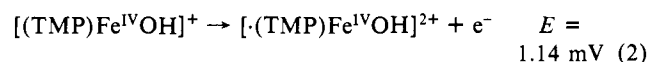
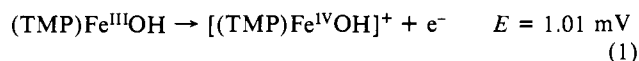


generated $[(\text{TMP})\text{Fe}^{\text{IV}}\text{OCH}_3]^+$ a species is formed with a Soret band at 423 nm, a major peak at 540 nm, and a minor peak at 575 nm. This spectrum is essentially identical with a spectrum reported by Groves^{3a} (5% $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$) who proposed the structure $(\text{TMP})\text{Fe}^{\text{IV}}(\text{OCH}_3)_2$.

Means for generating (porphinato)iron(IV)-oxo π -cation radical species in order to determine their spectral characteristics have not been available. It is this oxidation state that is of primary concern to those interested in the reactions of cytochrome P-450. The controlled-potential $1e^-$ oxidation of $[(\text{TMP})\text{Fe}^{\text{IV}}\text{OH}]^+$ was carried out at 1.22 V (vs. SCE). This is accompanied by a slight blue shift in the Soret band and a decrease in its molar absorptivity as an absorbance peak develops at 398 nm which is very diagnostic of a π -cation radical. The broad secondary absorbance peaks (605, 670 nm) are also diagnostic of a π -cation radical (Figure 1). The cyclic voltammogram of the product $[(\text{TMP})\text{Fe}^{\text{IV}}\text{OH}]^{2+}$ establishes that it has been formed from an iron(III) species by two reversible $1e^-$ oxidation steps.

In conclusion, $(\text{TMP})\text{Fe}^{\text{III}}\text{OH}$ undergoes two reversible $1e^-$ oxidations. The first oxidation step must be metal-centered because it is not accompanied by a blue shift in the Soret band and the spectrum of the product is quite similar to those reported previously for iron(IV) porphyrins. The visible spectrum of the product formed in the second $1e^-$ oxidation step clearly supports the conclusion that a π -cation radical is being formed. This can be summarized in eq 1 and 2. The conclusion²⁻⁴ that ligation



of a strongly basic oxyanion to an iron porphyrin results in metal-centered oxidation being favored over porphyrin-centered oxidation is borne out by these spectral and electrochemical investigations. Further extension of these observations are current being pursued by this laboratory.

Acknowledgment. This work was supported by grants from the National Institutes of Health and the National Science Foundation.

Photocatalysis of Oxygen Transfer from *p*-Cyano-*N,N*-dimethylaniline *N*-Oxide to *meso*-(Tetraphenylporphinato)chromium(III) Chloride

Lung-Chi Yuan, Thomas S. Calderwood, and Thomas C. Bruice*

University of California at Santa Barbara
Santa Barbara, California 93106

Received July 15, 1985

In recent studies we have shown that *p*-cyano-*N,N*-dimethylaniline *N*-oxide (NO) transfers oxygen to the metal centers of iron(III) and manganese(III) tetraphenylporphyrins to yield higher valent oxoiron and oxomanganese porphyrin species plus *p*-cyano-*N,N*-dimethylaniline (DA).¹ In the interim, Murray and Sligar² have reported results of a model study of cytochrome P-450_{sec} based upon the quantitative oxidation of 1-phenyl-1,2-ethanediol (PED) by NO in the presence of *meso*-(tetraphenylporphinato)chromium(III) chloride $[(\text{TPP})\text{Cr}^{\text{III}}\text{Cl}]$ as catalyst to yield benzaldehyde and DA.³ At the same time we defined the relationships between $(\text{TPP})\text{Cr}^{\text{III}}\text{Cl}$ and the oxo-complexes $(\text{TPP})\text{Cr}^{\text{IV}}\text{O}$ and $(\text{TPP})\text{Cr}^{\text{IV}}\text{OH}$ and reported that oxygen transfer from NO to $(\text{TPP})\text{Cr}^{\text{III}}\text{Cl}$ requires photoexcitation.³ We report

