J. Am. Chem. Soc. **2000,** *122,* 8083−8084

Experimental Observation of Non-Aufbau Behavior: Photoelectron Spectra of Vanadyloctaethylporphyrinate and Vanadylphthalocyanine[†]

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Received November 16, 1999

The oxidation and reduction behavior of metalloporphyrin and related macrocycle-containing biomolecules is central to oxygen transport,[1] electron transfer,[2] charge-separation in photosynthesis,[3] oxygen atom transfer,[3] and many other life processes. Oxovanadium(IV) porphyrinates, VO(por), have been studied extensively, partly because of their relationship to the reactive oxoiron(IV) porphyrinate intermediate in oxygen atom transfer.[4] One advantage of studying vanadyl molecules is the simple electron configuration of a single d electron on the vanadium(IV) center. For VO(oep) [oep = dianion of octaethylporphyrin] in the condensed phase, EPR studies have shown that the unpaired electron is in the metal $b_2(d_{xy})$ orbital,[5] that oxidation removes an electron from the porphyrin ligand rather than from the $b_2(d_{xy})$ orbital,[6] and that one-electron reduction places an electron into an empty porphyrin-based orbital rather than with the single electron in the $b_2(d_{xy})$ orbital.[7] Similar behavior has been observed for oxoiron(IV) porphyrinates.[8] These observations have been interpreted in the past to mean that the valence porphyrin orbitals are very close in energy to the metal-based orbitals.

To determine the relative energies and nature of the positive ion states of VO(oep) in the gas phase, we have collected the valence photoelectron spectra of this and related porphyrin and phthalocyanine molecules.[9] The photoelectron spectra show that the lowest energy ionization of VO(oep) and of vanadyl phthalocyanine, VO(pc), in the gas phase is from a filled ligand-based orbital, as found for the oxidation of VO(oep) in the condensed phase.[6] The spectra also show the unusual result that ionization from the singly occupied metal d orbital of these molecules requires considerably more energy than ionization from certain doubly occupied ligand orbitals, and that the energies associated with high-spin stabilization are extremely small. These observations imply a non-Aufbau occupation of the molecular orbitals. Electronic structure calculations indicate that this non-Aufbau behavior is strongly favored by the electron−electron repulsion energies, regardless of electron relaxation energies with ionization, correlation energies, exchange energies, or other contributions. The large energy associated with this non-Aufbau behavior of vanadyl porphyrins suggests that such behavior is important in the chemistry of other metalloporphyrins, and the fundamental basis for this behavior has important implications for the most stable states of other molecules.

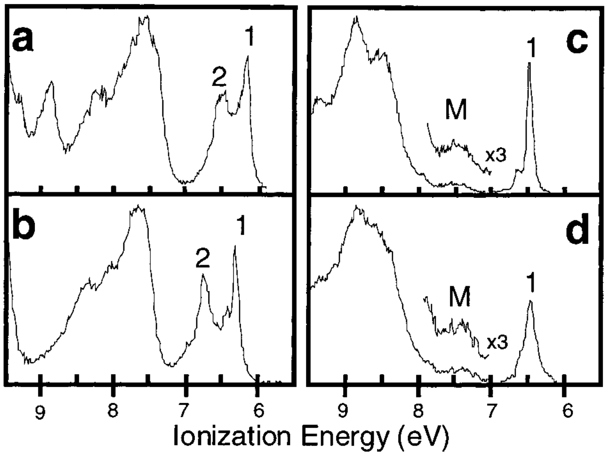

Figure 1. He I gas-phase photoelectron spectra of (a) Mg(oep), (b) VO(oep), and (c) VO(pc) and (d) He II spectrum of VO(pc).

