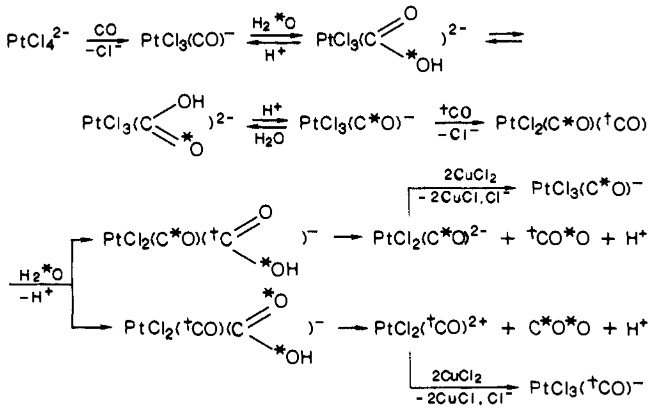
Scheme II



ports the notion that half the carbon dioxide is derived from gaseous CO and the other half from $PtCl_3(CO)^-$. In addition, the isotopic distribution data exhibit a significant difference in ^{18}O content between $^{13}CO_2$ and $^{12}CO_2$. The values of n, obtained from the ^{18}O isotopic distribution data and eq 15 and 16, are 0.99 for $^{13}CO_2$ and 2.15 for $^{12}CO_2$, respectively. These results again lead us to conclude that the CO group in $PtCl_2(CO)_2$ originally from $PtCl_3(CO)^-$ is sufficiently long-lived to reach complete isotopic equilibrium with water before attack by water. On the contrary, the carbonyl group derived from the gaseous CO in the dicarbonyl species does not exchange oxygen with water at all, presumably due to the irreversible attack of water at $PtCl_2(CO)_2$. For comparison the calculated n values based on this model are 1.02 and 1.90 for $^{13}CO_2$ and $^{12}CO_2$, respectievly. The results obtained from this double-labeling experiment may be summarized according to eq 21.

$$PtCl_4^{2-} \xrightarrow[-Cl^-]{CO} PtCl_3(CO)^- \xrightarrow[H_2{}^{18}O]{^{13}CO} {}^{13}CO^{18}O + C^{18}O^{18}O \ (1:1) \qquad (21)$$

Mechanism. The labeling studies described in this paper have uncovered detailed mechanistic information that is difficult to obtain by other methods for the oxidation of CO to CO_2 catalyzed by a $PtCl_4^{2-}$–CuCl–$CuCl_2$ system. On the basis of these results, a detailed mechanism for the catalytic reaction is proposed and is depicted in Scheme II. An interesting aspect of this mechanism is that $PtCl_3(CO)^-$ undergoes oxygen scrambling with water rapidly with negligible decomposition to give carbon dioxide, but the reverse is true for $PtCl_2(CO)_2$. The divergence in the rate of decarboxylation for the two platinum species may be understood in terms of the difference in ability to stabilize low oxidation state metal complexes between a carbonyl group and a chloride ligand. The decarboxylation of $PtCl_3(COOH)^{2-}$ (eq 22) is not favored

$$PtCl_3(COOH)^{2-} \rightarrow PtCl_3{}^{3-} + CO_2 + H^+ \qquad (22)$$

$$PtCl_2(CO)(COOH)^- \rightarrow PtCl_2(CO)^{2-} + CO_2 + H^+ \qquad (23)$$

because of the inability of Cl^- to stabilize Pt(0) in the presumed product of $PtCl_3{}^{3-}$. On the other hand, the presence of a carbonyl group in $PtCl_2(CO)(COOH)^-$ facilitates the decarboxylation of the species (eq 23) by decreasing the electron density in the transition state through back-donation. The recent results of an investigation[19] of the stability of hydroxycarbonyl complexes are in accord with our observation that strong π-acid ligands accelerate decomposition to give CO_2.

Conclusion

The results of our ^{13}C labeling study have unambiguously established that $PtCl_2(CO)_2$ is the species that reacts with water to give CO_2 in the present catalysis even though the dicarbonyl is not directly observed. In addition, the ^{18}O and double-labeling experiments have shown that the two structurally equivalent, but historically different carbonyl groups in $PtCl_2(CO)_2$ may be distinguished. On reacting with water, one carbonyl gives CO_2 product of which all oxygens come from water, while the other carbonyl yields CO_2 with only one oxygen derived from water. The ^{13}C experiment appears to be a new and powerful method for determining the number of carbonyl groups in the active species, while ^{18}O and double-labeling experiments are very useful in elucidating the paths for CO_2 formation.