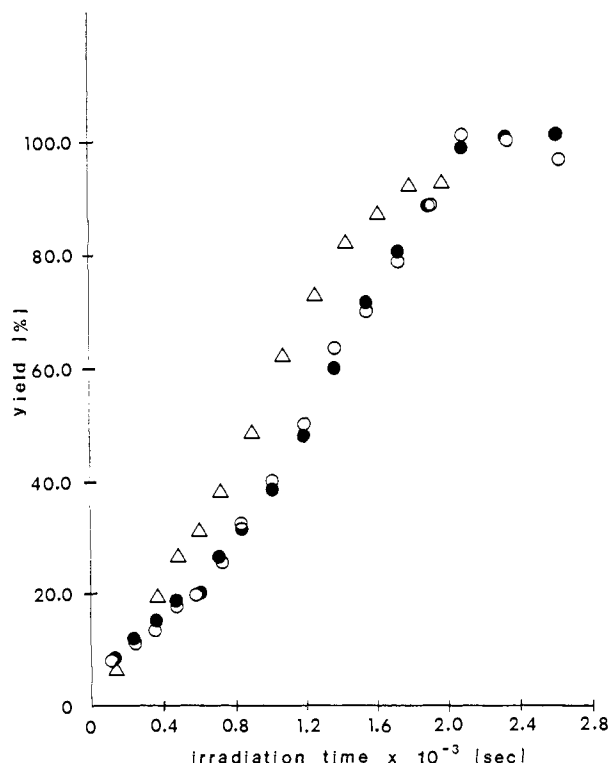


Figure 1. Plots of yields of benzaldehyde (●) and DA (○) vs. irradiation time: (A) $[\text{PED}] = 3.0 \times 10^{-2} \text{ M}$, $[\text{NO}] = 1.2 \times 10^{-3} \text{ M}$, and $[(\text{TPP})\text{Cr}^{\text{III}}\text{Cl}] = 1.0 \times 10^{-4} \text{ M}$ in CH_3CN at room temperature. (B) same as plot (A), but including DA at $1.2 \times 10^{-3} \text{ M}$ and analyzing for benzaldehyde with time (Δ).

herein preliminary studies which show that the oxochromium species proposed as the reactive oxidant for PED oxidation² is most likely $(\text{TPP})(\text{Cl})\text{Cr}^{\text{IV}}\text{O}$ and that the rate of reaction reported by Murray and Sligar was severely limited by an absence of specific photocatalytic activation.

That oxygen transfer from the *N*-oxide to chromium(III) porphyrin requires photocatalysis is shown by the following experiment. The visible absorbance, monitored with time at the λ_{max} of $(\text{TPP})\text{Cr}^{\text{IV}}\text{O}$ (429 nm), was found to be unchanged over an 18-h period when an acetonitrile solution containing $(\text{TPP})\text{Cr}^{\text{III}}\text{Cl}$ ($1.0 \times 10^{-4} \text{ M}$)⁴ and NO ($1.2 \times 10^{-3} \text{ M}$) was maintained in the dark. Irradiation by diffuse room fluorescent light for only 2 min resulted in a change of the green color of $(\text{TPP})\text{Cr}^{\text{III}}\text{Cl}$ to orange. The spectrum of the spent reaction solution exhibited a broad absorption with maxima at 426 and 412 nm characteristic of a mixture of $(\text{TPP})\text{Cr}^{\text{IV}}\text{O}$ and $(\text{TPP})(\text{Cl})\text{Cr}^{\text{IV}}\text{O}$.⁵ Transfer of the reaction from acetonitrile to dichloromethane provided similar results and from the spectrum it could be estimated that $(\text{TPP})\text{Cr}^{\text{IV}}\text{O}$ was formed in a 95% yield. Since the photocatalysis results in a very rapid reaction with reactants at low concentrations when the light source is meager it appears obvious that the quantum yield must be much greater than 1.0. From this it follows that oxygen transfer from NO to $(\text{TPP})\text{Cr}^{\text{III}}\text{Cl}$ should be anticipated as a photoinitiated chain reaction.

