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Base-Promoted Autoreduction of Iron(III) Porphyrins in Dimethyl Sulfoxide Solution: Magnetic Resonance Spectroscopy of Hydroxoiron(II) Porphyrin Complexes

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Under anaerobic conditions iron(III) porphyrin complexes in dimethyl sulfoxide solution are reduced to the iron(II) state by addition of hydroxide ion, alkoxide ion, or solid sodium hydride. Excess hydroxide ion serves to generate the hydroxoiron(II) complex, as confirmed by titration of the square-planar iron(II) tetraphenylporphyrin contained in toluene solution with a solution of tetrabutylammonium hydroxide. Changes in the NMR spectra are consistent with a 1:1 hydroxide ion–metal ion binding stoichiometry. The five-coordinate hydroxoiron(II) porphyrin exists in the high-spin $S = 2$ state on the basis of solution magnetic measurements. The pyrrole proton NMR chemical shift value of 32.8 ppm is relatively less downfield as compared to those of high-spin iron(II) porphyrin complexes of substituted imidazoles and alkylmercaptide ions. Variation in paramagnetic chemical shift values likely reflects greater contribution of a porphyrin π-spin delocalization pathway.

Introduction

Ferrous porphyrin complexes with hydroxide ion have been cited in the literature since 1949.[1] More recently, Traylor and Coworkers[2] reported generation of both the five- and six-coordinate hydroxoiron(II) complexes through addition of a sodium dithionite 18-crown-6 complex and protohemin dimethyl ester to a nonaqueous solution that contained hydroxide ion. Lexa et al.[3] have also described electrochemical generation of hydroxoiron(II) complexes of "basket-handle" porphyrin derivatives. Optical spectral and redox potential measurements have provided the major basis for description of hydroxide binding. The putative hydroxoiron(II) porphyrin complexes have not otherwise been thoroughly characterized.

Herein is reported additional spectroscopic and magnetic characterization of the hydroxoiron(II) tetraphenylporphyrin, $(TPP)Fe(OH)^-$, and the hydroxoiron(II) etioporphyrin I, $(Etio)Fe(OH)^-$, complexes in nonaqueous solution. The measurements were stimulated by our observation that hydroxide ion in dimethyl sulfoxide (DMSO) solution promotes the autoreduction of ferric porphyrins to the ferrous state. Thus, the hydroxoiron(II) porphyrin anion is generated by addition of ≥ 2 equivalents of base to a DMSO solution of the chloroiron(III) porphyrin derivative. We were further intrigued by an independent literature report that described stoichiometric hydroxide ion promoted iron(III) porphyrin reduction in pyridine solution, but not in DMSO solution.[4] Nuclear magnetic resonance methods have been utilized to clarify the effects of excess base addition to solutions of iron porphyrins.

Experimental Section

Toluene-d_8 (99+ atom % ^2H), DMSO-d_6 (99.9 atom % ^2H), sodium hydride (60% dispersion in mineral oil), sodium methoxide (25% in methanol), and tetrabutylammonium hydroxide ((TBA)OH, as a 1 M solution in methanol) were purchased from Aldrich. Potassium *tert*-butoxide was purchased from Alfa. All solvents were degassed through freeze–pump–thaw cycles prior to introduction into the argon-filled Vacuum Atmospheres glovebox. The contents of freshly opened vials of DMSO-d_6 and toluene-d_8 were stored over activated 3-Å molecular sieves.

Proton and deuterium NMR spectra were recorded on a Bruker WM-360 spectrometer. Iron porphyrin concentrations ranged from 1.0 to 5.0 mM. Electronic absorption spectra were measured with a Cary 219 spectrophotometer. Electron spin resonance measurements at 80 K were performed with a Varian E-104A EPR spectrometer. Electrochemical measurements were carried out with a standard three-electrode arrangement that employed the PAR Model 173 potentiostat and programmer. The DMSO solution contained 1.0 mM iron porphyrin and 0.10 M tetrabutylammonium perchlorate supporting electrolyte under an argon atmosphere.

