J. Phys. Chem. A **2004,** *108,* 10997−11000

Gas-Phase Metallation Reactions of Porphyrins with Metal Monocations

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Received: May 18, 2004; In Final Form: September 22, 2004

The gas-phase reactions of octaethylporphyrin (H_2P, III) with 12 metal monocations, which were produced by laser ablation of Al, V, Cr, Fe, Ni, Nb, Mo, Hf, W, Re, Pt, and Au targets in an ICR−FTMS instrument, revealed three possible reaction pathways: (i) charge transfer; (ii) metal incorporation (ligation) with loss of H_2; and (iii) "dimerization" of the ligation product from pathway ii by addition of another porphyrin without further loss of H_2. The differences in metal behavior are discussed. The reaction of a mixture of hexaethyldimethylporphyrin (H_2P, I) and pentaethyltrimethylporphyrin (H_2P, II) with neat Fe^+ was also investigated; it was found that more than half of the Fe^+ reacts by charge exchange and that the lower-alkylated porphyrin (I), which has the higher ionization energy (IE), reacts more slowly in charge exchange but with the same rate in the both ligation and "dimerization" reactions as the higher alkylated porphyrin (H_2P, II).

Introduction

Naturally occurring porphyrins and metalloporphyrins are constituents of many important biological molecules and they play a significant role in the chemistry of living systems.[1,2] Large numbers of synthetic porphyrinoid molecules have been prepared as model systems to investigate the complex biological functions exhibited by porphyrins.[3−5] In metalloporphyrins, the metal center often plays a key role in such processes as electron transfer,[6] oxidation,[7] and other chemical transformations that involve association or dissociation of a ligand at the metal center.[1,8] Because of the great importance of metalloporphyrins, investigations of the intrinsic reactivity of the entities that form them is of interest. Porphyrins in nature are usually synthesized in a metal free form, the metal ions being subsequently inserted. This latter process is catalyzed by enzymes.[9]

The reaction of a porphyrin molecule (H_2P) with M^{2+} ions in solution proceeds by release of two protons

$$M^{2+} + H_2P \rightarrow (M + P) + 2H^+$$

The existence of a "sitting-atop" (SAT) intermediate, which deforms the H_2P and enables proton dissociation, has been demonstrated; a second metal ion can then be incorporated from the axial (distal) side in several steps, SAT formation being the slowest and proton dissociation an I_d process[10] (i.e., a dissociative interchange reaction; identical with Ingold's S_N1 reaction[11]). It is known that this reaction is highly solvent dependent. Indeed, in solvents of low basicity, such as acetonitrile, the released protons cannot be readily stabilized.[12] Metalloporphyrins are of low volatility and thus have not been subject to intense study in the gas phase. However, gas-phase metalloporphyrin ions, MP^+, have been known since the early days of mass spectrometry.[13] Such gas-phase studies, ones unaffected by solvent environment, are the central concern of this work.

All experiments were carried out in a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. The formation and characteristics of complexes formed from metal monocations, M^+, and neutral ligand molecules in a laser desorption ionization, LDI−FTICR, mass spectrometry experiment have been described previously.[14−18] Irikura and Beauchamp[19] have shown that metal monocations react rapidly (ca. millisecond) with gaseous neutral porphyrin (H_2P) molecules to produce positively charged complexes MP^+ in such a way that H_2 is released from the central nitrogen of the H_2P molecule.

$$M^+ + H_2P \rightarrow (M + P)^+ + H_2$$

When the ionization energy of the metal is larger than that of neutral porphyrin, the metal monocation may react with porphyrin by charge exchange to produce H_2P^+ ions. Consequently, mass spectrometric observations of the competition by different M^+ ions can lead to relative ligation rates. Such gas-phase studies of ion−molecule reactions allow determination of the intrinsic properties of the bare charged species, unaffected by solvation, ion pairing, and other effects common to solution chemistry. We report here the results of two series of experiments: in one experiment, various metal monocations were allowed to react with octaethylporphyrin in the gas phase and, in the other, Fe^+ ions were allowed to react with a mixture of two porphyrins differing only by one methylene group on a side chain. The first series is concerned with discrimination of the effects of the metal ion, whereas the second concerns the effects of the porphyrin (H_2P) ionization energy (IE). It is known that higher alkylation decreases the IE of porphyrins and that the missing electron in the $(M + P)^+$ moiety derives from metal and not from porphyrin.[20,21]