The low-energy valence photoelectron spectra of VO(oep) and Mg(oep) are shown in Figure 1. In previous photoelectron studies of Mg(oep)[10] and the free-base porphyrin, H_2(oep),[11] the assignment of the initial ionizations (6−7 eV) was straightforward because the porphyrin π electrons are the only low-valence electrons in these molecules. Bands 1 and 2 in the spectrum of Mg(oep) are due to ionizations from the filled porphyrin $a_{1u}(\pi)$ and $a_{2u}(\pi)$ orbitals (D_{4h} symmetry). These ionizations shift slightly from 6.24 and 6.47 eV for H_2(oep) to 6.16 and 6.52 eV for Mg(oep). For VO(oep), the characteristic shapes of these porphyrin-based ionizations[11] are again observed as bands 1 and 2 (6.32 and 6.76 eV). The similar relative intensities of bands 1 and 2 for Mg(oep) and VO(oep) show that the $a_{1u}(\pi)$ and $a_{2u}(\pi)$ orbitals retain occupations of two electrons in the neutral molecules. The porphyrin-based ionizations of VO(oep) can be split into singlet and triplet states because of the unpaired d electron, but the similar intensities of bands 1 and 2 in both spectra relative to the ionizations above 7 eV show that the spin state splitting is less than the width of the ionizations. This places an upper bound on the spin stabilization of the triplet states of about 0.05 eV (400 cm^{-1}), which is in agreement with previous estimates.[12]

Comparison of the ionization bands 1 and 2 of VO(oep) with those of H_2(oep) and Mg(oep) shows that the initial ionizations of VO(oep) do not correspond to removal of the single vanadium d electron from the $b_2(d_{xy})$ orbital, but the specific location of this metal ionization is not apparent in this spectrum because of the large number of porphyrin-based ionizations from 6 to 9 eV.

[†] Portions of this work were presented at the 217th National Meeting of the American Chemical Society, March, 1999, Anaheim CA, Abstract INOR418.

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10.1021/ja994018p CCC: $19.00

To aid in locating the vanadyl $b_2(d_{xy})$ ionization, the spectra of the related phthalocyanine complexes were also examined. The spectrum of Mg(pc) has been reported previously.[13] In comparison to Mg(oep), the ionization of Mg(pc) that corresponds to band 2 is stabilized to greater than 8 eV because of the orbital character on the extra nitrogen atoms of phthalocyanine. As a consequence of this stabilization, the spectrum of Mg(pc) has a “window” without ionizations from the $a_{1u}(\pi)$ ionization of the phthalocyanine at 6.35 eV to the next band of phthalocyanine ionizations starting near 8 eV. The spectrum of VO(pc) shown in Figure 1c is similar to that of Mg(pc), with band 1 located at 6.49 eV. Most significantly, the VO(pc) spectrum contains a broad ionization at 7.50 eV that is not seen in the spectrum of Mg(pc). The area of this ionization increases by 80% with respect to ionization 1 with He II excitation (Figure 1d), similar to the behavior observed for the vanadium-based ionizations of other vanadyl complexes.[14,15] The band labeled M is therefore identified as the metal $b_2(d_{xy})$ ionization.

The He II photoelectron spectrum of VO(oep) suggests that the $b_2(d_{xy})$ ionization of this molecule also is between 7.3 and 8 eV, because an increase in ionization intensity is observed in this region. However, because of the relatively low intensity of the $b_2(d_{xy})$ ionization as seen for VO(pc) and because of the presence of other oep ionizations partially obscuring this region, the $b_2(d_{xy})$ ionization of VO(oep) is not clearly observed.

The observation that considerably less energy is required to remove electrons from filled orbitals than to remove an electron from a singly occupied orbital indicates that the Aufbau principle[16] is being violated in this system. Although the Aufbau principle strictly applies only in independent particle models, the concept is inherent in the understanding of much of molecular behavior. Non-Aufbau electron configurations are occasionally invoked in theoretical calculations, but experimental observation of non-Aufbau behavior for a molecule is unusual. In previous photoelectron studies of cobalt(II) and copper(II) phthalocyanines[13] and other metalloporphyrins with unpaired metal electrons,[10,17] the initial ionizations also were assigned to ligand-based orbitals. However, those assignments were challenged computationally,[18] and the possibility was raised that the photoionization cross-sections of the metal orbitals are simply too small to be observed in the previous studies.[10]