Porphyrin compounds were prepared by literature methods,[5] and iron incorporation with conversion to the chloroiron(III) complex followed established routes.[6] All reactions designed to generate ferrous porphyrins were carried out in an inert-atmosphere chamber under an argon atmosphere. Crystalline iron(II) porphyrins were prepared from the corresponding chloroiron(III) derivatives by zinc metal reduction.[7] Typically 200 mg of the iron(III) porphyrin in 150 mL of toluene was stirred over excess mercury-activated zinc powder until the optical spectrum indicated complete loss of the iron(III) porphyrin bands. The solution was filtered through a medium glass frit and concentrated to half the original volume. The product was crystallized by the addition of heptane.

Solutions of $[Bu_4N][(TPP)Fe(OH)]$ for NMR spectroscopy were prepared by two routes. The first method involved autoreduction of the iron(III) porphyrin through use of various strong bases. Typically, 2 mg of (TPP)FeCl or (Etio)FeCl was dissolved in 0.5 mL of DMSO-d_6, and at least 2 equiv of 1 M (TBA)OH in methanol was added. Other strong bases, to include NaH or K(*t*-BuO) suspended in DMSO, or a methanol solution of $NaOCH_3$, were effectively utilized to generate an iron(II) porphyrin complex spectroscopically identical with that observed for hydroxide ion treatment. A second method for preparation of the hydroxoiron(II) porphyrin complex involved addition of (TBA)OH to a toluene solution of the square-planar iron(II) porphyrin.

Solution magnetic moments were determined by the NMR method[8] with toluene solvent and tetramethylsilane as the reference substance. The concentration of $(TPP)Fe(OH)^-$ was determined indirectly by exposure of the solution to air and by conversion to (TPP)FeCl with HCl vapor. A second determination of the reference peak splittings permitted calculation of the concentration, assuming that the magnetic moment for (TPP)FeCl is 5.92 μ_B.

Results and Discussion

Autoreduction Reactions. The autoreduction of iron(III) porphyrins in DMSO was monitored by proton and deuterium NMR spectroscopy. Upon dissolution of (TPP)FeCl in DMSO-d_6, pyrrole proton NMR signals are observed at 79.3 and 72.2 ppm for the respective high-spin iron(III) species (TPP)FeCl and $(TPP)Fe(DMSO)_2^+$. Addition of 2 equiv of (TBA)OH (1.0 M in methanol) under anaerobic conditions produced a new species with a pyrrole proton signal at 32.8 ppm, as shown in Figure 1. Absolute assignment of this signal to the pyrrole residue was accomplished by deuterium NMR spectroscopy of the corresponding pyrrole-d_8 derivative. A relatively sharp signal in this position is unprecedented for iron(III) tetraphenylporphyrin complexes, and hence an autoreduction reaction was suspected.

Evidence for formation of an iron(II) porphyrin product is supported in part by the absence of EPR signals for the hydroxide

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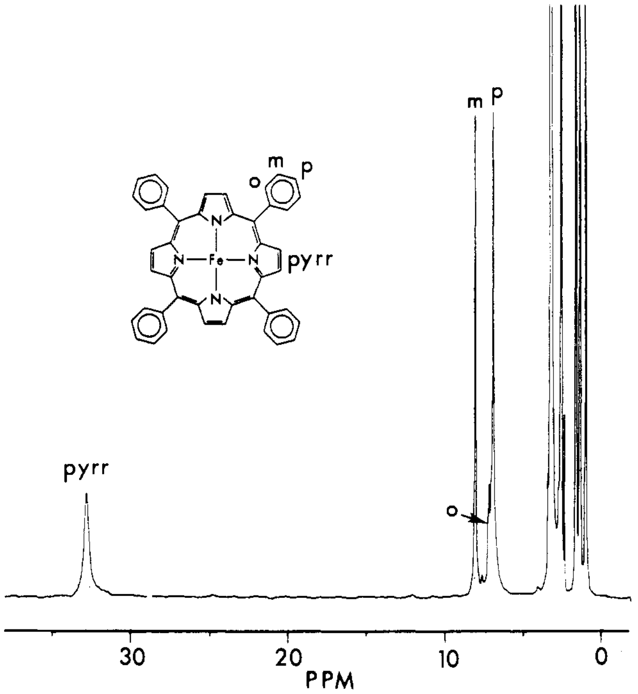

