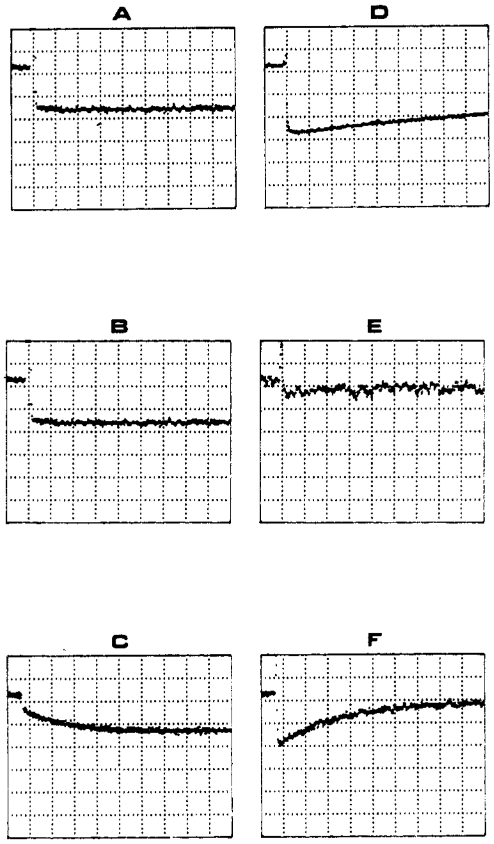

Figure 1. Change in optical transmission with time for N_2O-saturated solutions containing azide (1 M): (A) no tryptophan, 2×10^{-3} M *p*-methoxyphenol, 5 μs per horizontal division, 200 mV per vertical division, 410 nm; (B) 10^{-2} M tryptophan, 2×10^{-3} M *p*-methoxyphenol, 5 μs per horizontal division, 200 mV per vertical division, 410 nm; (C) 10^{-2} M tryptophan, 2×10^{-4} M *p*-methoxyphenol, 25 μs per horizontal division, 200 mV per vertical division, 410 nm; (D) 10^{-2} M tryptophan, no *p*-methoxyphenol, 100 μs per horizontal division, 50 mV per vertical division, 510 nm; (E) 10^{-2} M tryptophan, 2×10^{-3} M *p*-methoxyphenol, 10 μs per horizontal division, 50 mV per vertical division, 510 nm; (F) 10^{-2} M tryptophan, 2×10^{-4} M *p*-methoxyphenol, 25 μs per horizontal division, 50 mV per vertical division, 510 nm.

(3) We have attempted to repeat the measurement of the one-electron reduction potential of tryptophan. N_2O-saturated solutions were prepared containing 1 M sodium azide, 10^{-2} M tryptophan, and 2×10^{-3} and 2×10^{-4} M *p*-methoxyphenol, adjusted to pH values in the range 6.5–8.0. Observations were made at 410 nm (*p*-methoxyphenoxy radical) and 510 nm (oxidized tryptophan radical) after delivery of 1-Gy pulses using cells of 10-cm optical path length. The experimental setup was the same as employed in earlier work.[2,4] Typical changes in optical transmission are shown in Figure 1. In every case transfer of the electron from *p*-methoxyphenol to the oxidized tryptophan radical was complete ($k = 1 \times 10^8$ M^{-1} s^{-1}), showing no indication of equilibrium. If the one-electron reduction potential of the *p*-methoxyphenoxyl radical is accepted as 0.6 V at pH 7.5, these experiments are inconsistent with a one-electron reduction potential of the oxidized tryptophan radical of 0.64 V, but consistent with 0.87 V.

The oxidized guanosine radical was reported to react to completion with tryptophan,[1] but as the redox data for this species are unpublished, we have not attempted to repeat the experiments.

We conclude that there is no reason to doubt that the one-electron reduction potential of the oxidized tryptophan radical at neutral pH is above that of the oxidized tyrosine radical, in full agreement with the observed direction of transfer.

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Registry No. Tryptophan, 73-22-3; tyrosine, 60-18-4.