Acknowledgment. We thank the National Science Council of the Republic of China for support of this research.

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Nitrogen Atom Activation: The Influence of Porphyrin Ring Structure on the Kinetics of the Reaction of Trifluoroacetic Anhydride with Nitrido Manganese(V) Porphyrins

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Abstract: The kinetics of the reaction of (porphyrin)Mn(N) (where the porphyrin was octaethylporphyrin, Baldwin's capped porphyrin or one of several substituted tetraphenylporphyrins) with selected substituted acetic anhydrides to form the corresponding nitrenoid Mn porphyrin complex were determined under pseudo-first-order conditions. This reaction is the rate-determining first step in the nitrogen atom activation and transfer sequence that uses nitrido Mn porphyrins to convert olefins to the corresponding aziridines. The apparent rate constants, which varied over three orders of magnitude, were dependent upon porphyrin ring basicity, acetic anhydride substituent, and the steric environment about the nitrido–Mn reaction center.

The chemistry of high-valent metalloporphyrins has been actively pursued since the discovery that these materials are capable of oxidizing water.[1-3] Recently, workers in the field have focused their attention on the reactivity of oxo iron and oxo manganese porphyrins, models of the active site of cytochrome P-450.[4-12]

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0002-7863/88/1510-6748$01.50/0

From these studies, catalytic pathways involving oxygen atom transfer from high-valent oxo metalloporphyrins to olefins and paraffins have been elucidated.

Our efforts have centered on the study of the redox reactivity of nitrido metalloporphyrins where the central metal can be Fe,[13] Mn,[14] or Cr.[15] These high-valent metalloporphyrins are remarkable in their thermal, chemical, and redox stability as well as in their structural diversity.[13–22] Nitrido iron porphyrins are binuclear;[13,16–18,40] a single N atom bridges two equivalent Fe centers formally possessing a valence of 3.5. In contrast, the Mn and Cr complexes are mononuclear,[14,15,19–22] formally possessing a valence of 5. The Fe complexes can be electrooxidized in three, single-electron-transfer steps or electroreduced in three, single-electron-transfer steps with full retention of the binuclear structure.[13] These redox reactions produce changes in the valence of each Fe center as well as the charge on each porphyrin ring. The formal valence of each Fe in the Fe–N–Fe core ranges from IV–IV down to II–II. The mononuclear Cr and Mn complexes are also electroactive. Both can be electrooxidized or electroreduced in two, sequential single-electron-transfer steps.[14,15] But, unlike the binuclear Fe complex, all redox reactions are porphyrin ring centered.

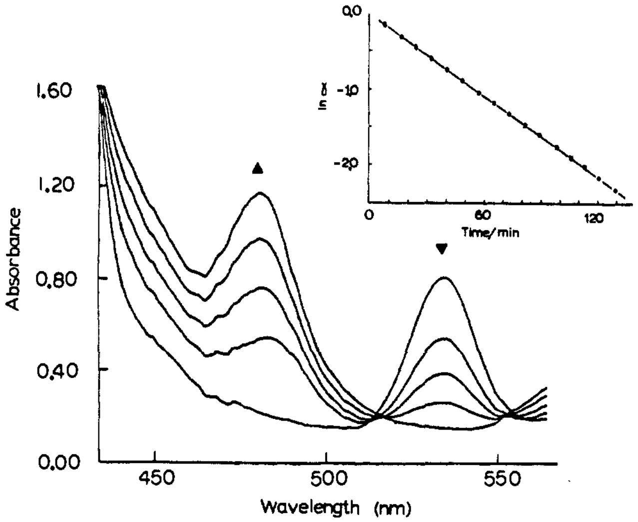

Figure 1. Electronic spectra acquired as a function of time after the addition of 20 μL of TFAA to 3.00 mL of 0.054 mM (4-methoxy-TPP)Mn(N) in 1,2-dichloroethane. This particular reaction reached completion in 120 min. The inset depicts a standard first-order analysis of the absorbance data as a function of time. α is the change in concentration of the reactant at any point in time computed from the change in absorbance at 479 and 538 nm.