Figure 1. Proton NMR spectrum of (TPP)Fe(OH)$^-$ formed from reaction of 1 mM (TPP)FeCl in DMSO-d_6 with 2.0 equiv of 1 M (TBA)OH in methanol under anaerobic conditions (spectrometer frequency 360 MHz; 25 °C; signals referenced to $(CH_3)_4Si$). The phenyl signals were assigned by examination of the tolyl analogues. No signal has been located for the coordinated hydroxide ion.

reaction product in frozen DMSO at 80 K. Monomeric iron(III) states are expected to show EPR signals, whereas the even-spin iron(II) states are not EPR active at liquid-nitrogen temperature. Solution magnetic susceptibility results for the (TPP)Fe product are also consistent with a high-spin iron(II) formulation in that an experimental magnetic moment of 4.7 ± 0.1 μ_B is in reasonable agreement with a spin-only value of 4.9 μ_B for an $S = 2$ state.

Other strong bases also served to cause autoreduction of (TPP)FeCl in DMSO solution, consistent with the alkoxide-induced reactions noted by other workers.[9-11] In our hands the iron(III) derivative in a stirred DMSO solution ultimately was reduced by solid sodium hydride or potassium *tert*-butoxide and was immediately reduced by addition of a sodium methoxide/methanol solution. Optical and NMR spectra for the reduced species were very similar to those for the iron(II) porphyrin generated by hydroxide ion reduction. The common iron porphyrin NMR spectra produced by the four bases suggests a common axial ligand(s) in each case. Evidence offered in the following section favors hydroxide coordination through a process in which the strong bases react with trace amounts of water in the DMSO solution to give more than stoichiometric quantities of hydroxide ion. A less likely possibility is that the various bases (hydroxide ion, alkoxide ion, and DMSO anion) form complexes with (TPP)Fe^{II} that have equivalent paramagnetic NMR chemical shift patterns. The importance of DMSO or trace impurities in DMSO as a reducing agent is demonstrated by the fact that autoreduction was not evident with (TBA)OH addition to tetrahydrofuran or dimethylformamide solutions of (TPP)FeCl.

Sawyer and co-workers have reported that addition of 1 equiv of hydroxide ion to (TPP)FeCl in pyridine is sufficient to bring about autoreduction, whereas, in agreement with our results, autoreduction did not take place with 1 equivalent of hydroxide ion in DMSO.[4] Sawyer et al. demonstrated by cyclic voltammetry that the reduction potential for the Fe(III)/Fe(II) couple moved from −0.21 to −0.70 V (SCE reference) with addition of 1 equiv of hydroxide ion. We confirmed this result and, in addition, examined the cyclic voltammetric patterns following reduction of the iron(III) porphyrin by addition of 2 equiv of hydroxide ion. The oxidative wave for (TPP)Fe(OH)$^-$ proved to be highly irreversible, presumably due to rapid conversion of the (TPP)Fe(OH) species to the μ-oxo dimeric iron(III) compound.

