Ltd. for their loan of K_2PtCl_4. C. Elie is thanked for recording CD spectra.

Registry No. d(T-C-T-C-G-T-G-T-C-T-C), 94891-00-6; *cis*-$PtCl_2(NH_3)_2$, 15663-27-1.

Department of Chemistry
Gorlaeus Laboratories
State University Leiden
2300 RA Leiden, The Netherlands

Jeroen H. J. den Hartog
Cornelis Altona
Hans van den Elst
Gijs A. van der Marel
Jan Reedijk*

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Oxygen Donation to Manganese(III) Tetraphenylporphyrin Chloride. Low Reactivity of Hydroperoxides as Oxygen Donors to Manganese(III) Porphyrins

Sir:

Modeling of peroxidases and cytochromes P-450 have focused on the preparation of high-valent oxometalloporphyrins as the active intermediates in catalytic oxidations. For this purpose (tetraphenylporphinato)iron(III) chloride ($ClFe^{III}TPP$) has been used with the "oxene" donors PhIO,[1] percarboxylic acids,[2,3] hydroperoxides,[3] *N*,*N*-dimethylaniline *N*-oxides,[4] and oxaziridines.[5] These studies have been logically extended to $ClCr^{III}TPP$ and $ClMn^{III}TPP$ salts. A puzzling observation is that, although $ClFe^{III}TPP$, $ClCr^{III}TPP$, and $ClMn^{III}TPP$ appear to be roughly comparable catalysts for oxidations involving PhIO and *m*-$ClC_6H_4CO_3H$, $ClMn^{III}TPP$ is at best a very poor catalyst with alkyl hydroperoxide.[3,6] We show in this paper that the low reactivity of $ClMn^{III}TPP$, compared with $ClFe^{III}TPP$ and $ClCr^{III}TPP$, with alkyl hydroperoxides is due to its much greater sensitivity to the acidity of the leaving group (YOH) as evidenced by Brønsted β_{1g} values.

The kinetics of the reaction of percarboxylic acids and hydroperoxides with $ClMn^{III}TPP$ were studied in dried benzonitrile under anaerobic conditions at 30 °C. From past experience,[7] benzonitrile has proven to be a solvent of choice for studies of oxygen transfer to manganese(III) porphyrin salts. Reactions were carried out under the conditions of 50–400 turnovers of metalloporphyrin. The concentration range of $ClMn^{III}TPP$ and of oxygen donor was chosen on the basis of the reactivity of the latter. The higher valent oxomanganese porphyrin species was trapped with 2,4,6-tri-*tert*-butylphenol (TBPH),[8] and the reactions were followed by monitoring the increase in absorbance of 2,4,6-tri-*tert*-butylphenoxy radical (TBP·) at 630 nm (eq 1). Formation

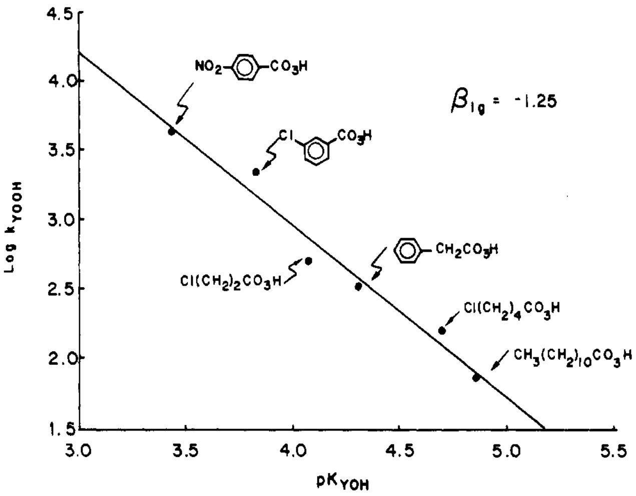


Figure 1. Plot of the log of the second-order rate constants (k_{YOOH}) for the reaction of $ClMn^{III}TPP$ with percarboxylic acids (YOOH) vs. pK_a of the carboxylic acid leaving groups (pK_{YOH}).

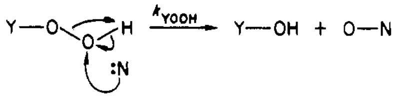
$$YOOH + ClMn^{III}TPP \xrightarrow[slow]{k_{YOOH}} YOH + O{=}Mn^{V}(Cl)TPP$$

$$2TBPH + O{=}Mn^{V}(Cl)TPP \xrightarrow{fast} 2TBP\cdot + H_2OMn^{III}(Cl)TPP \quad (1)$$