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Resonance Raman Spectroscopic Detection of Demetallation of Metalloporphyrin π Cation Radicals

Sir: Resonance Raman (RR) spectroscopy has been utilized to extract structural and electronic information from naturally occurring metalloporphyrin systems and their models and has recently been applied to synthetic metalloporphyrin π cation radicals ($MP^{\bullet+}$).[1-3] The preparative techniques for $MP^{\bullet+}$ generation, however, rarely produce a homogeneous sample.[4] Owing to the selective enhancement afforded by Soret excitation RR, it is possible to detect trace amounts (less than 3%) of porphyrin free base diacid salts in samples of $MP^{\bullet+}$ prepared by chemical and electrochemical oxidation in CH_2Cl_2. If unrecognized, the presence of the diacid salt may cause serious artifacts in the RR spectra of these samples that prevent accurate analysis of scattering from the $MP^{\bullet+}$.[1] Proper control of experimental conditions, particularly the choice of excitation frequency, can produce RR spectra of $MP^{\bullet+}$ free of contributions from the diacid.[3,5]

One-electron oxidation of Co and Zn octaethylporphyrin (OEP) in dry CH_2Cl_2 leads to divalent metal porphyrin π cations.[3,6] Laser excitations at 363.8 nm selects against resonance enhancement of possible residual starting materials and produces good quality RR spectra.[3] RR spectra of these $MP^{\bullet+}$ samples excited at 406.7 nm, however, are often dominated by bands not present in spectra at 363.8 nm and not assignable to parent MP modes.[7] The frequencies of these bands (most noteworthy are those at 1394 and 1558 cm^{-1}) show no metal dependency. These facts suggest the presence of an impurity which absorbs strongly near 406.7 nm.

Spectra a and b of Figure 1 show RR scattering excited at 406.7 nm from samples of $Co^{II}OEP^{\bullet+}ClO_4^-$ prepared with $AgClO_4$ and $Co^{III}OEP^{\bullet+}2ClO_4^-$ prepared with $Fe(ClO_4)_3$, respectively.[8]

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(7) Our results show the phenomenon to be widespread. In addition to examples presented here, we have observed similar artifacts when using Br_2 to oxidize CoOEP and MgOEP. Oxidation of NiTPP, CuOEP, and FeOEPCl by $Fe(ClO_4)_3$ in CH_2Cl_2 also produces significant amounts of analogous impurities.

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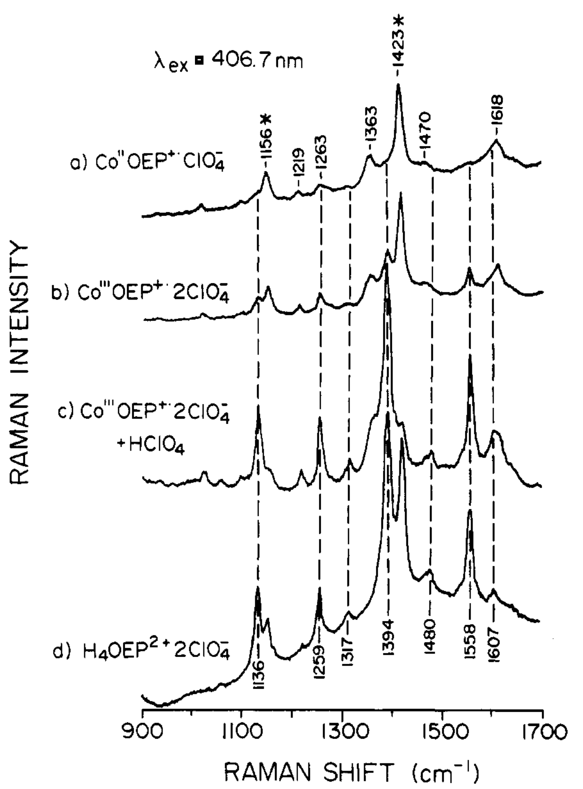

Figure 1. Resonance Raman spectra excited at 406.7 nm: (a) Co^{II}OEP$^{\cdot+}$ClO$_4^-$ prepared with AgClO$_4$; (b) Co^{III}OEP$^{\cdot+}$2ClO$_4^-$ prepared with Fe(ClO$_4$)$_3$; (c) Co^{III}OEP$^{\cdot+}$2ClO$_4^-$, prepared with Fe(ClO$_4$)$_3$ and a trace amount of HClO$_4$; (d) H$_4$OEP^{2+}2ClO$_4^-$, prepared from H$_2$OEP + HClO$_4$. All samples were dissolved in CH$_2$Cl$_2$. A spinning quartz cell and ~20-mW laser power were used. Solvent bands are labeled with an asterisk.