Although the N≡Mn core is isoelectronic with O═Fe, the reactivity of (POR)Mn(N)[23] is dissimilar to that of (POR)Fe(O). The nitrido compound is an air-stable material[19–22] whereas the crystallization of the oxo iron complex has proven elusive. Buchler[20] has converted the nitrido group to a phosphine imide by refluxing (POR)Mn(N) in the presence of triphenylphosphine. Groves and Takahashi[19,22] have shown that the inert N≡Mn moiety can be activated at ambient temperature upon treatment of (2,4,6-trimethyl-TPP)Mn(N) with TFAA,[23] producing a nitrenoid Mn^{V} porphyrin complex. When this material is exposed to cyclooctene, the imidoacyl group of the nitrenoid porphyrin is transferred to the olefin, yielding 9-(trifluoroacetyl)-9-azabicyclo[6.1.0]nonane, the corresponding aziridine of cyclooctene. Present methods[24,25] for producing aziridines involve reagents and

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(23) Abbreviations used: saturated calomel electrode = SCE; 1,2-dichloroethane = EtCl$_2$; benzonitrile = PhCN; porphyrin dianion = POR; nitrido[*meso*-tetrakis(2,4,6-trimethoxyphenyl)porphinato]manganese(V) = (2,4,6-trimethoxy-TPP)Mn(N); nitrido[*meso*-tetrakis(2,6-dimethoxyphenyl)porphinato]manganese(V) = (2,6-dimethoxy-TPP)Mn(N); nitrido[*meso*-tetrakis(2,4-dimethoxyphenyl)porphinato]manganese(V) = (2,4-dimethoxy-TPP)Mn(N); nitrido[*meso*-tetrakis(2-methoxyphenyl)porphinato]manganese(V) = (2-methoxy-TPP)Mn(N); nitrido[*meso*-tetrakis(4-methoxyphenyl)porphinato]manganese(V) = (4-methoxy-TPP)Mn(N); nitrido[*meso*-tetrakis(2,4,6-trimethylphenyl)porphinato]manganese(V) = (2,4,6-trimethyl-TPP)Mn(N); nitrido[*meso*-tetrakis(4-methylphenyl)porphinato]manganese(V) = (4-methyl-TPP)Mn(N); nitrido(phenylporphinato)manganeses(V) = (TPP)Mn(N); nitrido[*meso*-tetrakis(4-chlorophenyl)porphinato]manganese(V) = (4-chloro-TPP)Mn(N); nitrido[*meso*-tetrakis(2,6-dichlorophenyl)porphinato]manganese(V) = (2,6-dichloro-TPP)Mn(N); nitrido(octaethylporphinato)manganese(V) = (OEP)Mn(N); nitrido(5,10,15,20-pyromellitoyltetrakis(*o*-(oxyethoxy)phenyl)porphinato)manganese(V) = (C$_2$Cap)Mn(N); trifluoroacetic anhydride = TFAA; trichloroacetic anhydride = TCAA; dichloroacetic anhydride = DCAA; chloroacetic anhydride = MCAA; acetic anhydride = AA; ferrocene = Fc.

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conditions that often reduce other functional groups on the molecule. The nitrogen atom transfer route would provide a straightforward means for introducing the aziridine moiety and avoid these unwanted side reactions. This reaction, if generalized, would find widespread synthetic utility.

Our preliminary investigation[14a] into the reaction sequence

$$\mathrm{(POR)MnN + F_3C{-}C(O){-}O{-}C(O){-}CF_3 \rightarrow \{(POR)Mn(NC(O)CF_3)\}^+\{O(O)CCF_3\}^-} \quad (1)$$

$$\mathrm{\{(POR)Mn(NC(O)CF_3)\}^+\{O(O)CCF_3\}^- + olefin \rightarrow (POR)Mn(OC(O)CF_3) + aziridine} \quad (2)$$

showed that the rate of formation of the nitrenoid Mn porphyrin (reaction 1) was not significantly affected by the presence of olefin in the reaction mixture. This finding implied that the formation of the nitrenoid was rate determining. Thus, we focused our attention on determining the important factors governing the production of the nitrenoid Mn porphyrin. We viewed this as an important first step in generalizing the nitrogen atom transfer sequence. In this account, we demonstrate that the rate of formation of the nitrenoid Mn porphyrin is markedly dependent upon the basicity of the porphyrin ring and the steric environment about the N≡Mn moiety.