Experimental Section

A steady-state concentration of either a (1:3) mixture of pentaethyltrimethylporphyrin (H_2P, I) with hexaethyldimethylporphyrin (H_2P, II) or octaethylporphyrin (H_2P, III) was achieved in the FTICR mass spectrometer by sublimation from

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10.1021/jp0478514 CCC: \$27.50

TABLE 1: Gas-Phase Reaction Products of Metal Ions, M^+, with Octaethylporphyrin (H_2P, III)

metal ions	*m/z* H_2P^+	*m/z* $(M + P)^+$	*m/z* $(M + P + H_2P)^+$	ionization energy of atom/eV
Al^+: *m/z* 27 (100.0%)	none	559	1093	5.99
V^+: *m/z* 51 (100.0%)	534	583	1117	6.75
Cr^+: *m/z* 52 (100.0%), 53 (11.3%), 54 (2.8%)	534	584	1118	6.77
Fe^+: *m/z* 56 (100.0%), 54 (6.4%), 57 (2.3%)	534	588	1122	7.90
Ni^+: *m/z* 58 (100.0%), 60 (38.5%), 62 (5.3%), 61 (1.7%), 64 (1.4%)	534	590	none	7.64
Nb^+: *m/z* 93 (100.0%)	534	625	none	6.76
Mo^+: *m/z* 98 (100.0%), 96 (69.1%), 95 (66.0%), 92 (61.5%), 100 (39.9%), 97 (39.6%), 94 (38.3%)	534	630	none	7.09
Hf^+: *m/z* 180 (100.0%), 178 (77.8%), 177 (53.0%), 179 (38.8%), 176 (14.8%)	534	712	none	6.83
W^+: *m/z* 184 (100.0%), 186 (93.2%), 182 (85.7%), 183 (46.5%)	534	716	none	7.86
Re^+: *m/z* 187 (100.0%), 185 (59.7%)	534	719	none	7.83
Pt^+: *m/z* 195 (100.0%), 194 (97.3%), 196 (74.9%), 198 (21.3%), 192 (2.3%)	534	none	none	8.96
Au^+: *m/z* 197 (100.0%)	534	none	none	9.23

a small heated quartz tube mounted on the probe head. A pure metal or alloy target adjacent to this tube was exposed to a single pulse from a Nd:YAG Quanta Ray DCR-11 laser (Spectra Physics, Mountain View, CA) operating at 1064 nm. All but M^+ ions were removed from the cell by a synthesized wave inverse FT (SWIFT) procedure shortly after the laser pulse. The product FT mass spectra were recorded on an FT/MS 2001 DD Fourier transform mass spectrometer (Finnigan, Madison, WI) at different time delays ranging from 100 μs to 100 s. The difference of the IEs of porphyrins I and II was determined mass spectrometrically by electron impact ionization: a plot of individual molecular ion abundance versus electron impact voltage indicates that porphyrin I has an IE that is higher by some 0.2 eV. The reactions of Al^+, V^+, Cr^+, Fe^+, Ni^+, Nb^+, Mo^+, Hf^+, W^+, Re^+, Pt^+, and Au^+ ions with the neutral ligands pentaethyltrimethylporphyrin (H_2P, I), hexaethyldimethylporphyrin (H_2P, II), and octaethylporphyrin (H_2P, III) were carried out in an LDI FTICRMS experiment. Measurements were done at various time delays following the expulsion of all entities except the M^+ ions that were produced by the laser shot. The reaction pathways, the reaction products, and the ratios of these products were determined for each pair of reactants. We would have liked to determine the kinetic and thermodynamic parameters for the various reactions and, in fact, we made such an attempt. Unfortunately, because of the rather high temperatures (~300 °C) required for the production of gaseous porphyrins, our equipment could not maintain a constancy of temperature that was congruent with the generation of reproducible reaction rate constants. Nor could it permit sufficiently accurate measurements at the various temperatures needed to generate good thermodynamic data. Such measurements will have to wait for another day.

Results and Discussion

The gas-phase reactions indicate the presence of three different processes (Table 1): (i) charge transfer, (ii) metal ion incorporation, and (iii) "dimerization".

Of all 12 ions, only Al^+, as produced from the neutral metal by an IE < 6 eV, does not react by charge transfer from M^+ to H_2P (IE ≈ 6 eV) in a process that would generate H_2P^+ by

$$M^+ + H_2P \rightarrow H_2P^+ + M \qquad (1)$$

However, even for Al^+, this reaction can be observed immediately (i.e., at 100 μs) following the initial ion production. Presumably, the short-term ablation products of the laser pulse contain electronically excited Al^+ entities.

