# Correlation between Gas-Phase Electron Affinities, Electrode Potentials, and Catalytic Activities of Halogenated Metalloporphyrins

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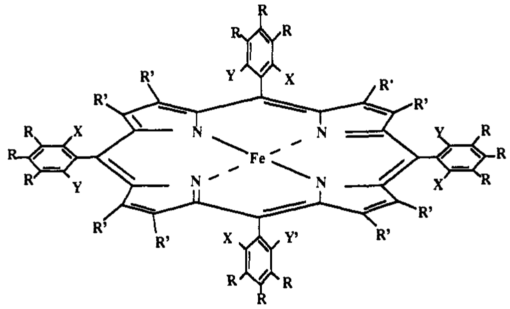
**Abstract:** The gas-phase electron affinities (EAs) of a series of halogenated iron tetraphenyl porphyrins determined using ion cyclotron resonance mass spectrometry are reported. The EAs of the Fe(II) species vary approximately linearly with their condensed-phase reduction potentials. The EAs of the Fe(III) species with axial Cl ligands vary approximately linearly with condensed-phase reduction potentials. The lines for the Fe(III) and Fe(II) data sets are quite different, however, suggesting substantial solvent effects on the condensed-phase reduction process. Analysis in terms of the Born equation suggests a smaller effective size for the two Fe(III) species with the lowest degree of halogenation, which suggests in turn that those species accept an electron into a metal-based orbital while the remaining species accept an electron into a ligand-based orbital. The available catalytic activities of the various metalloporphyrins for the oxidation of isobutane to *tert*-butyl alcohol are covariant with the electron affinities. This covariance is discussed in the context of a catalytic mechanism, and it is suggested that the gas-phase electron affinity is a useful measure of electronic effects on catalyst activity.

## Introduction

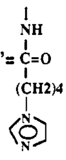
Polyhalogenated metalloporphyrins have been the object of a number of recent studies because of their potential as selective oxidative catalysts.[3-8] The activity of such heme-based biological oxidation catalysts as cytochrome P-450 suggested that metalloporphyrins might be effective homogeneous oxidation catalysts.[9-12] Readily available iron tetraphenylporphyrin (FeTPP), **1**, is essentially ineffective as a catalyst for air oxidation of alkanes to alcohols, but halogenated FeTPPs have been found to be effective and selective catalysts for conversion of isobutane to *tert*-butyl alcohol.[3-5] Both the stability and activity of the catalysts increase with extent of halogenation. In probing the origin of the dependence of catalytic activity on halogenation, it was found that catalytic activity increased with the Fe(III)/Fe(II) electrode potential of the catalyst.[5] The correlation of catalytic activity with the electrode potentials of halogenated FeTPPs led us to measure the gas-phase electron affinity (EA) of each of a number of iron porphyrin species. We report the results of those measurements here.



1: X=Y=Y'=R=R'=H

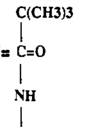
2: R=R'=H, X=Y=Y'=Cl

3: X=Y=R=R'=H, Y'=



$-NH-C(=O)-(CH_2)_4-$imidazolyl

4: X=R=R'=H, Y=Y'=



$-NH-C(=O)-C(CH_3)_3$

5: X=Y=Y'=R=F, R'=H

6: X=Y=Y'=R=R'=Cl

7: X=Y=Y'=R'=Cl, R=H

8: X=Y=Y'=R=F, R'=Cl

9: X=Y=Y'=R=Cl, R'=H

## Experimental Section

The measurements were done using the same methods that were used to measure the EAs of nickel porphyrins.[13] Syntheses of the halogenated porphyrins have been described elsewhere.[4,7] A selected halogenated FeTPP chloride (FeTPP$^{i}$Cl) was introduced into the vacuum chamber of a Fourier transform ion cyclotron resonance (FT-ICR) spectrometer[14] (FTMS 2000,[15] Millipore Extrel, Madison, WI) using a heated probe.