Experimental Section

Chemicals. All sterically unencumbered Mn porphyrins used herein were prepared by the method of Adler.[27] Since yields less than 1% were obtained for the 2,6-disubstituted porphyrins, repeated preparations were necessary to collect sufficient quantities of material for this study. The following nitrido Mn(V) porphyrins were prepared from the corresponding Mn(III) porphyrins by the method of either Buchler[20] or Takahashi:[19] (2,4,6-trimethoxy-TPP)Mn(N), (2,6-dimethoxy-TPP)Mn(N), (2,4-dimethoxy-TPP)Mn(N), (2-methoxy-TPP)Mn(N), (4-methoxy-TPP)Mn(N), (2,4,6-trimethyl-TPP)Mn(N), (4-methyl-TPP)Mn(N), (TPP)Mn(N), (4-chloro-TPP)Mn(N), (2,6-dichloro-TPP)Mn(N), and (OEP)Mn(N). The free base form of Baldwin's capped porphyrins was synthesized and purified by the method of Almog et al.[28] Manganese was inserted into the free base by the method of Bruice.[4] The purity of all porphyrinic materials was verified by UV–vis, NMR, and mass spectral measurements.

Apparatus. The electrochemical instrumentation and techniques were identical with those previously reported.[26] Experiments were carried out at ambient temperature (21 ± 1 °C). Unless otherwise noted, all solutions were deoxygenated with solvent saturated nitrogen and blanketed with nitrogen during all experiments. All electrochemical experiments were carried out with an SCE[23] as the reference electrode. The potentials reported herein are referenced to the $\mathrm{Fc^+/Fc}$[23] redox couple (present in solutions as an internal standard) to correct for day-to-day variations in liquid junction potentials. The EPR experiments were performed on a Varian E3 spectrometer. UV–vis spectra were acquired with a Tracor-Northern Model 1710 diode array rapid scanning spectrometer. Kinetic measurements were obtained in a septum-sealed three-port Pyrex cuvette. Aliquots of the substituted acetic anhydrides were delivered into the cuvette via syringe.

Results

Groves and Takahashi[19,22] have previously shown that the nitrido moiety on (2,4,6-trimethyl-TPP)Mn(N) is activated upon reaction with TFAA and forms a nitrenoid $\mathrm{Mn^V}$ species, $\mathrm{\{(2,4,6\text{-}trimethyl\text{-}TPP)Mn(NCOCF_3)\}^+\{OOCCF_3\}^-}$. The trifluoroacetate ion forms a coordinate covalent bond with the high-valent Mn center. We have found that this reaction is not specific to (2,4,6-trimethyl-TPP)Mn(N) but occurs with a variety of nitrido Mn porphyrins. The progress of this reaction may be monitored by voltammetry, by both NMR and EPR spectrometry, or by UV–vis and infrared spectrophotometry.

An example of the temporal dependence of the electronic spectrum of (4-methoxy-TPP)Mn(N) when treated with an excess of TFAA is given in Figure 1. The intense Soret band at 424 nm (not shown in Figure 1), characteristic of (POR)Mn(N) complexes, diminishes in intensity during the course of this reaction. The visible band at 538 nm is also reduced in intensity with a concomitant increase in a new band at 479 nm. The electronic spectrum of the nitrenoid is qualitatively similar to those normally encountered for π-cation radicals.[29] Similar changes in the electronic spectrum were obtained for all (POR)Mn(N) compounds investigated.

In contrast to the nitrido complex, the nitrenoid is paramagnetic. For (4-methyl-TPP)Mn(N), a single resonance at $g = 2.002$ is obtained when the EPR spectrum is acquired at ambient temperature and the nitrenoid is dissolved in $\mathrm{CH_2Cl_2}$. The intensity of this resonance is proportional to the concentration of porphyrin, the concentration of TFAA, and reaction time. Addition of cyclooctene to solution resulted in a rapid conversion of this spectrum into that obtained for $\mathrm{\{(4\text{-}methyl\text{-}TPP)Mn^{III}\}^+}$.