Electronic structure calculations on neutral, cation, and anion states of VO(por) agree with the non-Aufbau order of the ionizations observed for these vanadyl molecules and help to clarify the factors that contribute to this behavior. A wide variety of theoretical models and computational methods have been used.[19] According to the calculated total energies of the neutral molecule and ion states, the initial ionizations correspond to removal of an electron from the porphyrin-based $a_2(\pi)$ orbital to produce the $b_2(d_{xy})^1...a_1(\pi)^2a_2(\pi)^1$ configuration followed by removal of an electron from the porphyrin-based $a_1(\pi)$ orbital to produce the $b_2(d_{xy})^1...a_1(\pi)^1a_2(\pi)^2$ configuration. Ionization from the metal-based $b_2(d_{xy})$ orbital produces a closed shell ion state that is several electronvolts higher in energy. The $b_2(d_{xy})$ ionization is predicted to be with the ionizations in the band that starts at 7.5 eV. Calculation of the negative ion state of this molecule similarly favors addition of the electron to the lowest empty porphyrin orbitals, the $e(\pi)$, rather than pairing the electron in the metal b_2 orbital. Thus the calculated total energies of the ion states agree with the non-Aufbau behavior that is observed experimentally in both the condensed-phase EPR and the gas-phase photoelectron experiments.

Experimental ionization energies are related to the molecular orbital energies in the neutral molecule through Koopmans' theorem.[20] Besides neglect of the change in electron correlation energy with ionization, which is known to be small for metalloporphyrins,[21,22] Koopmans' theorem ignores the theoretical electron relaxation energy of the self-consistent-field (SCF) positive ion from the frozen ground-state orbital approximation. Electron relaxation energies associated with the porphyrin-based ionizations are less than 2 eV, whereas the electron relaxation energy associated with the $b_2(d_{xy})$ ionization is more than 5 eV. The larger electron relaxation energy associated with the metal d ionization means that this singly occupied orbital is *more* stable relative to the doubly occupied porphyrin orbitals than would be indicated by the theoretical SCF energies of the ion states or by the measured ionization energies, and thus consideration of electron relaxation energies strengthens the implication of a non-Aufbau configuration. Conversely, electronic structure calculations on many metal-containing molecules invoke non-Aufbau configurations with singly occupied metal orbitals that are more stable than doubly occupied ligand orbitals, but because of the large electron relaxation energies that move metal-based ionizations to lower energy, these molecules normally do not display non-Aufbau behavior experimentally as observed for the vanadyl molecules in this study.[14]

In an attempt to achieve a theoretical Aufbau filling of the molecular orbitals of VO(por), an electron was taken from the highest occupied orbital, the porphyrin $a_2(\pi)$, and paired with the electron in the more-stable $b_2(d_{xy})$ orbital to produce the $b_2(d_{xy})^2...a_1(\pi)^2a_2(\pi)^1$ configuration. It was found that this state is approximately 2 eV less stable than the non-Aufbau ground state at the Hartree−Fock level. The localized $b_2(d_{xy})$ orbital is destabilized more than 8 eV due to the electron−electron repulsion when two electrons are paired in this orbital, while the delocalized porphyrin $a_2(\pi)$ orbital is stabilized less than 3 eV with transfer of an electron from this orbital to the metal. As a consequence of these relative electron−electron repulsions, the lowest energy state of the molecule strongly prefers a non-Aufbau configuration with a single electron in a stable metal d orbital and double occupation of less stable porphyrin orbitals.

Acknowledgment. We thank J. L. Brédas, G. Crundwell, J. H. Enemark, and F. A. Walker for helpful discussions and N. R. Armstrong for providing the sample of VO(pc). D.L.L. and N.E.G. acknowledge the U.S. Department of Energy and the National Science Foundation. B.L.W. and L.J.M. acknowledge the Connecticut State University AAUP Research Grant.

Supporting Information Available: Atomic coordinates, calculated total energies and orbital eigenvalues with several different basis sets for a variety of different computational methods (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA994018P

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