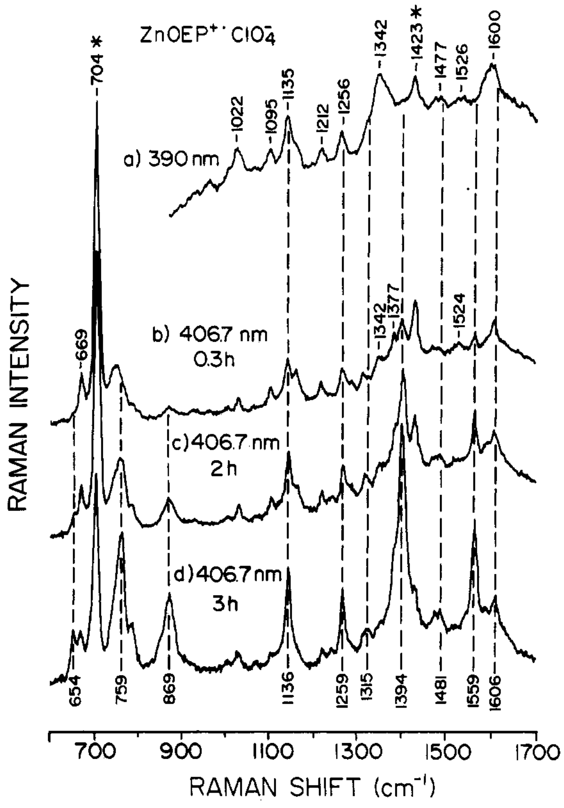

Figure 2. RR spectra of ZnOEP$^{\cdot+}$ClO$_4^-$: (a) λ_{ex} = 390 nm; (b) -(d) show a time course at λ_{ex} = 406.7 nm for ~1 mL of sample in a quartz spinning cell with a laser power of 16 mW. The time values indicate total irradiation time at the end of the scan.

Although the RR spectra of these two species excited at 363.8 nm are very similar,[3] with excitation at 406.7 nm additional bands appear in the spectrum of the cobaltic OEP$^{\cdot+}$ relative to the cobaltous sample. Figure 1c shows scattering from a sample of Co^{III}OEP$^{\cdot+}$2ClO$_4^-$ prepared with Fe(ClO$_4$)$_3$ and a trace amount of HClO$_4$. The added intensity of the spurious bands in this spectrum suggests that the impurity is caused by acid-promoted demetallation of the MP$^{\cdot+}$ and protonation of the resultant free base porphyrin. Figure 1d shows the RR spectrum of the diacid salt H$_4$OEP^{2+}2ClO$_4^-$, confirming this as the interfering species.

Thus, RR spectra of MP$^{\cdot+}$ samples excited at 406.7 nm may contain artifacts due to free base diacid salts present at concentrations too low to be obvious in the optical absorption spectrum yet high enough to dominate the RR scattering at 406.7 nm. This is clear from the Soret optical properties of the impurity: the Soret band sharpens dramatically and red shifts to 406 nm (ϵ = 430 mM^{-1} cm^{-1}) upon formation of the diacid from OEPH$_2$.[9] Thus, the narrowed bandwidth, the increased extinction coefficient ϵ, and the coincidence of the Soret transition energy with the laser line at 406.7 nm explain the selective scattering from the impurity.