Nitrenoid formation was also monitored by voltammetry. In the absence of TFAA, the nitrido Mn porphyrins display four single-electron-transfer processes within the accessible potential window of the solvent-supporting electrolyte system. These redox reactions involve sequential single-electron oxidations or reductions of the porphyrin ring to form π-cation radicals and dications (at anodic potentials) and π-anion radicals and dianions (at cathodic potentials). Details of an electrochemical and spectroelectrochemical investigation of the nitrido Mn porphyrins have been published elsewhere.[14b] Upon addition of a 100-fold excess of TFAA, the currents associated with the stepwise oxidation of the nitrido Mn porphyrin decrease in intensity with a corresponding increase in two new oxidation processes. Cathodic discharge of TFAA obscured the observation of the sequential reduction processes. The current magnitudes relative to those of the corresponding (POR)Mn(N) complexes were dependent upon the porphyrin ring structure, the potential at which the sweep was initiated, and the potential sweep rate. Oxidation processes were observed at 1.03 and 1.32 V vs SCE for (OEP)Mn(nitrene) and at 1.06 and 1.41 V vs SCE for $\mathrm{(C_2Cap)Mn(nitrene)}$. Analysis of the data obtained on these two complexes by a variable potential sweep rate study inferred that both oxidations are single electron charge transfers with a preceding chemical reaction, the reversible addition of TFAA to the corresponding (POR)Mn(N) complex. Indeed, Groves and Takahashi[19,22] have observed the rapid self-exchange between these two species by NMR. We have confirmed this mechanism spectroelectrochemically. For the other compounds investigated, the equilibrium lies too far toward the reactant, (POR)Mn(N), to obtain well-defined oxidations of the nitrenoid complexes.

The vibrational spectrum of the nitrido Mn porphyrin is comparable to that observed for other metalloporphyrins. The metal–ligand vibration is a band of medium intensity, centered at 1045 ± 10 $\mathrm{cm^{-1}}$. Upon reaction with TFAA, new bands were observed at 1695 and 1743 $\mathrm{cm^{-1}}$. These vibrations correspond to the carbonyl stretch of trifluoroacetate and of the trifluoroacylimido group, respectively. It is interesting to note that although the electronic spectrum of the nitrenoid is qualitatively similar to those normally encountered for π-cation radicals, the vibration diagnostic of cation radicals[30] (between 1260 and 1290 $\mathrm{cm^{-1}}$) is absent in the IR spectrum of the product. Thus, we postulate that the formation of the nitrenoid does not involve a change in the formal valence of the Mn center. This assignment concurs with that originally made by Groves and Takahashi[22] for $\mathrm{\{(2,4,6\text{-}trimethyl\text{-}TPP)Mn(NCOCF_3)\}^+\{OOCCF_3\}^-}$ but now is generalized for all complexes studied herein.

The nitrenoid species are unstable and slowly degrade with time producing the corresponding $\mathrm{(POR)Mn^{III}}$. Consequently, attempts to isolate single crystals of the nitrenoid have been unsuccessful.[31]

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(31) The degradation does not appear to be enhanced by UV radiation nor is it consistent in rate. The reaction with $\mathrm{TBA^+OH^-}$ serves as an indicator of the extent of degradation. The nitrenoid is sufficiently stable to permit investigation of the kinetics of nitrido activation.

Table I. Apparent Rate Constants[a] for the Reaction of Nitrido Mn Porphyrins with TFAA

porphyrin	k_{app} ($s^{-1} \times 10^4$)	substituent constant[b]	$E_{1/2}$ (V vs Fc^+/Fc)
(2,4,6-trimethoxy-TPP)	2.3	−4.20	0.37
(2,6-dimethoxy-TPP)	1.5	−3.12	0.42
(2,4-dimethoxy-TPP)	3.2	−2.64	0.44
(2-methoxy-TPP)	1.0	−1.56	0.50
(4-methoxy-TPP)	2.7	−1.08	0.48
(2,4,6-trimethyl-TPP)	0.68	−0.204	0.51
(4-methyl-TPP)	1.4	−0.068	0.52
(TPP)	1.1	0.00	0.55
(4-chloro-TPP)	0.43	0.92	0.60
(2,6-dichloro-TPP)	0.033	1.60	0.72
(OEP)	8.7	na[c]	0.35
(C_2CAP)	40	na[c]	0.42

[a] Determined under pseudo-first-order conditions. See text for details. [b] Values taken from ref 39. [c] Not applicable.

However, the lifetimes of the nitrenoid species are long enough to permit the determination of the kinetics of formation reaction. Apparent rate constants, k_{app}, were determined from analysis of the temporal dependence of the absorbance of both the Soret and visible bands characteristic of the nitrido Mn porphyrin reactant. Kinetic determinations were carried out under first-order conditions, i.e., over the ranges 0.05 mM < [porphyrin] < 1.0 mM and 1.0 mM < [TFAA] < 1000 mM. These conditions were used in this study to enhance the rate of the reaction, avoid any complications due to degradation of the reaction product,[32] and minimize the contribution of any adventitious water which may have been present.[33] A typical data set, given in the inset of Figure 1, confirms the fit of the first model to the data. The value of k_{app} is derived from the slope of the line. Table I lists the k_{app} values obtained for each of the porphyrins investigated.