Metal incorporation proceeds, as expected, by expulsion of H_2 from H_2P to produce metalloporphyrin $(M + P)^+$ ions according to

$$M^+ + H_2P \rightarrow (M + P)^+ + H_2 \qquad (2)$$

This reaction was observed for all metal ions except Pt^+ and Au^+. Reactions **1** and **2** occur within 100 ms.

"Dimerization" was observed for M = Al, V, Cr, Fe, and Ni. The $(M + P)^+$ ions, after ~500 ms, add another H_2P molecule to form $(M + P + H_2P)^+$ ions according to

$$H_2P + (M + P)^+ \rightarrow (M + P + H_2P)^+$$

A fourth process may also be observed: proton transfer, presumably arising from the presence of ubiquitous water in the instrument, to the neutral porphyrin. This is a very slow process producing H_3P^+ ions which do not react any further. Thus, spectra recorded after a delay of several seconds or more show no further reaction.

In summary, the metal ions V^+, Cr^+, Fe^+, and Ni^+ undergo all three reactions delineated above, whereas Pt^+ and Au^+ exhibit only the charge-transfer reaction. While the inability of Al^+ to ionize H_2P is a result of the low IE of Al, the very high IE's of platinum and gold, on the other hand, make charge exchange with H_2P much faster than ion incorporation.

The reason for "dimerization", which only the $(M + P)^+$ ions of Al, V, Cr, Fe, and Ni undergo, is less clear. The presence of Al^+ in this group might suggest an effect of ion size. However, unlike the PAH^+ cations of the polycyclic aromatic hydrocarbons, H_2P^+ ions do not form charged dimers with neutral H_2P in the gas phase; this observation suggests a crucial role for the metal. Indeed, recent comparative computations on the electronic structures of Fe-, Co-, and Ni-porphyrins and their ions by Liao and Scheiner[21] place the outer valence electrons on the metal for Fe and Co but on the ring for Ni. Although these calculations refer to unsubstituted porphyrin rings and the compounds used here are octaalkyl-substituted entities, the Liao/Scheiner studies should still apply: Dedieu and co-workers[22] conclude that vinyl, alkyl, and phenyl substituents seem to have little or no effect on the electronic structure of porphyrins. However, alkyl substitution does cause an inductive lowering of the IP and, as a result, one can expect that $(Ni + P)^+$ is also formed by removal of a metal electron. Indeed, the related metallophthalocyanines all lose a ring electron when they form the corresponding monocations. Thus, it appears that the Al^+ dimerization is not a matter of size but rather an effect of the low IE of Al. Thus,