Figure 2 shows scattering excited at 390 and 406.7 nm of ZnOEP$^{\cdot+}$ClO$_4^-$. The absence of bands at 1394 and 1558 cm^{-1} indicates no contributions from the impurity with 390-nm excitation.[10] Spectra excited at 406.7 nm show bands at 1394 and 1559 cm^{-1} as depicted in Figure 2b. Unlike the Co^{III}OEP$^{\cdot+}$2ClO$_4^-$ sample, which appears to be stable to prolonged laser irradiation, the contributions from the impurity (marked by the dashed lines) increase dramatically with repeated scanning of the ZnOEP$^{\cdot+}$ClO$_4^-$ sample until they dominate the spectrum as shown in Figure 2c–d. The solvent bands at 704 and 1423 cm^{-1} show the opposite trend and decrease in intensity, indicating stronger absorbance at 406 nm as the impurity concentration increases. Indeed, for this MP$^{\cdot+}$ sample with the Soret band at 387 nm, the Soret absorbance at 406 nm of the protonated porphyrin was easily seen to increase in parallel with the changes in the RR spectrum.[11]

These results suggest a number of conclusions: (1) oxidation of MP samples in CH$_2$Cl$_2$ often results in the formation of free base diacid impurities which can be detected by RR at 406.7 nm; (2) owing to trace amounts of aqueous acid impurities in reagents, oxidation with Br$_2$ or Fe(ClO$_4$)$_3$ is more likely to cause demetallation and diacid formation than oxidation with AgClO$_4$ or electrochemical techniques; (3) MOEP$^{\cdot+}$ complexes prepared by electrochemical or AgClO$_4$ oxidation show detectable diacid formation for M = Mg or Zn but not for Co^{II} or Ni, suggesting

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(8) OEPH$_2$ was prepared according to Wang, C. B.; Chang, C. K. *Synthesis* **1979**, 548–549. Insertion of metals was carried out by standard methods: Falk, J. E. *Porphyrins and Metalloporphyrins*; Elsevier: New York, 1964; p 798. The metalloporphyrins were purified by recrystallization and/or chromatography to eliminate traces of free base. CH$_2$Cl$_2$ freshly distilled from CaH$_2$ was used as a solvent for all preparations. Details of oxidations are presented in ref 3 and 5. Raman measurements on spinning samples at 406.7 nm were made as described by Ondrias, M. R.; Babcock, G. T. *Biochim. Biophys. Res. Commun.* **1980**, *93*, 29–35.

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(10) Excitation of 390 nm was provided by a pulsed laser system described by Oertling, W. A.; Babcock, G. T. *J. Am. Chem. Soc.* **1985**, *107*, 6406–6407. The RR spectral contribution from the diacid impurities are less obvious with pulsed excitation than with CW excitation at similar wavelengths, most likely reflecting a long-lived Soret excited state of the diacid species not in resonance at 390 nm.

(11) ZnOEP$^{\cdot+}$ClO$_4^-$ was prepared by oxidation with AgClO$_4$. Use of Fe(ClO$_4$)$_3$ as an oxidant for ZnOEP is more difficult to control as an excess will rapidly oxidize the sample to the dication. Along with this a copious amount of the diacid impurity is produced as is evidenced by the rapid growth of a sharp absorption band at 405 nm. Three control RR experiments at 406.7 nm were performed: degassed ZnOEP in CH$_2$Cl$_2$ showed no sign of the impurity (ref 1), whereas anaerobic samples of ZnOEP$^{\cdot+}$ClO$_4^-$ exhibited behavior like that shown in Figure 2, and OEPH$_2$ in CH$_2$Cl$_2$ rapidly became protonated during the same time period of laser irradiation. The band at 1377 cm^{-1} in Figure 2b is from unoxidized starting material and indicates the presence of the diacid under conditions of incomplete oxidation. Samples containing no detectable trace of neutral ZnOEP showed the same behavior. Samples of ZnOEP$^{\cdot+}$ClO$_4^-$ not exposed to laser light showed no sign of diacid formation detectable by optical absorption spectra.