$$H_2OMn^{III}(Cl)TPP \xrightarrow{fast} H_2O + ClMn^{III}TPP$$

of TBP· was found to follow the first-order rate law at all [YOOH] employed. That oxygen transfer to $ClMn^{III}TPP$ is rate determining is shown by the linear dependence of the observed first-order rate constant (k_{obsd}) on [$ClMn^{III}TPP$] and its independence on [TBPH] and [YOOH] (when [TBPH $\gg$ [YOOH] $\gg$ [$ClMn^{III}TPP$]). The species $H_2OMn^{III}(Cl)TPP$ has been shown, by a radiochemical technique,[7] to be very unstable in even wet benzonitrile so that its breakdown is expected to be quite rapid. Values of k_{YOOH} were determined as slopes of plots of k_{obsd} vs. [$ClMn^{III}TPP$]. The reactions with percarboxylic acids were found to be rapid and to involve heterolytic O–O bond cleavage.[9] Also, at completion of the turnover of all peracids, $ClMn^{III}TPP$ was found (spectrally) to be intact. Reactions of $ClMn^{III}TPP$ with alkyl hydroperoxides could not be detected. The hydroperoxides employed included those previously shown to react with $ClCr^{III}TPP$ and $ClFe^{III}TPP$, ranging from the previously found most reactive diphenylhydroperoxyacetonitrile to the least reactive *tert*-butyl and cumyl hydroperoxides.[5]

A dependence upon leaving group pK_a is an established characteristic for nucleophilic displacements upon the terminal oxygen of percarboxylic acids and hydroperoxides when accompanied by heterolytic O–O bond scission (eq 2).[10] For the reactions of eq



(2)

2, log k_{YOOH} is a linear function of the pK_a of YOH (eq 3; β_{1g}

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(9) $ClMn^{III}TPP$ (8.86×10^{-3} M) and $C_6H_5CH_2CO_3H$ (2.53×10^{-3} M) were allowed to react for 90 min in dry PhCN under N_2 when an excess of an etherial solution of CH_2N_2 was added. GC analysis showed that the peracid had been converted to the corresponding carboxylic acid, which was recoverable in 95% yield as the ester $PhCH_2CO_2CH_3$. Had the percarboxylic acid undergone homolysis, the resulting $PhCH_2CO_2\cdot$ would have undergone immediate decarboxylation: Barlett, P. D.; Ruchardt, C. *J. Am. Chem. Soc.* **1960**, *82*, 1756.

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$$\log k_{\mathrm{YOOH}} = \beta_{\mathrm{lg}}\, \mathrm{p}K_{\mathrm{YOH}} + C \qquad (3)$$

= −0.6),[10] and both percarboxylic acids and alkyl hydroperoxides are correlated by the same line for any given nucleophile. In Figure 1 there is plotted log k_{YOOH} for reaction of percarboxylic acids with $\mathrm{ClMn^{III}TPP}$ vs. the pK_a of the carboxylic acid leaving groups. The correlation line of Figure 1 is provided by eq 3 with $\beta_{\mathrm{lg}} = -1.25$ and $C = 8.0$. For reaction of both percarboxylic acids and alkyl hydroperoxides with $\mathrm{ClCr^{III}TPP}$, $\beta_{\mathrm{lg}} = -0.34$ and $C = 4.90$.[5] For $\mathrm{ClFe^{III}TPP}$ the rates of heterolysis of the YO–OH bond accompanying oxygen transfer from peracids and hydroperoxides are correlated by eq 3 with $\beta_{\mathrm{lg}} = -0.34$ and $C = 4.66$.[5] In comparing the linear free energy expressions that correlate the rates of oxene transfer, one must be aware that different solvents were employed in each case. Thus, for $\mathrm{ClCr^{III}TPP}$ the solvent was $\mathrm{CH_2Cl_2}$ (25 °C), and for $\mathrm{ClFe^{III}TPP}$ the solvent was $\mathrm{CH_3OH}$ (30 °C), while for $\mathrm{ClMn^{III}TPP}$ the solvent was PhCN (30 °C). Nevertheless, the lack of reactivity of $\mathrm{ClMn^{III}TPP}$ with hydroperoxides (in such divergent solvents as benzene and dichloromethane) would appear to find an explanation in the relatively large but negative β_{lg} value of −1.25 when compared to a value of −0.34 for both $\mathrm{ClCr^{III}TPP}$ and $\mathrm{ClFe^{III}TPP}$.

A full appreciation of the meaning of β_{lg} for metalloporphyrin nucleophilic displacements upon YOOH species awaits studies of other metallotetraphenylporphyrins and a determination of the dependence of β_{lg} upon the solvent and axial ligand for a given metalloporphyrin cation. (The importance of ligand is shown by our observation that $\mathrm{Mn^{III}TPP}$ reacts readily with alkyl hydroperoxides when the ligand is imidazole due to a change in β_{lg} of fivefold.) At present, we may tentatively suppose that the large negative β_{lg} for $\mathrm{ClMn^{III}TPP}$ in PhCN solvent reflects a full negative charge on the departing group in the transition state so that the rds involves the formation of the intimate pair $[\mathrm{TPP(Cl)Mn^{V}OH{\cdot}YO^-}]$.