Nitrogen atom activation by reaction of (POR)Mn(N) with other anhydrides was investigated utilizing the limited series TFAA, TCAA, DCAA, MCAA, and AA and the porphyrin (OEP)Mn(N). The relative rate of reaction decreased in the order TFAA > TCAA > DCAA. The k_{app} values for TCAA and DCAA relative to that of TFAA were 0.56 and 0.16, respectively. The substituted anhydrides MCAA and AA were found to be unreactive with (OEP)MnN. The products of the reaction with TCAA and DCAA displayed electronic spectra virtually identical with those obtained from the reaction with TFAA.

Voltammograms acquired on the product gave two sequential oxidations at potentials shifted positively from those of the starting material. The magnitude of the potential shift for the first redox reaction of the nitrenoid (OEP)Mn relative to the potential of the corresponding redox reaction of (OEP)MnN was 262 mV for TFAA, 250 mV for TCAA, and 214 mV for DCAA. Similarly, the potential of the second redox process of the nitrenoid (OEP)Mn relative to the potential of the corresponding redox reaction of (OEP)MnN shifted 135 mV for TFAA, 103 mV for TCAA, and 75 mV for DCAA. Thus, the potential shift magnitude was dependent upon anhydride structure and decreased in the same order as the k_{app}. However, when (C_2Cap)Mn(N) was used as the porphyrin, the potential of both redox reactions shifted positively by 250 mV and the potential shifts were independent of anhydride structure.

Discussion

From the rate data presented in Table I, several inferences can be drawn. The first involves the stereochemistry of (C_2Cap)-Mn(N). The nitrido moiety can potentially be located under the cap or opposite the cap relative to the Mn–pyrrole nitrogen core. In the former case, the reaction rate should be significantly decreased relative to that of the unhindered porphyrins. In the latter case, the observed reaction rate should be comparable to that observed for porphyrins with similar phenyl ring substituents. Since the observed reaction rate for (C_2Cap)Mn(N) is two orders of magnitude greater than (o-OCH_3TPP)Mn(N), we conclude that the nitrido moiety on (C_2Cap)Mn(N) is located opposite the cap.

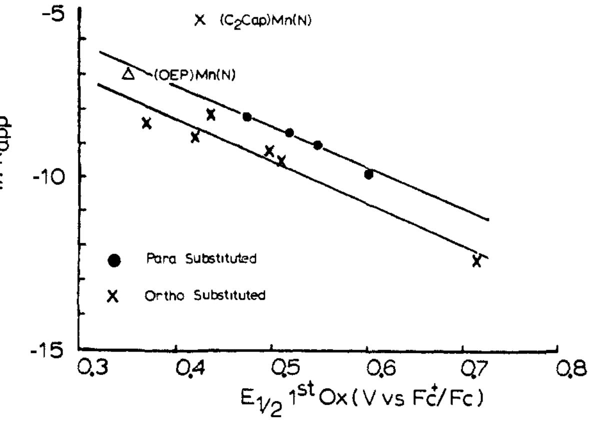

Figure 2. Plot of ln k_{app} vs $E_{1/2}$ of the first oxidation of the corresponding (POR)Mn(N) referenced to the Fc^+/Fc couple present as an internal standard. The circles denote values obtained for (para-substituted TPP)Mn(N), crosses denote values obtained for (ortho-substituted TPP)Mn(N) or the (ortho- and para-substituted TPP)Mn(N), and the triangle denotes the value obtained for (OEP)Mn(N).

Second, qualitative examination of the k_{app} values listed in Table I reveals that the reaction rate varies directly with porphyrin ring substituent. The k_{app} values for both the para-substituted and ortho-substituted porphyrins decrease with increasing Hammett–Taft substituent constant. However, the k_{app} values for the para-substituted porphyrins are somewhat greater than those for the ortho-substituted porphyrin with comparable Hammet–Taft substituent constants. This concurs with our expectations. It has also been well established that the phenyl rings of the TPP family rapidly rotate at ambient temperatures.[34] Optimal induction occurs when the phenyl rings are oriented coplanar with the porphyrin macrocycle establishing good π-overlap. Bulky ortho substituents hinder this rotation and, consequently, reduce the inductive effect of a particular substituent.

