pendence of *both* d_{hy} and enantioselectivity on coaggregate composition is immediately apparent. Enantioselectivity responds directly and sensitively to variations in coaggregate structure that can be monitored by dls.

Separate experiments demonstrated that the maximum value of d_{hy} (690 ± 10 Å) observed at composition A, where enantioselectivity is also maximized, is not greatly affected (≤10%) by the addition of appropriate quantities of L- or D-**1**, catalyst **2**, or their reaction products. The properties of the $2C_{14}$/CTAB coaggregates are therefore innate, and not induced by addends as is the case in the diastereoselective thiolyses of dipeptide esters.[3]

What is the structure of the coaggregates and how do they exert control over enantioselectivity? These questions cannot now be answered definitively, but informed speculation is possible. Stopped-flow fluorescence experiments were carried out with $2C_{14}$/CTAB coaggregates and 1-anilino-8-naphthalene sulfonate.[8] $\tau_{1/2}$ for ANS permeation decreased from 720 ms in pure $2C_{14}$ vesicles, to 150 ms at 23 mol % CTAB, to 27 ms at 33% CTAB. At higher CTAB, specifically at composition A, "instantaneous" development of ANS fluorescence (i.e., binding without measurable permeation) was observed. Our interpretation is that $2C_{14}$/CTAB coaggregates lose vesicular structure somewhere above 33% CTAB, a conclusion supported by the inability of differential scanning calorimetry to detect a critical temperature for a phase change in coaggregates richer than 23% in CTAB.

The coaggregates were also examined by monitoring the fluorescence of 5×10^{-5} M solubilized pyrene.[5,8,9] From the near constancy (0.70 ± 0.02) of the fluorescence intensity ratio at 385 nm, relative to that at 375 nm, the micropolarity[9a] of the coaggregates appears to be independent of composition all across the abscissa of Figure 1. On the other hand, the microviscosity, as reflected by the intensity of pyrene excimer (475 nm) relative to pyrene monomer (393 nm) fluorescence,[9b] shows a maximum in the region of 67-83% CTAB (I_{475}/I_{393} = 0.21-0.11) when compared to either other coaggregate compositions or to pure $2C_{14}$ or CTAB (I ratios 0.43 or 0.42). Similar conclusions follow from fluorescence polarization studies using solubilized 1,6-diphenyl-1,3,5-hexatriene.[4]

Variable-angle (45-135°) dls reveals the coaggregates of composition A to be markedly nonspherical. They are characterized by a strong dependence of d_{hy} on scattering angle, whereas coaggregates containing 83%, 75%, 41%, 33%, 13%, or 0% CTAB exhibit little or no angular dependence of d_{hy} and are presumably spherical or nearly spherical micelles or vesicles.

Taking the evidence together, we suggest that upon admixture of $2C_{14}$, CTAB micelles undergo successive transitions to large rodlike or cylindrical micelles,[10] then to extended lamellae, and finally to spherical vesicles when $2C_{14} \geq 70\%$.[11] We suggest that the highly enantioselectivity-supportive coaggregates at composition A are rodlike micelles.[10] It would be conceptually attractive if the crystalline coaggregate (66-42% CTAB) lay between rod micelles at composition A and lamellae at <42% CTAB.

Crucially, *both* enantioselectivity and d_{hy} peak just before the coaggregate composition crosses an obvious phase boundary. Near this boundary, i.e., at composition A, d_{hy} does not reflect the hydrodynamic diameter of spherical particles, but more probably the correlation range of large extended aggregates.[12] Moreover, we suggest that the increasingly correlated, extended molecular alignment within coaggregates on the verge of phase separation may impose ordered relative arrangements on solubilized host molecules (such as substrate **1** and catalyst **2**) that engender highly amplified enantioselectivities.

An important implication of this hypothesis is that various types of selectivity (stereo, regio, or even chemo) expressed by reactions occuring in micelles or vesicles might be augmented in coaggregates held at compositions close to phase boundaries. We are investigating these possibilities.

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(7) We used a Nicomp TC-100 computing autocorrelator, an argon laser light source (488 nm), and a Hazeltine microcomputer fitted with the cumulant program. This directly afforded a nominal value of d_{hy} based on the *assumption* of a spherical aggregate. Data were collected at a 90° scattering angle unless otherwise specified, and d_{hy} was reproducible to better than ±10% in duplicate preparations.

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Oxidative Cleavage of 1-Phenyl-1,2-ethanediol by 4-Cyano-*N*,*N*-dimethylaniline *N*-Oxide and Chloro(5,10,15,20-tetraphenylporphinato)-chromium(III): A Model for Cholesterol Side-Chain Cleavage by Cytochrome P-450$_{SCC}$[1]

Ralph I. Murray and Stephen G. Sligar*

Department of Biochemistry
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801
Received September 14, 1984

Exogenous oxidant supported substrate oxidations by metalloporphyrins have been used extensively as simplified model systems for the corresponding enzyme-catalyzed oxidations by cytochrome P-450. Documented reactivities include epoxidations,[2-4] hydroxylations,[2-5] N-demethylation.[6] and oxidation of alcohols and ethers to aldehydes or ketones.[7] In this paper we report the oxidative cleavage of 1-phenyl-1,2-ethanediol (PED) by chloro(5,10,15,20-tetraphenylporphinato)chromium(III) (Cr(TPP)Cl) and the exogenous oxidant 4-cyano-*N*,*N*-dimethylaniline-*N*-oxide (CN-DMANO),[8] stoichiometrically producing benzaldehyde.[9] This carbon-carbon lyase reaction is analogous to the third step in the removal of the side chain of

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(8) Nee, M. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 6123-6125. In preliminary experiments iodosobenzene was chosen as the exogenous oxidant for the cleavage reaction. In this case, however, it was demonstrated that iodosobenzene was active in oxidative cleavage of PED in the absence of porphyrin catalyst (Egeberg and Sligar, unpublished observation). Initial reaction rates were 70 μM product min^{-1} for iodosobenzene and 4 μM product min^{-1} with 100 μM Cr(TPP)Cl and CN-DMANO as oxygen donor. With the *N*-oxide as exogenous oxidant, no detectable reaction was found in the absence of catalyst.

