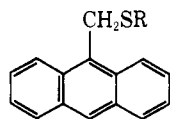


V, X = Br
VI, X = CH₃

surprisingly, cleaved less rapidly than V or VI. In DMF, using 10 equiv of the sodium salt of methyl mercaptan, cleavage of VII and VIII is about 90%



VII, R = 1-hexyl
VIII, R = benzyl

complete after 5 hr at 25°. When, however, HMPA is employed as the reaction medium, deblocking is complete in less than 2 hr at 25° and *n*-hexyl mercaptan and benzyl mercaptan are isolated in 68 and 74% yields.

A dioxane solution containing 10 equiv of trifluoroacetic acid is without effect on ether IV, even after 1 hr at 25°; but after 10 min at 0° the ether is completely cleaved by trifluoroacetic acid in methylene chloride. On the other hand, thioether VI is recovered quantitatively after being treated with trifluoroacetic acid in methylene chloride for 10 min at 0°.⁶

The possibility of utilizing the 9-anthrylmethyl system for protecting amines and alcohols is being studied. Also under investigation are a number of interesting questions relating to other nucleophiles and to the matter of mechanism.

Acknowledgment. We are indebted to the National Science Foundation and to Eli Lilly and Co. for support of this research.

(6) Both IV and VI are unaffected by ethylamine in DMF, even after 24 hr at room temperature. The thioether (VI) was also recovered quantitatively after being treated with lithium hydroxide in aqueous dioxane for 8 hr at 25°.

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X-Ray Photoelectron Spectroscopic Studies of Silver(III) Octaethylporphyrin

Sir:

The redox properties of metalloporphyrins¹⁻³ are of recent interest because of their potential relevance as models in biological redox systems. Two points are of special interest. One is the question of whether or not an electron can be removed (or added) directly to the central metal ion or whether the electronic levels of the porphyrin ring are involved. The second is to what extent changing oxidation states of the metal ions

(1) J. Manassen and A. Wolberg, *J. Amer. Chem. Soc.*, **92**, 2982 (1970).

(2) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Amer. Chem. Soc.*, **92**, 3451 (1970).

(3) J. Fuhrhop, K. M. Kadish, and D. G. Davis, *J. Amer. Chem. Soc.*, **95**, 5140 (1973), and references therein.

affects the porphyrin ring charge and therefore its reactivity. The latter question has been considered theoretically.⁴ The technique of X-ray photoelectron spectroscopy (XPS or ESCA) has been suggested to be an appropriate tool for probing the charge distribution of these systems⁵ since in the absence of complicating factors like atomic relaxation and gross structural differences, chemical shifts of core electron binding energies directly reflect the nuclear charge felt by these electrons. In this study we wish to present the ESCA spectra of several silver porphyrins. These results establish unequivocal evidence for the existence of a stable Ag(III) complex and illustrate the power of using the binding energies of the metal, N 1s, and C 1s electrons in understanding the electron distribution in these systems.

All compounds were prepared by previously reported synthetic methods.³ Samples were prepared for spectral analysis by smearing several micrograms of material onto a gold plate and burnishing it into a very thin film with a sapphire ball. Samples burnished to a very thin film did not show any signs of charging as evidenced by (a) a high reproducibility of results (± 0.1 eV) from one sample preparation to the next and by (b) a lack of movement of the peaks during exposure to low-energy electrons flooding the sample. Unlike the previous ESCA study on porphyrins,⁵ we found the compounds to be very easy to handle and the measured binding energies to be very reproducible.

To interpret chemical shifts of the silver porphyrins in terms of their charge distribution, we have studied a series of molecules with similar structure. A compilation of these results is given in Table I. The binding

Table I. Binding Energies^a (eV) of Silver Porphyrins and Related Compounds

	Ag 3d _{5/2}	Ag 3d _{3/2}	C 1s	N 1s
Ag(0)	374.0	367.9		
H ₂ OEP			284.5	399.4 397.3
H ₂ TPP			284.0	399.1 397.0
Ag ^{II} OEP	374.3	368.3	284.3	397.6
Ag ^{II} TPP	373.7	367.6	284.3	398.3
Ag ^{III} OEP(ClO ₄)	377.1	371.0	284.2	398.7

^a All spectra were recorded on a Hewlett-Packard 5950A ESCA spectrometer. Binding energies were all reproducible to ± 0.1 eV.

energy for the 3d_{5/2,3/2} electrons of evaporated silver are shown as 374.0 and 367.9 eV, respectively, vs. the gold 4f_{7/2} electrons at 84.0 eV and are presented as a reference value. The binding energy values for the C 1s and N 1s electrons of octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP) free bases are also shown in order to characterize the system in the absence of metal ion. The N 1s spectrum exhibits a doublet due to the selective protonation of two of the central nitrogens. This result is in agreement with a previous study⁵ and settles a long standing controversy over the configuration of the attached protons. The C 1s

(4) (a) M. Zerner, M. Gouterman, and H. Kobayashi, *Theor. Chim. Acta*, **6**, 363 (1966); (b) M. Zerner and M. Gouterman, *ibid.*, **4**, 44 (1965); **8**, 26 (1967); (c) A. M. Schaffer and M. Gouterman, *ibid.*, **18**, 1 (1970).

(5) M. V. Zeller and R. G. Hayes, *J. Amer. Chem. Soc.*, **95**, 3855 (1973).

