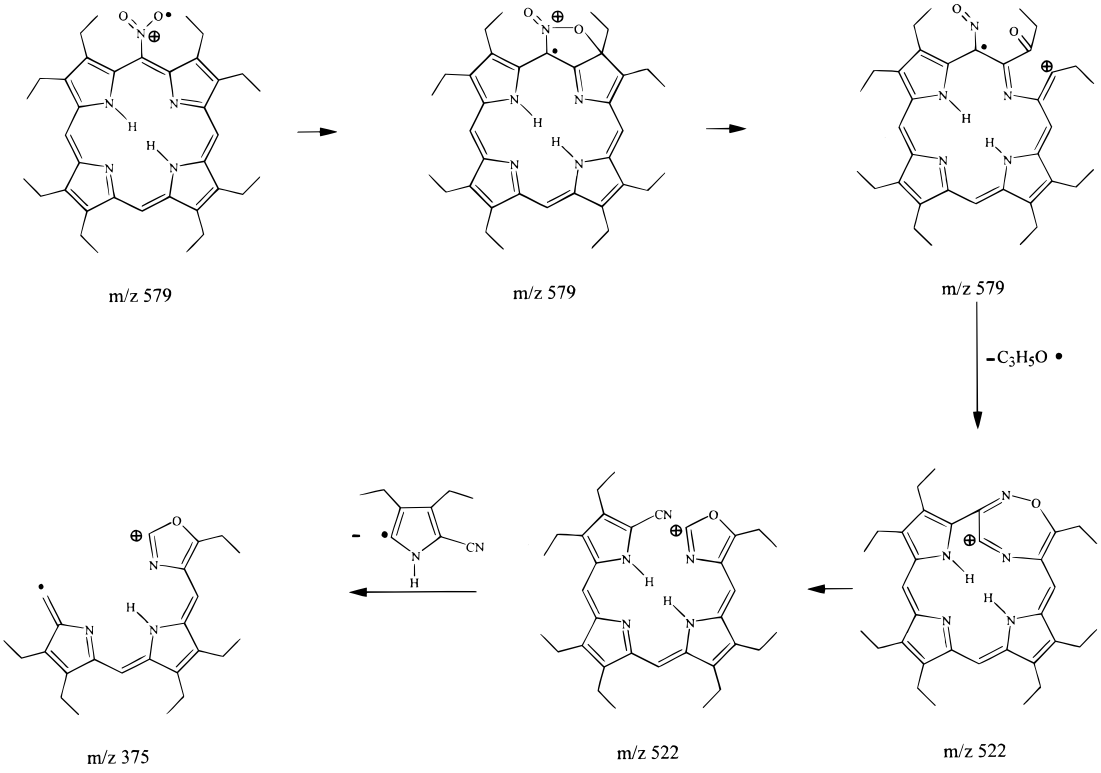

Figure 2. Plausible scheme for ring scission process of 5-nitro OEP.

compositions C_3H_4O and C_3H_6O respectively. The *m/z* 375 ion has the elemental composition $C_{24}H_{29}N_3O$, i.e. it is formed by loss of $C_{12}H_{16}N_2O$ (Table 1). The loss of two nitrogens indicates that the ion must be formed by cleavage of at least one pyrrolic ring. Such fragmentation processes have previously been observed only as a surface-induced fragmentation process in CIMS.[2–5] It would appear that *m/z* 375 is *not* produced via a loss of nitric oxide, NO, because the fragmentation pathway to the *m/z* 522 parent ion already involved a loss of an oxygen. To account for these data, it is necessary to invoke a cleavage of a carbon from the macrocycle such as that shown in Fig. 2. If this hypothesis is correct, then it appears that oxygen migration is an important step in the pyrrole ring cleavage process, but loss of NO is not significant in forming the *m/z* 375 ion. In view of the unusual nature of the fragmentation processes and the masses of the neutral losses, it was necessary to prepare isotopically labeled samples of 5-nitro OEP and study their fragmentation pathways to examine the hypothesis more carefully.