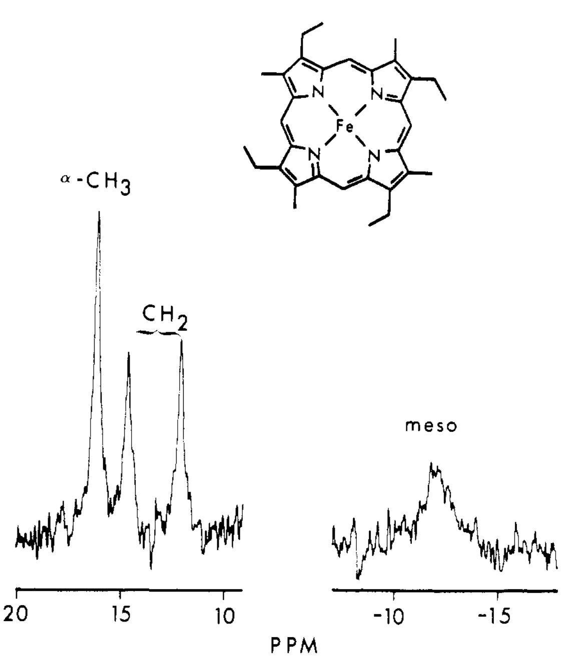

Figure 2. Downfield and upfield regions of the proton NMR spectrum for (Etio)Fe(OH)$^-$, recorded within minutes of preparation to avoid deuterium exchange of the CH_3 moiety (prepared by anaerobic dissolution of (Etio)Fe^{II} in DMSO-d_6 with subsequent addition of 5.0 equiv of 1 M (TBA)OH in methanol; 360 MHz; 25 °C; signals referenced to $(CH_3)_4Si$).

The formation of μ-oxo dimeric iron(III) porphyrin upon oxidation of (TPP)Fe(OH)$^-$ is perhaps relevant to the mechanism of the autoreduction process. In particular, the order of mixing of (TPP)FeCl, DMSO, and (TBA)OH is highly important in that if base is added to the DMSO before the (TPP)FeCl is dissolved, only μ-oxo iron(III) dimer is produced. However, the addition of 1 equiv of (TBA)OH to (TPP)FeCl in DMSO does not produce the μ-oxo dimer nor iron(II) porphyrin but rather produces an iron(III) species with a broad pyrrole proton NMR signal at 82 ppm. The line width and chemical shift value are indicative of iron(III) coordination by a strong base.[14] A reasonable explanation would involve coordination by the DMSO anion, wherein attack by a second hydroxide ion would produce the DMSO radical and the (TPP)Fe(OH)$^-$ complex. Hydroxide ion is a sufficiently strong base (in pure DMSO solution) to generate the DMSO anion, and the resulting anion can be readily oxidized.[15] The ultimate DMSO product from iron(III) porphyrin oxidation has not been identified but presumably is a sulfone or a radical–radical coupling product.

Iron(III) octaalkylporphyrin compounds were also reduced to the ferrous state in DMSO upon addition of excess hydroxide ion. The downfield and upfield proton NMR spectral regions of the hydroxide ion induced reduction product of (Etio)FeCl shown in Figure 2 are reminiscent of those for other high-spin, five-coordinate ferrous porphyrin derivatives as described below. The extreme basicity of hydroxide ion in the nonprotic DMSO solvent is demonstrated by the fact that facile base-catalyzed exchange

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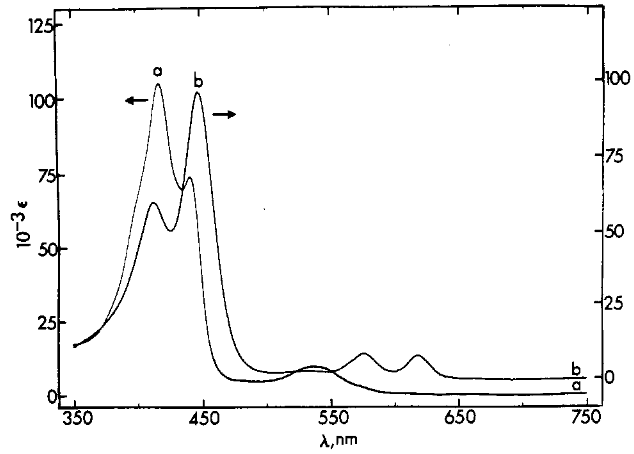