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**Table 1.** Electron Affinities, Reduction Potentials, Radii, and Catalytic Activities of Metalloporphyrins

| species[a] | EA (eV)[b] | $E_{1/2}$ (V)[c] | $r_e$ (Å)[d] | TON[e] |
|---|---|---|---|---|
| NiTPP | 1.51 ± 0.01[f] | −1.370[g] | 3.5 | |
| $H_2$TPP | 1.69 ± 0.01[f] | −1.280[g] | 3.7 | |
| NiTPPCHO | 1.74 ± 0.01[f] | −1.165[g] | 3.5 | |
| **1** (FeTPP) | 1.87 ± 0.03 | −1.010[i] | 3.5 | |
| **2** (FeTPPo$Cl_8$) | 1.86 ± 0.03 | −1.05[h] | 3.6 | |
| **3** (FeTPP-val) | 1.97 ± 0.03 | | | |
| **4** (FeTPP-piv) | 2.07 ± 0.03 | −0.866[i] | | |
| **5** (FeTPP$F_{20}$) | 2.15 ± 0.15 | | | |
| **6** (FeTPP$Cl_{28}$) | 2.59 ± 0.11 | | | |
| **8** (FeTPP$F_{20}\beta Cl_8$) | 3.21 ± 0.03 | | | |
| **1**-Cl (FeTPPCl) | 2.15 ± 0.15 | −0.221[j] | 2.7 | 0 |
| **2**-Cl (FeTPPo$Cl_8$Cl) | 2.10 ± 0.19 | −0.221[j] | 2.7 | |
| **5**-Cl (FeTPP$F_{20}$Cl) | 3.14 ± 0.03 | 0.07[j] | 3.9 | 1160 |
| **7**-Cl (FeTPPo$Cl_8\beta Cl_8$Cl) | 2.82 ± 0.03 | 0.10[h] | 3.2 | |
| **8**-Cl (FeTPP$F_{20}\beta Cl_8$Cl) | 3.35 ± 0.03 | 0.28,[j] 0.27[h] | 3.7 | 1800 |
| **9**-Cl (FeTPP$Cl_{20}$Cl) | 2.93 ± 0.23 | | | |

[a] The species indicated as chlorides (-Cl) correspond to Fe(III) complexes having an axial Cl ligand coordinated to the metal in the numbered structures. [b] Present results except as indicated. [c] From cyclic voltametry. Potentials for $M/M^-$ couples, where M is the indicated neutral species. Reversible half-wave potentials in $CH_2Cl_2$ relative to the SCE except as noted. [d] Effective radius from eq 4. [e] Catalyst turnover numbers from ref 5 for oxidation of isobutane to tertiary butyl alcohol at 60 °C under 100 psig of $O_2$ (mol $O_2$ consumed in 6 h)/(mol catalyst used). [f] From ref 13. [g] Measurements done in $CH_2Cl_2$ from the following: Hagan, T. E. Ph.D. Thesis, University of Delaware, 1992. Potentials measured relative to the ferrocene/ferrocenium couple. Values relative to SCE obtained as described in the text. [h] Measurements done in benzonitrile from ref 7. [i] Measurements done in 1,2-$C_2H_4Cl_2$ from the following: Guentin, C.; Lexa, D.; Momenteau, M.; Saveant, J.-M.; Xu, F. *Inorg. Chem.* **1986**, *25* (23), 4294–4306. [j] Measurements done in $CH_2Cl_2$ from ref 5.