Selection and EIHRMS Analyses of Isotopically labeled 5-nitro octaethylporphyrin

In order to determine the source of the two nitrogen atoms that are lost in generating the *m/z* 375 ion, it was necessary to prepare a sample of 5-nitro OEP labeled with ^{15}N at the *meso* nitro group and another sample with the pyrrolic nitrogens fully labeled with ^{15}N. Additionally, the compounds were used to confirm that the fragmentation pathway to the *m/z* 522 ion, which is a parent ion of *m/z* 375, did not involve the loss of NO from the *meso* nitro group. In order to determine the number of *meso* (bridge) carbons that are lost in the fragmentation process, it was necessary to prepare 5-nitro OEP fully labeled with ^{13}C at the bridge positions.

The EIHRMS analyses of the $^{15}NO_2$ 5-nitro OEP confirmed that the nitrogen of the nitro group was lost en route to the *m/z* 375 ion. The data for the determination of the proposed pathway to the *m/z* 522 ion in the unlabeled material were less satisfactory. An ion at *m/z* 523 was observed; however, the Δ-value of 7.1 for the only feasible elemental composition of $C_{33}H_{40}N_4O^{15}N$ was too high to be definitely correct. Analysis of the spectrum also revealed a neutral loss of CH_2O as well as NO. Thus the *m/z* 549 ion in the unlabeled material is generated by two distinct fragmentations rather than being solely the product of loss of NO as might have been expected.

The EIHRMS analysis of the tetra ^{15}N-labeled 5-nitro OEP revealed that only one pyrrolic nitrogen was lost in the formation of the *m/z* 375 ion. The *m/z* 526 ion, which is the tetra ^{15}N analog of *m/z* 522 in the unlabeled compound, was generated without loss of NO (Table 1), which provides further corroboration of the fragmentation pathway to that ion.

Analysis of the EIHRMS data for the *meso* ^{13}C-labeled 5-nitro OEP confirmed that only one *meso* carbon is lost in forming the analog *m/z* 375, providing more support for the fragmentation pathway shown in Fig. 2. Similarly, no *meso* carbon was lost in the formation of the analog of the *m/z* 522 ion.

Significance of Data

There are three possible explanations for the differences in the fragmentation pathways between OEP and

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5-nitro OEP. First, the nitro group may be more labile than the alkyl groups. While this proposal accounts for the low relative abundance of the $[M - 15]^+$ daughter ion, it does not explain the α-cleavage of the alkyl moieties or the cleavage of the macrocycle. A second possibility is that the electron-withdrawing effects of the nitro group might modify the properties of the aromatic ring by reduction of the electron density, thereby modifying the fragmentation patterns. It is well known that porphyrinogens (hexahydroporphyins) and tetraoxaporphyrinogens readily undergo cleavage of a pyrrolic ring,[20,21] so it is conceivable that decreasing electron density might generate an analogous result. A third possibility is that the NO_2 group causes the macrocycle to become non-planar, which might cause a significant modification of the fragmentation process. At this point it is not clear which of the latter two factors is dominant in producing the anomalous fragmentations for 5-nitro OEP. There is circumstantial support for the macrocyclic distoration argument. Cycloalkano geoporphyrins bearing five-, six- and seven-membered exocyclic rings that cause some macrocyclic distortion are known to generate some unusual daughter ions in EIMS/MS.[22] Studies are under way on the synthesis of analogous systems to help resolve this issue.

It will be especially exciting if the anomalous fragmentation behavior of 5-nitro OEP is the result of the influence of macrocyclic distortion. This is a facet of porphyrin chemistry that is of growing importance because of its role both in biological chemistry and in the design of catalysts. It would be beneficial if mass spectrometry would provide researchers with another tool to probe the effect of macrocyclic distortion in porphyrin chemistry.

CONCLUSIONS

The EIMS fragmentation pathways of 5-nitro OEP and its isotopically labeled analog have been investigated using a combination of EIMS, EIMS/MS and EIHRMS. The data show that the classical β-cleavage mechanism is largely suppressed. Instead, the porphyrin undergoes a rather complex fragmentation process involving skeletal rearrangements and α-cleavages. Most significantly, the molecule undergoes scission of a pyrrolic sub-unit, which is a novel fragmentation pathway in the EIMS of porphyrins. The reason for the anomalous behavior is attributed to macrocyclic distortion and/or the electron-withdrawing effect of the nitro group. Studies are under way to prepare model compounds that will determine which of these factors is dominant in controlling the fragmentation pathway.

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