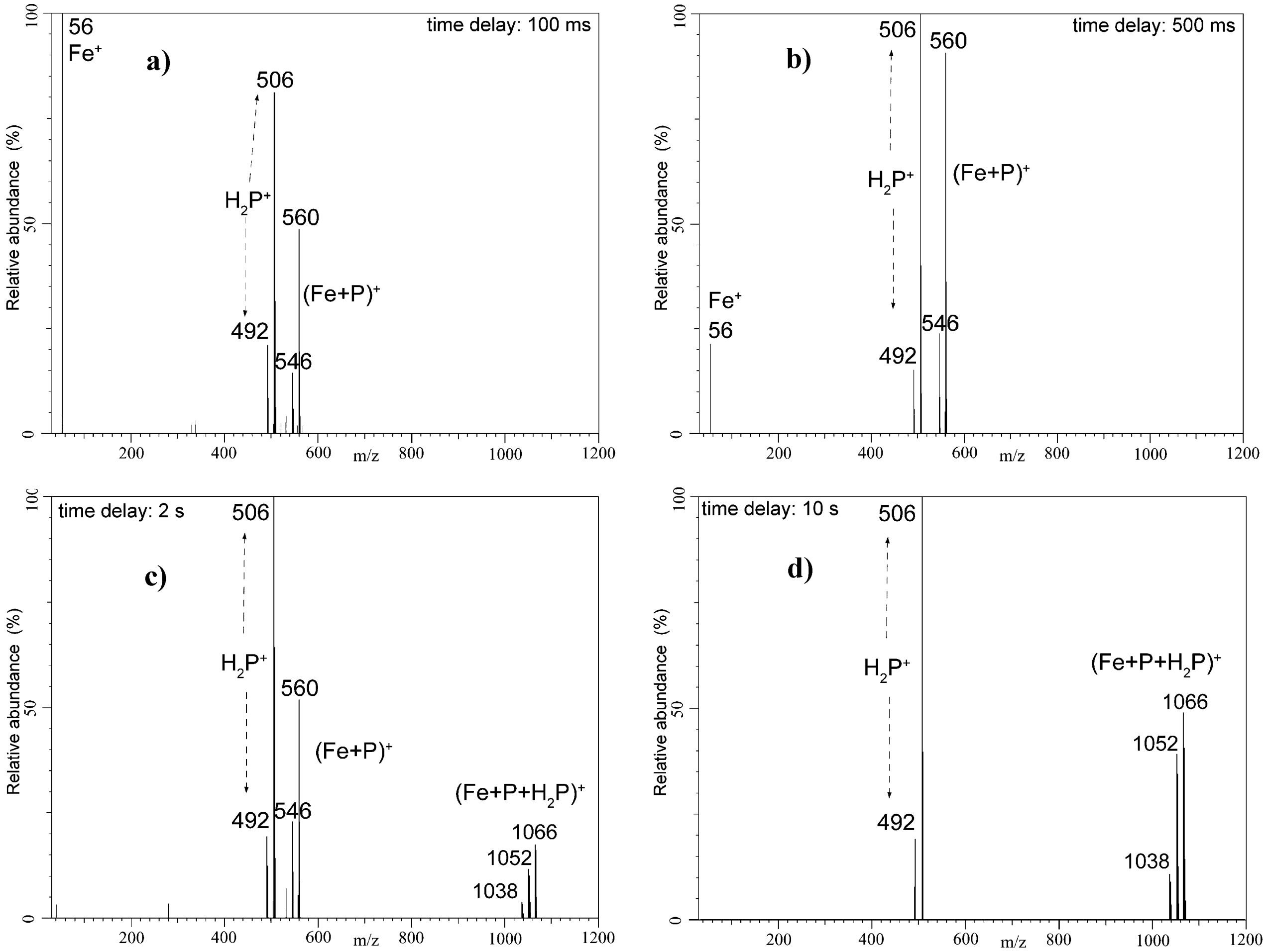

Figure 1. LDI-FT mass spectrum of reaction products of Fe^+ ions with a (1:3) mixture of pentaethyltrimethylporphyrin (*m*/*z* 492) and hexaethyldimethylporphyrin (*m*/*z* 506): (a) after 100 ms, (b) after 500 ms, (c) after 2 s, and (d) after 10 s reaction time.

we hypothesize that the metal ion is the reactive site in the dimerization reaction.

Another set of experiments was aimed at the study of the influence of porphyrin structure, particularly that of IE, on reaction rates. For this purpose, neat Fe^+ ions were allowed to react with a 3:1 mixture of porphyrins II and I, respectively, and the products were monitored after given time delays (i.e., reaction times). Reaction products of Fe^+ with H_2P I and II, for time delays of 100 ms, 500 ms, 2 s, and 10 s are shown in Figure 1a–d. It is found that Fe^+ reacts in the same way as it does with unsubstituted porphyrin,[17] namely a loss of H_2 in the first ligation step and a considerable amount of porphyrin I and II cation formation by charge transfer. However, in the case of the substituted porphyrins, charge exchange is much faster than ligation because of the lower IEs. After 100 ms (Figure 1a), the Fe^+ ions still constitute the base peak but, of the two reactions (i.e., ligation and charge transfer), which have progressed for longer than their half-lives, charge transfer is the faster. After 500 ms (Figure 1b), both the charge transfer and ligation reactions have effectively ended and their ratio is close to unity. It is also seen that the lower alkylated H_2P I (i.e., of higher IE) reacts more slowly in charge exchange and somewhat faster in the ligation reaction than the higher alkylated H_2P II. At 2 s delay (Figure 1c), the ratio of the two ligation products $(Fe + P)^+$ of *m*/*z* 560 and *m*/*z* 546 drops from an initial value of 3 to almost 2, and "dimerization" is well underway. The ratio of "dimerization" products at *m*/*z* 1066, 1052, and 1038 already shows deviations from the statistical 9:6:1 distribution for a 3:1 mixture. As Figure 1d shows, the reaction is complete after 10 s and the product distribution is 5:4:1, which indicates a preference for the lower alkylated porphyrin I in dimer formation. However, since the product is formed from a 2:1 ratio of precursors with a 3:1 mixture of reactants then, statistically, the product ratios should be 6:5:1, close to that which is observed and confirmatory of the fact that it is metal and not porphyrin ring orbitals that are decisive for the "dimerization" reaction.

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