The chlorides have an axial chloride ligand and are formally Fe(III). A reference electrophile such as $NO_2$ was introduced into the spectrometer through a fixed leak. Combined pressures of the two samples in the vacuum chamber were on the order of $10^{-7}$ Torr, as indicated by an ionization gauge. The ratio of the pressures of the species present was estimated from their relative ionization cross sections and a 70-eV positive ion mass spectrum of the mixture in the vacuum chamber. When necessary, ionization cross sections were estimated from polarizabilities,[16] which in turn were estimated using group additivities methods.[17] Negative ions formed by a 5-ms, 4-eV electron beam pulse were confined in the ion trap for a variable reaction time, after which a spectrum was obtained revealing the relative concentrations of the ions. The ions observed usually included the parent anions of the selected halogenated FeTPP, $FeTPP^{i-}$, the halogenated FeTPPCl, $FeTPP^iCl^-$, and the reference electrophile. These ions grew in over a few tenths of a second reaction time, indicating that they were formed as the neutrals present captured slow electrons scattered from the electron beam. The $FeTPP^i$ neutral was presumably formed by thermolysis of the $FeTPP^iCl$ on the heated probe. In some instances the parent anions of only $FeTPP^i$ (**7** and **9**) or only the halogenated $FeTPP^iCl$ (**3**, **4**, and **6**) were observed. EAs could not be obtained for those neutrals corresponding to anions not observed. As reaction time increased, the relative concentrations of the various anions changed as a result of charge-transfer reactions. At long reaction time either one ion became predominant or two ions achieved a time independent steady-state ratio. In the former case, the neutral corresponding to the ion predominant at long time was taken as the neutral with the highest EA. In the latter case the steady-state concentrations were taken as equilibrium concentrations, and an equilibrium constant for the charge-transfer reaction relating the two ions was determined. By assuming that $\Delta G = \Delta H$ for the charge-transfer reaction, the difference between the electron affinities of the neutrals involved in the equilibrium was deduced. These results together with the known electron affinities of the reference electrophiles[18] were used to determine the electron affinities in Table 1.

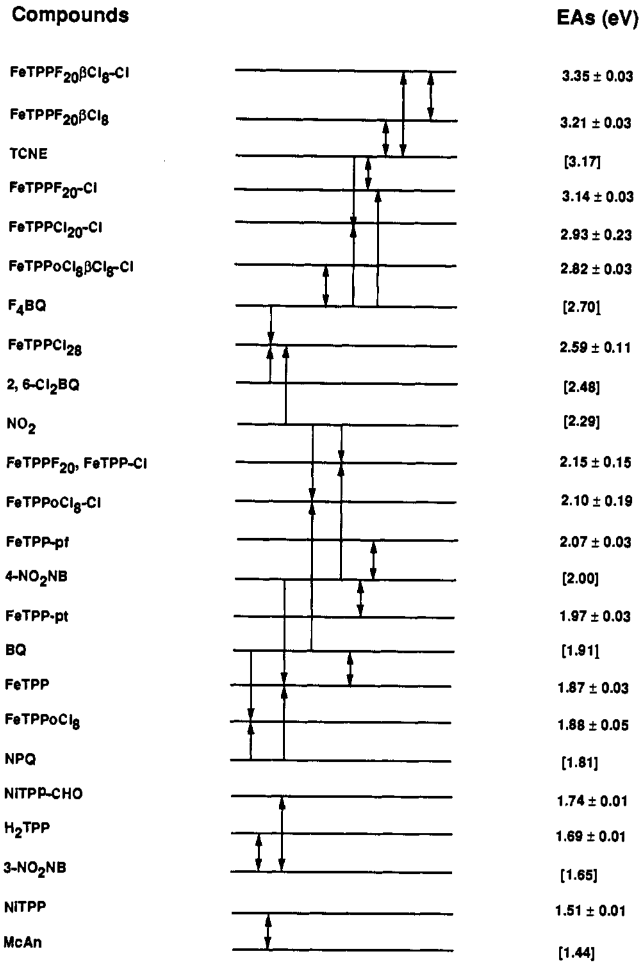

**Figure 1.** Electron affinity ladder. Bracketed EAs of standards are from ref 18. TCNE = tetracyanoethylene, $F_4BQ$ = tetrafluorobenzoquinone, 4-$NO_2NB$ = 1,4-dinitrobenzene, BQ = benzoquinone, NPQ = naphthoquinone, 3-$NO_2NB$ = 1,3-dinitrobenzene, and McAn = maleic anhydride. The porphyrins are identified by the codes used in Table 1. Double-headed arrows represent an equilibrium constant measurement. Single-headed arrows represent determination of an upper or lower limit on an equilibrium constant.