In the $(\text{TPP})\text{Cr}^{\text{III}}\text{Cl}$ photocatalyzed oxidation of PED with NO the final products are benzaldehyde, formaldehyde, DA, and $(\text{TPP})\text{Cr}^{\text{III}}\text{Cl}$ (plus less than 1% *p*-cyano-*N*-methylaniline formed upon demethylation of DA). The autocatalytic nature of this reaction is shown by the following experiment. Five milliliters of a CH_3CN solution containing PED ($3.0 \times 10^{-2} \text{ M}$), NO ($1.2 \times 10^{-3} \text{ M}$), and $(\text{TPP})\text{Cr}^{\text{III}}\text{Cl}$ ($1.0 \times 10^{-4} \text{ M}$) under N_2 was

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(2) Murray, R. I.; Sligar, S. G. *J. Am. Chem. Soc.* 1985, 107, 2186.

(4) The Soret band of $(\text{TPP})\text{Cr}^{\text{III}}\text{Cl}$ in CH_3CN showed two peaks at 450 and 459 nm, and the ratio of these two peaks was dependent on the concentration of $(\text{TPP})\text{Cr}^{\text{III}}\text{Cl}$ employed.

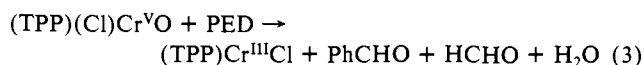
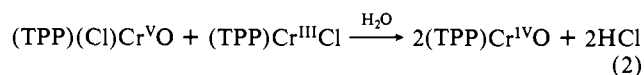
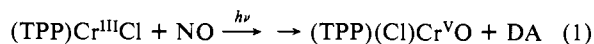
(5) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C.; Butler, W. M. *Inorg. Chem.* 1982, 21, 1363.

irradiated by room fluorescent light. Another identical solution was stored in the dark. At given intervals of time, 200- μ L aliquots of the irradiated reaction solution were transferred under N_2 to 2-mL cap-sealed bottles with a gas-tight syringe and these samples were stored on dry ice. Each sample was carefully (to avoid light) analyzed by HPLC.⁶ The results are shown in Figure 1. Inspection of Figure 1 shows that the plots of the yields of benzaldehyde and DA vs. irradiation time exhibit the shape anticipated for an autocatalytic reaction. Analysis of the reaction solution stored in the dark after 4.5 h showed that no benzaldehyde or DA had been formed. Irradiation of this solution provided a quantitative yield of benzaldehyde and DA after 40 min. In a separate experiment, a solution of (TPP)Cr^{III}Cl (8.0×10^{-6} M) and NO (1.1×10^{-4} M) in CH_2Cl_2 was subjected to intermittent exposure to room fluorescent light followed by monitoring in the dark at 429 nm. It was found that the reaction continued for up to 2 min in the dark after each period of light exposure. In order to determine if DA, a product of oxygen transfer from NO, might play a role as an autocatalytic agent, the experiment of Figure 1 was repeated with the inclusion of 1.2×10^{-3} M DA. The time course for this reaction was followed by HPLC analysis of benzaldehyde and is included in Figure 1. By inspection of the figure there is seen to be a shortening of the lag phase and a small rate enhancement. DA seems to play some minor role in the photoinduced autocatalysis.