that the ease of demetallation is core size dependent for $MP^{\bullet +}$ as it is for the parent MP,[12] (4) demetallation of $ZnOEP^{\bullet +}ClO_4^-$ is enhanced by laser light in the Soret region of the spectrum; and (5) though diacid formation may be limited to chlorinated solvents and use of another solvent may minimize demetallation, the utility of CH_2Cl_2 for RR spectroscopy and porphyrin oxidations may not be easily replaced. Recognition and elimination of these artifacts is essential to characterizing the vibrational spectra of the $MP^{\bullet +}$ species. Excitation at 363.8 nm produces RR spectra free of these artifacts and illustrates vibrational similarity of $^2A_{1u}$ and $^2A_{2u}$ radical types.[5,13] This similarity was obscured by the occurrence of diacid impurities in RR samples of the presumed $^2A_{1u}$ species of previous studies.[1]

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Registry No. CoOEP, 17632-19-8; ZnOEP, 17632-18-7; $Co^{II}OEP^{\bullet +}ClO_4^-$, 55845-55-1; $Co^{III}OEP^{\bullet +}{}_2ClO_4^-$, 33058-44-5; $ZnOEP^{\bullet +}ClO_4^-$, 103904-51-4; $H_4OEP^{2+}{}_2ClO_4^-$, 51319-02-9.

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Work Function Measurability and the Absolute Half-Cell Potential

Sir: Reiss recently reviewed the subject of the absolute half-cell potential.[1] This has been a very controversial subject,[1-5] with several different approaches being discussed in the literature,[1-3] and the absolute half-cell problem is even widely considered insoluble.[4,5] Reiss's article gives a careful discussion of the problem while advocating a particular point of view. In a somewhat different approach it has been suggested that the absolute half-cell potential be defined in terms of the Gibbs free energy of the reaction[3]

$$M(\text{solid}) \rightarrow M^+(\text{solution}) + e^-(\text{gas}) \tag{1}$$

A common feature of most treatments of absolute half-cell potentials is the need to know a work function. Reiss carefully pointed out several difficulties in work function measurability and has thus brought into focus a crucial issue, inspiring the present comment. While his discussion is very important, it could lead to some confusion, since he overlooked mentioning that reliable measurements *are* possible.

The photoelectric method of work function measurement was criticized because the photoelectric threshold is not sharp at nonzero temperature. The Fowler method was designed to deal with this problem,[6,7] as were some related methods.[7] There are some assumptions used in these methods, so the literature should be consulted for details.

A second objection was that work function measurements are not thermodynamically reversible. The effusion method[7-9] largely answers this objection. This method is a close analogue of the heated cavity method of studying blackbody radiation. In both experiments particles of interest (photons or electrons) equilibrate inside a heated cavity. The equilibrium number density is given by well-established statistical mechanical expressions, the blackbody law for photons, and eq 27 of Reiss's paper for electrons. The cavity contents are sampled by effusion from a small hole. Some irreversibility exists (effusion), but the rate of effusion is too small to significantly perturb the equilibrated cavity, and effusion is well understood from kinetic theory. Both the effusion method of work function measurement and the heated cavity method of studying blackbody radiation use statistical thermodynamics and kinetic theory and are thus not *pure* thermodynamic methods. However, troublesome quantities like reflection coefficients are avoided entirely and the relevant equations are based on fundamental physical theory. Therefore these methods are reliable if properly applied. The heated cavity is of course the preferred method of studying blackbody radiation. In like manner Fomenko considers the effusion method to be preferred for work function measurements.[9]

The issue of electronic entropy of metals was raised as a factor in work function measurability. However, if one knows the electronic entropy as a function of temperature and the work function at a single temperature, one can integrate

$$\frac{\partial \bar{\mu}}{\partial T} = -S \tag{2}$$

to obtain the work function at any temperature. Since at 0 K the photoelectric threshold yields the work function,[1] and the electronic entropy is obtainable from the absolute thermoelectric power of the metal,[10] the work function is well measurable. The absolute scale of thermoelectricity is known quite accurately,[11] so this method may be of practical as well as theoretical interest. Once the work function of a single metal is known, all other work functions are obtainable from measurements of contact potentials.

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