Figure 3. Optical absorption spectra of iron(II) tetraphenylporphyrin species (toluene solution; iron porphyrin concentration 0.0185 mM; 0.5-cm optical cell): (a) square-planar (TPP)Fe; (b) $(TPP)Fe(OH)^-$ generated from spectrum a with 20 mM (TBA)OH. Peak maxima and millimolar absorptivity values, λ (ϵ_{mM}): 412 (60), 448 (97), 534 (1.1), 576 (8.6), 618 (7.6).

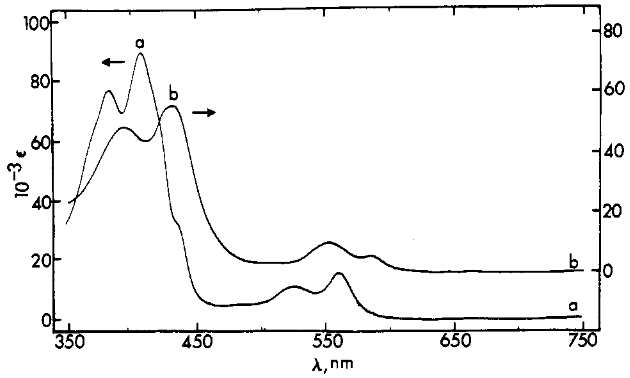

Figure 4. Optical absorption spectra of iron(II) etioporphyrin I species (toluene solution; iron porphyrin concentration 0.0187 mM; 0.5-cm optical cell): (a) square-planar (Etio)Fe; (b) $(Etio)Fe(OH)^-$ generated from spectrum a with 20 mM (TBA)OH. Peak maxima and millimolar absorptivity values, λ (ϵ_{mM}): 394 (50), 432 (56), 553 (10.2), 586 (5.8).

of porphyrin-ring-adjacent methyl and methylene groups occurs with solvent deuterons of DMSO-d_6.[16] This exchange reaction has been exploited for synthesis of deuteriated octaalkylporphyrins and natural porphyrin derivatives.

Characterization of Hydroxoiron(II) Porphyrin Complexes. Optical spectra for the putative $(TPP)Fe(OH)^-$ autoreduction product in DMSO solution and the species produced by titration of square-planar ferrous (TPP)Fe with (TBA)OH in toluene are equivalent. The spectrum of $(TPP)Fe(OH)^-$ in the latter solvent is shown in Figure 3. This spectrum resembles those reported earlier for the products formed by reaction of (TBA)OH and basket-handle ferrous porphyrins,[3] although splitting of the Soret band is much more distinctive for the unsubstituted $(TPP)Fe(OH)^-$ complex. The corresponding spectrum for the $(Etio)Fe(OH)^-$ derivative in toluene is reported in Figure 4. The optical spectrum of $(Etio)Fe(OH)^-$ also resembles in part the spectrum for the putative five-coordinate hydroxyprotoheme dimethyl ester,[2] but the Soret band is split more distinctively for the synthetic complex described here.

Questions about the nature and binding stoichiometry of axial ligands in the iron(II) porphyrin complex were addressed by titration of the square-planar (TPP)Fe derivative in toluene with a 1 M methanol solution of (TBA)OH. Results are shown in Figure 5. Addition of less than 1 equiv of hydroxide ion causes the appearance of a broad signal in the 30 ppm region. The signal is sharpened with addition of a full 1 equiv of base. The chemical shift value and line width are unchanged for addition of between 1.0 and 10.0 equiv of (TBA)OH. These results may be interpreted to indicate that the stoichiometry for hydroxide ion coordination at low hydroxide levels in toluene is 1:1. A less likely possibility is that a second hydroxide ion binds but causes no NMR spectral change. The essentially identical NMR chemical shift patterns for both toluene and DMSO solutions infer the existence of a common hydroxide complex for both noncoordinating and coordinating solvents. No role for coordination of DMSO or DMSO anion is evident under conditions where a moderate excess of hydroxide ion has been added.