Electrochemical measurements were made using a conventional three-electrode configuration consisting of a reference electrode (a silver wire to contact with a 0.01 M $AgNO_3$/0.10 M tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) dimethylformamide solution, which was connected to the main cell compartment by a Luggin capillary), a counter electrode (a coiled platinum wire), and a working electrode (a 200-μm-diameter platinum electrode). The cyclic voltammograms were run at scan speeds varying from 2 to 200 mV/s. All the reported potentials correspond to $E_{1/2}$ for reversible processes. The potentials were measured relative to $E_{1/2}$ for the ferrocene/ferrocenium couple. For comparison to potentials measured relative to the SCE in the literature the values obtained in the present study were increased (made more positive) by 0.43 V, the difference between our measurement of the first oxidation potential of tetraphenylporphine in methylene chloride relative to the ferrocene/ferrocenium couple (0.52 V) and a literature value[19] of the same oxidation potential relative to the SCE (0.95 V). This introduces an unknown but probably small (*ca.* ± .05 V) systematic error into the numbers. We note that the difference between the potentials of the aqueous SCE and ferrocene/ferrocenium in acetonitrile has been reported to be 0.40 V.[20]

## Results

The EA measurements are listed in Table 1 and summarized in the ladder illustrated in Figure 1. The reference electrophiles

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and the metalloporphyrins are listed in order of decreasing EA, as determined in the study. An arrow points down from a reference electrophile to a metalloporphyrin found to have a lower EA in the competitive electron transfer studies described above. An upward pointing arrow connects a reference electrophile to a metalloporphyrin of higher EA, as determined by competitive electron transfer. A double-headed arrow connects two species for which equilibrium was observed in competitive charge transfer. The overall consistency of the charge-transfer studies is clearly evident from the ladder.

In addition to the EAs Table 1 lists the condensed-phase reduction potentials for $\mathrm{FeTPP^iCl}$ (Fe(III) to Fe(II)) and for $\mathrm{FeTPP^i}$ (Fe(II) to Fe(I)). For some of the species the reduction potentials have yet to be obtained because of the insufficient material, insufficient purity, or insufficient solubility. It is evident from Table 1 that the electron affinities and the reduction potentials vary together. The electron affinities are plotted against the reduction potentials in Figure 1. The Fe(II) to Fe(I) reduction potentials vary approximately linearly with the electron affinities of the neutral halogenated FeTPP. The data for Ni(II) to Ni(I) reduction potentials and the corresponding electron affinities from our earlier study fall approximately on the same line. The Fe(III) to Fe(II) reduction potentials vary approximately linearly with the $\mathrm{FeTPP^iCl}$ electron affinities, but the line through the III–II data is not collinear with the line through the II–I data. Several of the Fe(III) porphyrins are more easily reduced in solution than would be expected from the gas-phase electron affinities. This suggests that reduction of the Fe(III) species is mediated by some solvent effect. The solvent effect also decreases the range of reduction potentials for Fe(III) species (0.50 V) relative to the range of their electron affinities (1.25 eV).

Finally we note that for those cases for which we have the III–II reduction potential, the EA, and the catalytic activity all three quantities are listed in Table 1.

## Discussion

**Reduction Potentials and EAs.** The comparison between gas-phase electron affinities and the solution reduction potentials of neutral electrophiles has been the subject of recent studies by Heinis *et al.*,[21] by Shalev and Evans,[20] and by Richardson.[22] We follow their lead and discuss the comparison in terms of the standard thermodynamic cycle:

$$\begin{tikzcd}
\mathrm{FeTPP^i(g)} + \mathrm{e(g)} \arrow[r, "\Delta G^\circ_a"] \arrow[d, "\Delta G_{solv}^\circ(\mathrm{FeTPP^i})"] & \mathrm{FeTPP^{i-}(g)} \\
\mathrm{FeTPP^i(s)} + \mathrm{e(g)} \arrow[r, "\Delta G^\circ_r"] & \mathrm{FeTPP^{i-}(s)} \arrow[u, "\Delta G_{solv}^\circ(\mathrm{FeTPP^{i-}})"']
\end{tikzcd}$$