The use of Hammett–Taft linear free energy relationships permits comparisons, but only within the TPP family. In an effort to permit a more quantitative comparison of the influence of porphyrin ring structure on the observed reaction rates, the ln k_{app} was plotted against the half-wave potential for the oxidation of the corresponding (POR)Mn(N), as depicted in Figure 2. The rationale behind our construction of such a plot and the subsequent interpretation is as follows. For sterically unencumbered porphyrins, redox potentials for charge-transfer reactions involving the porphyrin ring have been correlated with Hammett–Taft substituent constants.[35] Porphyrin ring basicity has also been correlated with Hammett–Taft substituent constants.[36] Since the site of charge transfers involving (POR)Mn(N) occurs exclusively at the porphyrin ring, the oxidation potential can be used as a measure of porphyrin ring basicity. In this way, the inductive effects of a variety of porphyrin ring structures can be compared.

Two separate but linear relationships can be discerned from Figure 2. Although the data set is limited, ln k_{app} for both the

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[32] Groves and Takahashi have shown that (2,4,6-trimethyl-TPP)Mn(N) is regenerated by addition of TBA^+OH^- to a solution containing $\{(2,4,6\text{-trimethyl-TPP})Mn(NCOCF_3)\}^+\{(OOCCF_3)\}^-$. We utilized this reaction as a test of significant nitrenoid decomposition. Kinetics analyses were performed on absorbance data only when the reactant could be quantitatively regenerated by treatment with TBA^+OH^-.

[33] Any traces of water present in the reaction mixture would quantitatively react with TFAA and produce 2 equiv of trifluoroacetic acid. We verified that (POR)Mn(N) was unreactive to trifluoroacetic acid, even at molar ratios of acid to porphyrin of up to 1000.

[34] (a) Gottwald, L. K.; Ullman, E. F. *Tetrahedron Lett.* **1969**, 3071. (b) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 3660–3666 and references therein.

[35] Kadish, K. M. *Prog. Inorg. Chem.* **1987**, *34*, 435 and references therein.

[36] Bottomley, L. A.; Olson, L.; Kadish, K. M. In *Electrochemical and Spectrochemical Studies of Biological Redox Components*; Kadish, K. M. Ed.; American Chemical Society: Washington, DC, 1982; Chapter 13 and references therein.

para-substituted and ortho-substituted porphyrins correlate reasonably well with half-wave potential. Within experimental error, both slopes are equivalent. This confirms that the inductive effect of phenyl ring substituents is an important factor governing the rate of nitrogen atom activation and is in accord with expectations. The nitrenoid formation reaction involves nucleophilic attack of the N≡Mn moiety on the electron deficient carbonyl carbon of TFAA. Thus, increasing the basicity of the porphyrin ring should increase the nucleophilic character of the N≡Mn core and increase the rate of the reaction. Since the intercept for the ortho-substituted porphyrins is less than that for the para-substituted porphyrins, a significant steric effect is indicated. The OEP macrocycle is more basic than the TPP macrocycle. Interestingly, the k_{app} value for (OEP)Mn(N) lies near the trace through the para-substituted tetraphenylporphyrins, yet the OEP macrocycle is devoid of the phenyl substituents at the meso positions. This implies that the apparent steric effect observed within the TPP family (between ortho-substituted and para-substituted TPP's) is generated exclusively by the ortho substituent on the phenyl rings.

Ortho-substituted nitrido Mn tetraphenylporphyrins possess six interconvertable atropisomers. The least sterically hindered atropisomer would have all four o-OCH_3 groups oriented anti to the nitride. By using the nomenclature usually employed for porphyrins that exhibit atropisomerism, this would be the β,β,β,β isomer.[34,37] The most sterically hindered atropisomer would have all four o-OCH_3 groups oriented syn to the nitride, i.e., the $\alpha,\alpha,\alpha,\alpha$ isomer. The anticipated rate of nitrenoid formation for (o-OCH_3TPP)Mn(N) would be less than that of another porphyrin with comparable basicity but without ortho substituents. The decrease reflects the additional time required for the molecule to achieve the favored conformation by the rotation of one or more phenyl rings. Substituted tetraphenylporphyrins with relatively small ortho substituents are known to isomerize at ambient temperature and at rates comparable to or greater than the observed rates for the nitrenoid formation.[34,37] Statistically, 6.25% of the molecules of (o-OCH_3TPP)Mn(N) should be in the favored conformation, the β,β,β,β atropisomer, at any point in time. If one views the cap functionality on (C_2Cap)Mn(N) strictly as a molecular device to prevent isomerization of the β,β,β,β atropisomer, then the observed reaction rate for (o-OCH_3TPP)Mn(N) should be 6.25% of that observed for (C_2Cap)Mn(N). If more than one atropisomer is capable of reaction, then the relative reaction rate for (o-OCH_3TPP)Mn(N) should increase. The observed reaction rate for (o-OCH_3TPP)Mn(N) is 2.7% of that observed for (C_2Cap)Mn(N). This infers that only one atropisomer is undergoing reaction. On the other hand, if the relative rate for (o-OCH_3TPP)Mn(N) is less than that predicted from statistical considerations, then what other factor(s) is responsible for the increased rate of (C_2Cap)Mn(N) relative to that of (o-OCH_3TPP)Mn(N)? Perhaps the increase in rate is due to the greater accessibility of the N≡Mn core. From single-crystal X-ray diffraction studies on (C_2Cap)Fe(Cl),[38] the presence of the cap is known to ruffle the porphyrin. If the same extent of ruffling of the porphyrin observed for (C_2Cap)Fe(Cl) is also present in (C_2Cap)Mn(N), then the N≡Mn core in the capped porphyrin is displaced even further from the mean porphyrin plane as compared to porphyrins without the steric superstructure. This displacement results in a more accessible reaction center.