That (TPP)Cr^{IV}O is not the oxidant for the rapid reaction with PED reported above is shown by the following experiments. The formation of benzaldehyde was followed by HPLC after mixing of a solution composed of (TPP)Cr^{IV}O (4.52×10^{-4} M) and a 100-fold excess of PED in CH_2Cl_2 . After 24 h there still remained more than 50% of unreacted (TPP)Cr^{IV}O. This result establishes that the oxidation of PED by ground-state TPPCr^{IV}O is far too slow to be a competent component of the mechanism of the photocatalytic reaction, since the photocatalytic reactions of Figure 1 go to completion in a short period of time. The species (TPP)Cr^{IV}O is a rather stable oxo metalloporphyrin as shown by the fact that it has been isolated and characterized by X-ray crystallography.⁷ Though this species is known to oxidize alcohols to aldehydes the rate of reaction with PED is, as shown, quite slow. The species (TPP)(Cl)Cr^VO is a much stronger oxidizing agent⁸ than (TPP)Cr^{IV}O and is stable in CH_2Cl_2 for a few hours at room temperature.⁹ Controlled-potential oxidation of (TPP)Cr^{IV}O was used to provide a stable CH_2Cl_2 solution of (TPP)(ClO₄)Cr^VO (4.4×10^{-5} M). To this solution there was added PED (to a concentration of 6.2×10^{-4} M) and the decrease in (TPP)(ClO₄)Cr^VO (412 nm) and increase in (TPP)Cr^{III}ClO₄ (450 nm) was followed at 30 °C in the dark. The reaction was found to obey the first-order rate law ($k_{obsd} = 6.7 \times 10^{-2} s^{-1}$) and the isobestic points at 374 and 439 nm established the absence of any accumulated intermediate. The oxidation of PED produced quantitative yields of benzaldehyde (95% by HPLC)⁶ and formaldehyde (100% by Nash procedure).¹⁰ The rapid rate of reaction of PED with the oxo-Cr^V porphyrin species allows this reaction to be a competent component of the photocatalysis of PED oxidation by NO.

We have shown (loc. cit.) that both (TPP)Cr^{IV}O and (TPP)(Cl)Cr^VO are present following the irradiation of solutions of (TPP)Cr^{III}Cl and NO. The formation of (TPP)Cr^{IV}O is known³ to occur by disproportionation of (TPP)Cr^{III}Cl with (TPP)(Cl)Cr^VO. High monooxygen donation potential compounds react with (TPP)Cr^{III}Cl to afford principally (TPP)(Cl)Cr^VO and low monooxygen donation potential compounds can only afford (TPP)Cr^{IV}O.

Since in the photocatalytic reaction the spectra of the spent reaction solution is that of both (TPP)(Cl)Cr^VO and (TPP)Cr^{IV}O and the reaction of percarboxylic acids with (TPP)Cr^{III}Cl provides a similar composition of Cr(IV) and Cr(V) species,¹ we may conclude that the photocatalytic oxygen transfer from NO to (TPP)Cr^{III}Cl is as efficient as the oxygen transfer from percarboxylic acids to (TPP)Cr^{III}Cl in the dark. Though the nature of the photoautocatalysis is not understood the essence of the overall oxidation of PED may be expressed as shown in eq 1-3.



In summary, unlike the facile and dark transfer from NO to iron(III) and manganese(III) *meso*-tetraphenylporphyrins, the oxygen transfer to chromium(III) occurs only by photocatalysis. While aniline *N*-oxides have been shown to undergo photoinitialized deoxygenation,¹¹ it has been demonstrated previously that *p*-cyano-*N,N*-dimethylaniline *N*-oxide does not react with our trap (PED).³ While the product of the photocatalysis oxidizes PED very rapidly, (TPP)Cr^{IV}O does not; and since (TPP)(Cl)Cr^VO does, the latter must be the initial product of oxygen transfer and, thus, is converted to (TPP)Cr^{IV}O by comproportionation with (TPP)Cr^{III}Cl.

Acknowledgment. This work was supported by a grant from the National Institutes of Health and The American Cancer Society.

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A Vinyltrimethylenemethane Intermediate in the 1,3-Sigmatropic Rearrangement of the 6-Methylenebicyclo[3.1.0]hex-2-enyl System

Steven Pikulin and Jerome A. Berson*

Department of Chemistry, Yale University
New Haven, Connecticut 06511

Received September 9, 1985

Because the barriers to internal rotation and cyclization of biradicals usually are very small,¹⁻⁵ the identification of these species as true intermediates in thermal rearrangements has been difficult. We conjectured that a stabilizing structural alteration of the biradical should deepen the local potential minimum and facilitate detection of the intermediate. This paper describes the experimental consequences of such an alteration, in which the putative partially conjugated biradical **1** of the bicyclo[3.1.0]hex-2-ene rearrangement⁶⁻⁸ is converted to the fully conjugated vinyltrimethylenemethane (VTMM) species **2** derived from 6-

(6) HPLC was performed as described in ref 1c. The retention time of each product follows: benzaldehyde (5.5 min), DA (8-9 min), and *p*-cyano-*N*-methylaniline (20 min).

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