From this cycle it follows that

$$\Delta G^\circ_a = \Delta G^\circ_r + \Delta G_{solv}{}^\circ(\mathrm{FeTPP^i}) - \Delta G_{solv}{}^\circ(\mathrm{FeTPP^{i-}}) \quad (1)$$

The free energy of electron attachment ($\Delta G^\circ_a$) is approximately the negative of the EA. The free energy of reduction of the neutral halogen substituted Fe(II) porphyrin ($\mathrm{FeTPP^i}$) in solution by a gas-phase electron ($\Delta G^\circ_r$) is the negative of the standard electrode potential ($E^\circ$) of the $\mathrm{FeTPP^i/FeTPP^{i-}}$ couple plus a constant ($C$) which depends on the reference electrode. Equation 1 can thus be recast to give

$$\mathrm{EA} = E^\circ + \Delta\Delta G_{solv}{}^\circ + C \quad (2)$$

where the difference ($\Delta\Delta G_{solv}$) between the solvation free energy of $\mathrm{FeTPP^{i-}}$ and that of $\mathrm{FeTPP_i}$ is given by

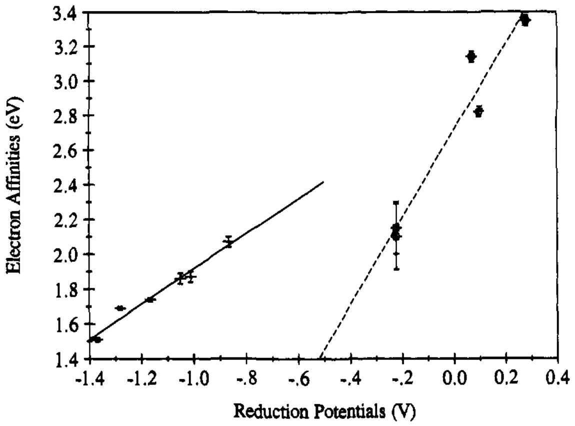

**Figure 2.** Gas-phase electron affinities (EA) vs reversible half-wave one-electron reduction potentials ($E_{1/2}$) of metalloporphyrins. The data points marked with an open square are Fe(III)/Fe(II) potentials and EAs of species with an axial chloride. The remaining points are Fe(II)/Fe(I) potentials and EAs of Fe(II) species. The solid line is a fit to data for M(II) species and the dashed line to the M(III) species.

$$\Delta\Delta G_{solv} = \Delta G_{solv}{}^\circ(\mathrm{FeTPP^{i-}}) - \Delta G_{solv}{}^\circ(\mathrm{FeTPP^i}) \quad (3)$$

Hence, the fact that a plot of the reduction potentials vs the electron affinities of the Fe(II) and Ni(II) species is linear with a slope near unity (1.05) as shown in Figure 2 indicates that $\Delta\Delta G_{solv}{}^\circ$ for those species are all nearly the same. The larger slope of the line through the data for the Fe(III) species indicates that $\Delta\Delta G_{solv}{}^\circ$ for these species depends on the ligand.

The degree of charge delocalization in the anion can be important in determining $\Delta\Delta G$. If the charge is more delocalized, the average distance of interaction between the solvent and the charge is increased. The addition of electron-withdrawing halogen substituents to the ligand could, of course, increase charge delocalization in the anion, giving rise to the observed solvent dependent $\Delta\Delta G_{solv}{}^\circ$. This effect could make it relatively difficult to reduce the heavily halogenated **5**-Cl, **7**-Cl, and **8**-Cl, since the corresponding anions would have delocalized charge not strongly stabilized by the solvent.