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Department of Chemistry
University of California at Santa Barbara
Santa Barbara, California 92106

Lung-Chi Yuan
Thomas C. Bruice*

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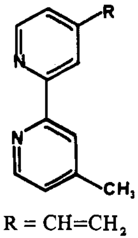
Improved Synthesis of 4-Vinyl-4′-methyl-2,2′-bipyridine

Sir:

The recent surge in the study of chemically modified electrodes has been due in part to the advent of electroactive polymer films that allow for extensive variation in electrode modification.[1] A particularly versatile reagent in this respect has been 4-vinyl-4′-methyl-2,2′-bipyridine (**1**),[2-4] first reported by Spiro.[5,6] Unfortunately, we and others[7] have found the preparation of **1** difficult to execute. We report herein modifications of Spiro's original synthesis that have allowed us to prepare multigram quantities of **1**. Subsequent to the completion of this work, a closely related procedure was reported in the patent literature.[8]



1, R = $\mathrm{CH{=}CH_2}$
2, R = $\mathrm{CH_3}$
3, R = $\mathrm{CH_2CH_2OCH_3}$

Experimental Section. Diisopropylamine was distilled over calcium hydride under nitrogen. Tetrahydrofuran (THF) was distilled over Na/benzophenone. The *t*-BuOK, (chloromethyl)methyl ether, and *n*-BuLi/hexane were obtained from Aldrich Chemical Co. and used as received. The 4,4′-dimethyl-2,2′-bipyridine was obtained from Strem Chemical Co. and used without further purification. Proton NMR spectra were recorded on a 100-MHz Varian CFT-20 spectrometer, and carbon-13 spectra were recorded on a JEOL FX90Q. Chemical shifts are reported in ppm relative to internal tetramethylsilane standards. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

4-Vinyl-4′-methyl-2,2′-bipyridine. To a solution of diisopropylamine (11.4 mL, 81 mmol) in THF (90 mL) at 0 °C under nitrogen was added 1.5 M *n*-BuLi in hexane (54.3 mL, 81.5 mmol) followed by dropwise addition of 4,4′-dimethyl-2,2′-bipyridine (**2**: 15 g, 81.5 mmol) in tetrahydrofuran (350 mL). After the resulting deep brown reaction mixture was stirred for 15 min at 0 °C, (chloromethyl)methyl ether (6.90 mL, 90.9 mmol) in 60 mL of dry THF was added dropwise. The homogeneous, pale yellow reaction was stirred at 0 °C for 30 min and then quenched with water (90 mL) and partitioned between saturated $\mathrm{NaHCO_3}$ (50 mL) and diethyl ether (150 mL). Following two additional 150-mL ether extractions, the combined ethereal layers were dried over sodium sulfate and concentrated in vacuo to afford a pale yellow oil. After the oil was filtered through flash grade silica gel (ether elution), concentrated in vacuo, and let stand at 25 °C for 2–3 days, all remaining traces of unreacted **2** deposited as white crystals. Bipyridine **3** (12.6 g, 68% yield) was isolated as a spectroscopically homogeneous, colorless oil: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 8.50 (br t, J = approximately 4 Hz, 2 H), 8.19 (br s, 2 H), 7.11 (br t, J = approximately 4 Hz, 2 H), 3.63 (t, J = 6.6 Hz, 2 H), 3.30 (s, 3 H), 2.91 (t, J = 6.6 Hz, 2 H), 2.37 (s, 3 H); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$) δ 156.6, 156.5, 149.1, 147.6, 124.7, 124.5, 122.2, 121.9, 72.2, 58.2, 35.9, 20.8; MS (CI) *m/z* 229 (M + 1, 100%).

To a solution of **3** (12.6 g, 55.2 mmol) in THF (325 mL) at −78 °C under nitrogen was added *t*-BuOK (12.4 g, 110.4 mmol) in THF (210 mL) dropwise. After the mixture was stirred for 1.5 h at −78 °C and at room temperature for an additional 15 min, the reaction was quenched with water (150 mL) and extracted with ether (3 × 300 mL). The combined ethereal layers were dried over sodium sulfate and stripped to a yellow solid. Following filtration through a 2-in. column of 230–400 mesh silica gel (ether elution) to remove polymeric impurities, the resulting yellow solid was recrystallized from ether/hexane, affording analytically pure **1** (5.40 g, 35% overall yield from **2**) as a white, crystalline solid that exhibited the reported[5,6] physical properties as well as the following: $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$) δ 149.8, 149.2, 135.4, 124.8, 124.6, 122.3, 120.8, 118.6, 118.1, 20.9. Anal. Calcd for $\mathrm{C_{13}H_{12}N_2{\cdot}{}^1/_4H_2O}$: C, 77.81; H, 6.29; N, 13.96. Found: C, 78.11; H, 6.31; N, 13.97.

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