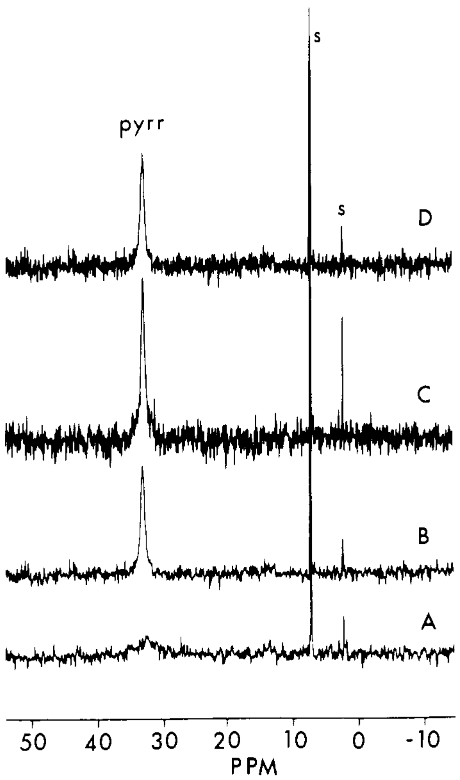

Figure 5. Deuterium NMR spectra of pyrrole-d_8 $(TPP)Fe^{II}$ with sequential addition of 1 M (TBA)OH in methanol under anaerobic conditions (toluene solvent; 55-MHz spectrometer frequency; 25 °C; signals referenced to $(CD_3)_4Si$). Total molar equivalents of (TBA)OH: (A) 0.5; (B) 1.0; (C) 2.0; (D) 5.0.

Features in the proton NMR spectrum of $(Etio)Fe(OH)^-$ in DMSO-d_6 in Figure 2 are also indicative of single hydroxide ion coordination. The downfield ring methyl signal at 18.3 ppm has been partially exchanged with the solvent deuterons.[16] Ring methylene signals at 14.9 and 12.5 ppm are indictive of diastereotopic CH_2 protons due to inequivalent axial ligand sites on the iron porphyrin. This rules out the possibility of dihydroxy ligation where the hydroxide groups would be equivalent and would be in a trans configuration. The relatively large methylene splitting of some 2.5 ppm is reminiscent of the 4.0 ppm splitting observed for the putative five-coordinate mercaptoiron(II) etioporphyrin analogue.[17] The downfield ring methyl and methylene signals parallel those previously observed for high-spin iron(II) porphyrin derivatives, consistent with a predominant σ-unpaired spin delocalization mechanism from the singly occupied $d_{x^2-y^2}$ orbital.[18,19] The methine proton signal in $(Etio)Fe(OH)^-$ is decidedly further upfield at −12.0 ppm than is the case for mercaptide (−0.4 ppm) or imidazole complexes (1.0 ppm) of ferrous porphyrins. The importance of a π-spin delocalization mechanism that puts significant positive spin density at the methine carbon atom and

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negative spin density at the bound proton is thus evident.

Proton NMR spectra of the hydroxoiron(II) tetraarylporphyrin complexes differ from those previously reported for high-spin iron(II) derivatives in that the pyrrole proton signal at 32.8 ppm is shifted less downfield. The pyrrole chemical shift values range from approximately 50 to 60 ppm (25 °C, $(CH_3)_4Si$ reference) for respective 2-methylimidazole[18,19] and alkylmercaptide[17] complexes. The upfield bias for the signal in the hydroxide complex seemingly does not reflect a large upfield dipolar shift contribution, as the phenyl signals show only small shifts from the diamagnetic values. Upfield chemical shift contribution from a diamagnetic state in chemical or magnetic equilibrium with the high-spin state is ruled out by both the magnetic susceptibility determination and approximate NMR Curie law behavior. As was the case for hydroxoiron(II) octaalkylporphyrins, the importance of a π-spin delocalization pathway in the porphyrin ring can serve to explain the upfield bias of the pyrrole proton signal in that positive π-spin density at the β-pyrrole carbon position results in an upfield contribution for the attached proton. Presence of an anionic axial ligand is not necessarily associated with this upfield bias of the pyrrole proton signal (compare the value of 61.0 ppm for the mercaptide complex), but a small basic axial ligand may be responsible for the effect.