The magnitude of the delocalization required to account for the observed potentials of the heavily halogenated species can be estimated by assigning a value to $C$ in eq 2 and calculating $\Delta\Delta G$ for a given ion–neutral couple. If we then assume that $\Delta\Delta G$ is equal to the Born energy of the solvated ion, we can estimate an effective radius, $r_e$, for the ion by rearranging eq 2 to give

$$\mathrm{EA} - E^\circ - C = \Delta\Delta G_{solv} = \frac{-e^2(1 - 1/\epsilon)}{2r_e} \quad (4)$$

where e is the ion charge and $\epsilon$ is the solvent dielectric constant. We follow the lead of Heinis et al.,[20] and we assign $C = 4.71$ eV for the aqueous SCE and find values for $r_e$, listed in Table 1.

All but two of the $r_e$ values are in the range 3.2–3.7 Å. The two exceptional $r_e$ values are 2.5 Å for **1**-Cl and 2.7 Å for **2**-Cl. A simple explanation that suggests itself for this grouping of the values is that the larger $r_e$ values result from adding the electron to a ligand-based LUMO and the smaller $r_e$ values result from adding an electron to a metal-based LUMO. The exceptional $\mathrm{FeTPP^i}$ species have an axial Cl ligand and either no halogenation of the ligand (**1**-Cl, FeTPPCl) or only partial halogenation of the ligand's phenyl substituents (**2**-Cl, $\mathrm{FeTPPoCl_8Cl}$). The result is to lower the energy of vacant metal-based orbitals relative to the energy of vacant ligand orbitals.

These results show the extent to which reduction potentials of neutral electrophiles reflect properties other than the intrinsic electronegativity of the electrophile. In combination with the other measured properties, such as the EA, the reduction potentials yield useful information on a variety of molecular properties. On

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(21) Heinis, T.; Chowdury, S.; Scott, S. L.; Kebarle, P. *J. Am. Chem. Soc.* **1988**, *110*, 400–407.

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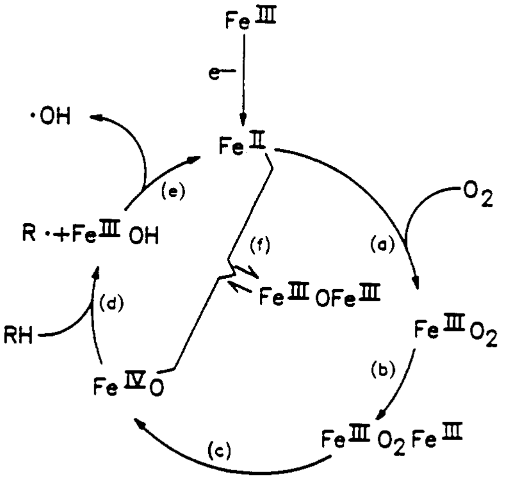

**Figure 3.** Postulated mechanism of the metalloporphyrin-catalyzed air oxidation of alkanes from ref 5. Dioxygen first adds to the reduced catalyst (a). The resulting dioxo species reacts with a second molecule of catalyst (b), giving two molecules of mono-oxo complex (c), which oxidizes the alkane (d and e). The mono-oxo complex equilibrates with reduced catalyst to give the inactive oxo dimer (f).

the other hand, the gas-phase EA provides a more direct measure of the intrinsic molecular electrophilicity. The EA thus provides a basis for any correlation between reactivity and electrophilicity.

**Catalytic Activity.** A mechanism proposed for the metalloporphyrin-catalyzed oxidation of 3-methylpropane to *tert*-butyl alcohol is shown schematically in Figure 3.[5] Overall reaction velocity will be maximized if equilibrium in

$$(\mathrm{FeTPP^i})_2\mathrm{O} \rightleftharpoons (\mathrm{FeTPP^i})\mathrm{O} + \mathrm{FeTPP^i} \qquad (5)$$

favors the active $(\mathrm{FeTPP^i})\mathrm{O}$ species and minimizes the amount of catalyst tied up as the inactive mono-oxo dimer. We suggest that as the electron-withdrawing capacity of the porphyrin increases, two effects ensue. First the stability of $\mathrm{FeTPP^i}$ relative to the oxo dimer increases, and second, the reactivity of $(\mathrm{FeTPP^i})\mathrm{O}$ toward substrate increases. The first effect increases the equilibrium constant for eq 5, and the second decreases the steady-state concentration of $(\mathrm{FeTPP^i})\mathrm{O}$.