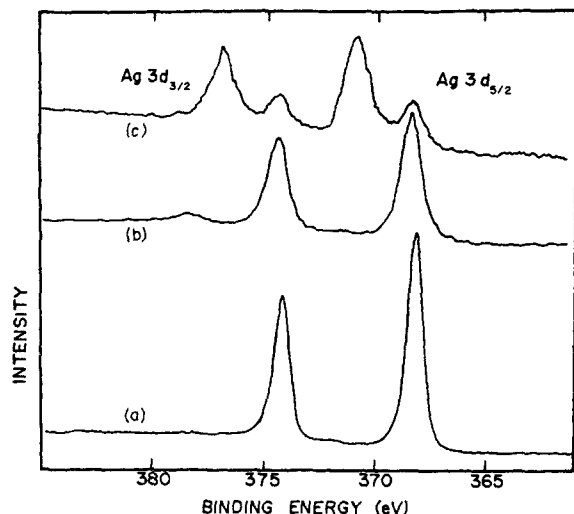


Figure 1. Silver $3d_{3/2}$ and $3d_{5/2}$ spectra of (a) silver foil evaporated onto a gold foil at 10^{-6} Torr, (b) $\text{Ag}^{\text{II}}\text{OEP}$, and (c) $\text{Ag}^{\text{III}}\text{OEP}\cdot(\text{ClO}_4)$ mixed with a small amount of b.

spectrum also shows a single peak presumably composed of both the porphyrin ring carbons and the substituent group carbons. The absence of any additional peaks due to charge differences in the porphyrin ring carbons is in general agreement with Gouterman's calculations⁴ indicating these differences to be less than 0.05 charge unit.

Complexing a metal ion with OEP causes noticeable chemical shifts in the binding energy of the metal, carbon, and nitrogen peaks. For $\text{Ag}^{\text{II}}\text{OEP}$ (Figure 1), the silver peaks are shifted a small amount (0.4 eV) to higher values indicating a slight increase in positive charge relative to silver metal. The spectrum for the (TPP) analog is similar in shape although the effect of the phenyl substituents is to shift the peaks to lower binding energy. This result is in general agreement with previous studies where only slight differences are noted between a variety of $\text{Ag}(0)$, $\text{Ag}(I)$, and $\text{Ag}(II)$ complexes.^{4b,6} The nitrogen 1s spectrum collapses to a single peak with a binding energy value directly in between the OEP doublet. For this molecule, the C 1s peak shows virtually no change indicating the nitrogen σ orbitals are, as predicted,⁷ weakly coupled to the porphyrin ring π system and the positive charge is primarily localized on the silver nitrogen.

The silver spectra of $\text{Ag}^{\text{III}}\text{OEP}(\text{ClO}_4)$ containing some $\text{Ag}^{\text{II}}\text{OEP}$ are shown in Figure 1 and the binding energies are given in Table I. The substantial chemical shift (2.7 eV vs. the $\text{Ag}(II)$ analog and 3.1 eV vs. $\text{Ag}(0)$) clearly confirms the previously assigned oxidized form⁸ to be $\text{Ag}(III)$ formed by removing an electron from the $\text{Ag}(II)$ rather than from the porphyrin ring to form a π cation radical as is believed to be the case for zinc, magnesium, and a number of other metalloporphyrins.¹⁻³ This shift is also in reasonable agreement with a similar shift recently reported for a $\text{Ag}(III)$ biguanide complex (4.2 eV vs. $\text{Ag}(0)$).⁹ The slightly smaller value observed for the porphyrin system may be attributable

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(9) D. A. Zatko and J. W. Pather, II, *J. Electron Spectrosc. Relat. Phenomena*, **2**, 190 (1973).

to the strongly coordinated perchlorate³ which would tend to reduce the net positive charge about the $\text{Ag}(III)$.

It is also of interest that the nitrogens are shifted noticeably (~ 1.0 eV) to higher energies thus obtaining a partial positive charge. This observation is consistent with the fact that the greater electronegativity of the $\text{Ag}(III)$ species promotes greater electron withdrawal from the nitrogen through the σ bond which is not replaced by the π system due to poor coupling. The small, reproducible shift to lower binding energy of the porphyrin carbon 1s electrons is somewhat surprising since this result indicates that in removing an electron from $\text{Ag}(II)$ by oxidation the π system slightly increases its electron density. This trend has been predicted^{4a} for an $\text{Fe}(II)/\text{Fe}(III)$ porphyrin system using an extended Hückel molecular orbital treatment.

On the basis of these results, we believe we have obtained conclusive evidence for the presence of a stable $\text{Ag}(III)$ species by preparing a series of complexes with similar structure and by monitoring the chemical shifts of the metal, nitrogens, and carbons. It is apparent that a similar approach on other metalloporphyrin or like compounds can be a valuable aid to estimating molecular charge densities for comparison to available theoretically calculated data.

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The Decomposition of *tert*-Butylperoxy Isobutyrate and Isotopic Derivatives

Sir:

We have developed methods for measuring deuterium secondary kinetic isotope effects in perester¹ and peroxide decompositions² with the twofold purpose of gaining a better understanding of the origin of these effects³ and of extending their use as mechanistic probes. Previous results indicated essentially no isotope effect on the overall rate of decomposition of *tert*-butyl peracetate.^{1a} In contrast, appreciable isotope effects were found for phenylacetates^{1b} ($k_{\text{H}}/k_{\text{D}} > 1.03$ per α deuterium) and *tert*-butyl perpivalate ($k_{\text{H}}/k_{\text{D}} = 1.02$ per β -deuterium). The latter results are consistent with expectations of the transition state for concerted decomposition of the perester in which the starting material and the alkyl-*tert*-butoxy radical pair are separated by a single free energy maximum (Scheme I

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(2) T. Koenig and R. Cruthoff, *J. Amer. Chem. Soc.*, **91**, 2562 (1969).

(3) T. Koenig and R. Wolf, *J. Amer. Chem. Soc.*, **91**, 2569 (1969).