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Variable-Energy Photoelectron Study of the Valence Levels of $Si(CH_3)_4$ and $Sn(CH_3)_4$ and the Sn 4d Levels of $Sn(CH_3)_4$

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By the use of monochromatized synchrotron radiation, the gas-phase photoelectron spectra of the valence levels of $Si(CH_3)_4$ and the valence and Sn 4d levels of $Sn(CH_3)_4$ have been obtained and compared between 21- and 70-eV photon energies. For both molecules, experimental valence-band branching ratios have been obtained and compared with theoretical branching ratios from MS–Xα calculations. The generally good agreement obtained between experiment and theory confirms the orbital assignment: $3t_2 < 1t_1 \simeq 1e \simeq 2t_2 < 2a_1$, in order of increasing binding energy. The theoretical and experimental results for both molecules are remarkably similar. For both $Si(CH_3)_4$ and $Sn(CH_3)_4$, resonances were predicted at ~4-, ~10-, and ~20-eV kinetic energies. The predicted resonance positions are in good agreement with experimental results for the high-energy resonance. In conjunction with other recent results on shape resonances in analogous large molecules (e.g. CF_4, SiF_4, SF_6, and SeF_6), these results indicate that shape resonance behavior for other than first-row central atoms (e.g. C) is determined mainly by the nature and symmetry of the ligands and that the resonances are not very sensitive to the detailed molecular potential. Interchannel coupling with Sn 4d photoemission is important for the outermost $3t_2$ orbital of $Sn(CH_3)_4$. The Sn $4d_{5/2}$:$4d_{3/2}$ ratio of $Sn(CH_3)_4$ deviates significantly from the statistical value of 1.5 in the low photon energy region.

Introduction

The tetramethyl compounds of group IV (14) (C, Si, Ge, Sn, Pb) elements have been the subject of a number of ultraviolet photoelectron studies.[1-6] These studies have primarily involved the assignment of the outer valence levels and, in particular, the location of the $2a_1$ and $3t_2$ metal–carbon bonding orbitals. The question of d-level participation in bonding has been widely debated in discussing the electronic structure of these compounds.[5,7-11]

In this study, we have obtained gas-phase photoelectron spectra of the valence levels of $Si(CH_3)_4$ and $Sn(CH_3)_4$ as a function of photon energy from 21 to 70 eV. We were able to include in our study the $1a_1$ and $1t_2$ molecular orbitals of primarily C 2s character that were inaccessible in previous He I photoelectron studies. We had four objectives: First, we expected that our study would confirm the valence-band assignment through a comparison of experimental branching ratios (BR's) with theoretical BR's obtained from MS–Xα calculations. Second, we wanted to examine the valence-band branching ratios for evidence of molecular shape resonances and to compare the shape resonance behaviors for the two analogous molecules. In a previous study, large differences in resonance behavior were observed between CF_4 and SiF_4.[12] The study of $Si(CH_3)_4$ was of particular interest since it is isoelectronic with SiF_4 and the valence band cross sections of SiF_4 exhibit a number of shape resonances.[12] Such resonances have been observed above the Si 2p threshold in absorption spectra of both SiF_4[13-17] and $Si(CH_3)_4$.[18] Third, we wanted to investigate further the role of core-level intershell coupling on valence-level cross

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