The forward reaction is a redox disproportionation reaction in which two Fe(III) centers become an Fe(II) and an Fe(IV) and will be favored to the extent that Fe(II) is stabilized with respect to Fe(III). Catalytic activity does increase with the stability of Fe(II) relative to Fe(III), as shown by the correlation between catalytic activity and the EAs and reduction potentials of Fe(III) catalysts. Of course, the halogenation that stabilizes Fe(II) might be expected to destabilize Fe(IV) and hence push the equilibrium of eq 5 to the left toward the unreactive dimer. We surmise from a previous study,[23] however, that halogenation increases the reactivity of the mono-oxo Fe(IV) species toward substrate, pulling the equilibrium to the right by diminishing the steady-state concentration of $\mathrm{Fe(TPP^i)O}$.

The previous study in question[23] showed that the reaction

$$\mathrm{Fe(TPP^i)^+} + \mathrm{NO_2} \rightarrow \mathrm{Fe(TPP^i)O^+} + \mathrm{NO} \qquad (6)$$

proceeds at an observable rate ($k > 10^{-12}$ cm$^3$ s$^{-1}$) for $\mathrm{Fe(TPP^i)}$ = **1**, **2**, **4**, and **5**, while **3**$^+$ was reported not to react at an observable rate. The failure of **3**$^+$ to react was attributed to the coordination of the tethered imidazole to the metal.[24] We have subsequently been able to examine the behavior of **6**$^+$ and **8**$^+$ and find that these highly halogenated species do not react at an observable rate. This suggests that D(FeO) is diminished by a porphyrin ligand with electron-withdrawing substituents, particularly if the metal is in a high oxidation state. Hence as halogenation increases, the mono-oxo product of eq 6 becomes more like the reactive $\mathrm{FeO^{\bullet}}$ and less like stable Fe=O, substantiating our assertion above that the reactivity of the mono-oxo Fe(IV) intermediate in the catalytic cycle increases with halogenation.

Whether it be the stabilization of the $\mathrm{FeTPP^i}$ relative to $\mathrm{FeTPP^i{}_2O}$, the activation of $\mathrm{FeTPP^iO}$, or some other effect, the catalytic activity of the halogenated iron porphyrins increases with their electrophilicity, as measured by their gas-phase EA. Analysis of the reduction potentials of the neutral Fe(III) complexes reveals that the electron affinities provide a better measure of intrinsic electrophilicity than the electrochemical measurements.

Correlation of the limited data on reactivity with electron affinities is better than with reduction potentials. Assuming a linear free energy type of relationship (ln(TON) proportional to EA), we would predict from the reactivity of **5** and **8** a very low TON (*ca.* 150) for the unreactive **1**. A similar extrapolation based on the reduction potentials would predict a much higher reactivity of **1** (TON *ca.* 600). We suggest on the basis of the present admittedly limited set of results that other effects of halogenation, such as steric effects, should emerge from the base line of electronic effects most clearly if electron affinities are used to measure electrophilicity. Attempts to generate more extensive data are underway in our laboratories.

**Acknowledgment.** Dennis Evans is acknowledged for helpful discussions. The Sun Co., the Delaware Research Partnership, the Morgentown Energy Technology Center of the Department of Energy, and the Gas Research Institute are acknowledged for financial support.

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[24] Chen, H. L.; Hagan, T. E.; Groh, S. E.; Ridge, D. P. *Org. Mass Spectrom.* **1991**, *26*, 173–174.