The last inference derives from the study of anhydride structure on the rate of formation and oxidation potential of the nitrenoid species. The k_{app} values for anhydride addition to (OEP)Mn(N) and the magnitudes of the potential shifts for the redox reactions of the nitrenoid (OEP)Mn relative to that of (OEP)MnN increased in the order DCAA < TCAA < TFAA. This order parallels the electron-withdrawing ability of the anhydride substituents on the α-carbon and is consistent with the proposed mechanism of nucleophilic attack by the nitride on the electron-deficient carbonyl carbon. Interestingly, the potentials for oxidation of the nitrenoid were dependent on anhydride structure with OEP but not for C_2Cap. We believe that this disparity is due to differences in the coordination sphere about the central Mn atom. For the nitrenoid OEP complex, the Mn core is six-coordinate; the substituted acetate ion is bound trans to the acyl moiety in a coordinate-covalent fashion. Since this change significantly alters the porphyrin to Mn π-orbital interactions, significant changes in the potentials for porphyrin ring centered oxidations are observed. However, in the Mn nitrenoid complex of the capped porphyrin, the Mn core is five-coordinate; the substituted acetate ion is prevented from forming a coordinate-covalent interaction with the Mn center by the presence of the pyromellitoyl cap. The Mn atom is out of the porphyrin plane and changes in the electron-withdrawing ability of the substituted acetate ion do not induce any changes in the porphyrin to Mn π-orbital interactions. The substituted acetate ion serves only as an ion pairing agent, with minimal influence on the observed oxidation potentials, at least in the medium investigated.

In summary, the rate of nitrenoid formation and, consequently, the rate of nitrogen atom transfer from nitrido Mn porphyrins to olefins is markedly dependent upon the basicity of the porphyrin ring and upon the steric environment of the nitrido Mn porphyrin reactant. In this study, we have shown that the rate of nitrenoid formation can be varied over three orders of magnitude through appropriate selection of the porphyrin ring structure. Porphyrins with strongly electron-donating substituents enhance the rate of nitrenoid formation. This trend is opposite to that observed for oxygen atom transfer reactivity of high-valent oxo Fe and oxo Mn porphyrins. The highest rates observed for nitrogen activation were with the (C_2Cap)Mn(N) complex. These rates were close to those required for use of high-valent nitrido Mn porphyrins as aziridine synthons. However, the synthetic complexity in preparing the capped porphyrin will be prohibitive. We are currently using the (OEP)Mn(N) complex exclusively to probe the kinetics and stereochemistry of the nitrogen atom transfer step with a variety of olefins. Also, we are extending our investigations to other macrocyclic systems that possess higher basicities than the porphyrins investigated herein and that possess the appropriate ring structure to force the Mn core from the center of the macrocyclic plane. In this manner, we hope to find a high-valent Mn macrocyclic complex with which we can probe the mechanism of the activation and atom transfer sequence. These findings should permit us to select the "optimum" nitrido Mn macrocycle for generalization of nitrogen atom transfer chemistry.

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(39) Zuman, P. *Substituent Effects in Organic Polarography*; Plenum: New York, 1967.

(40) **Note Added in Proof**: Nakamoto has very recently found spectroscopic evidence for the existence of mononuclear nitridoiron(V) porphyrins (*J. Am. Chem. Soc.* **1988**, *110*, 4044–4045).