(9) We have found that cleavage of the 3°,3° glycol, 1,1,2,2-tetraphenyl-1,2-ethanediol, produced 2 equiv of benzophenone for each CN-DMANO consumed, thus confirming the overall stoichioimetry of the reaction.

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Table I

time, h	CN-DMANO[a]	CN-DMA[a]	CN-NMA[a]	BZALD[a]	oxidative balance[b]
3.0	−0.8	0.72	0.01	0.60	−0.19
17.3	−1.7	1.64	0.04	1.24	−0.42
45.0	−10.8	10.63	0.13	9.00	−1.63

[a] Nanomoles consumed (−) or produced (+) per nanomole of Cr(TPP)Cl. [b] Until the reaction is complete, as much as 1 equiv of oxygen may be sequestered on the porphyrin.

cholesterol by cytochrome $P\text{-}450_{SCC}$.[10] Cleavage of the cholesterol side chain is the first step in the biosynthesis of steroid hormones and the primary regulatory site in steroidogenesis[11] during which cytochrome $P\text{-}450_{SCC}$ carries out three successive oxidations of cholesterol, with 22(*R*)- and 20-α-hydroxylations producing a vicinal diol oxidatively cleaved in the third step[10,12] at the expense of atmospheric dioxyygen and two reducing equivalents.

The title reaction was initiated by the addition of CN-DMANO to a CH_3CN solution of Cr(TPP)Cl and PED[13] and was monitored by HPLC and quatitated by integration of the UV chromatogram. The results of a typical experiment are presented in Table I. Glycol cleavage was stoichiometric at all time points. The endpoint oxidation balance showed 10.8 equiv of CN-DMANO consumed and 9.0 equiv of benzaldehyde (BZALD) produced. The competing N-demethylation reaction is minor (0.1 equiv of 4-cyano-N-methylaniline, CN-NMA) with 1.7 equiv of oxidation potential unaccounted for. All of the *N*-oxide consumed can be accounted for as 4-cyano-*N*,*N*-dimethylaniline (CN-DMA, 10.6 equiv) and CN-NMA. In contrast to the complete reaction mixture, omission of either CN-DMANO or CrTPPCl resulted in no detectable cleavage of PED.

Cr(TPP)Cl was chosen as a model metalloporphyrin for this study because it forms a spectrally defined, stable complex with an oxygen atom, oxo(5,10,15,20-tetraphenylporphinato)chromium (oxo-(TPP)Cr).[2,14] That this oxometalloporphyrin complex is the active species in diol cleavage was suggested by separation of the overall process into two sequential steps: transfer of an oxygen atom from CN-DMANO to Cr(TPP)Cl and the subsequent reaction of the oxo-(TPP)Cr with PED to cleave the diol and regenerate Cr(TPP)Cl. Addition of CN-DMANO to a solution of Cr(TPP)Cl in CH_2Cl_2[13] resulted in the rapid spectral transition shown in Figure 1, which is consistent with the spectrum of the compound generated from Cr(TPP)Cl and iodosobenzene and identified as oxo(5,10,15,20-tetraphenylporphinato)chromium(IV).[14] HPLC analysis of an aliquot of the mixture after addition of oxidant showed that N-demethylation occurred at a slow but significant rate during formation of oxo-(TPP)Cr, explaining the residual Cr(TPP)Cl seen in the optical spectrum. When decay of the spectrum indicated that the velocity of N-demethylation now exceeded the velocity of oxygen transfer, diol clevage was initiated by addition of PED. Concomitant with formation of benzaldehyde, the spectrum of Cr(TPP)Cl was regenerated. In our hands the rate of cleavage of PED by Cr(TPP)Cl is slightly higher than the rate of the corresponding alkene epoxidation reaction in which styrene oxide is produced from styrene.

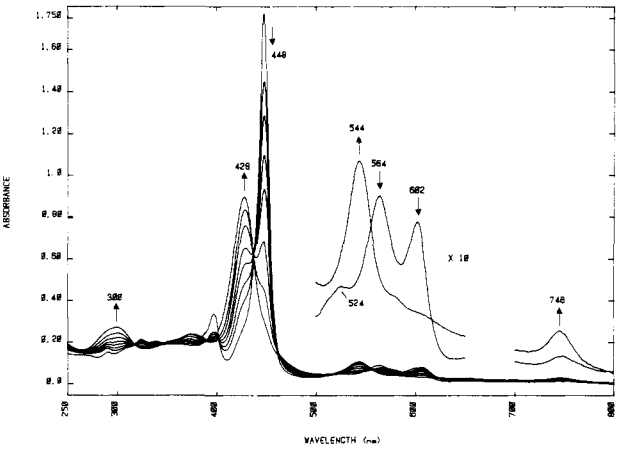

Figure 1. Formation of oxo(5,10,15,20-tetraphenylporphinato)chromium. One equivalent of CN-DMANO was added to Cr(TPP)Cl (8 μM) in CH_2Cl_2. Initial spectrum is prior to addition of CN-DMANO; arrows indicate direction of change with time following addition of CN-DMANO. The expanded sensitivity (500–650, 700–800 nm) shows the initial and final (60 min) spectra.

The exogenous oxidant supported cleavage of the vicinal diol PED by Cr(TPP)Cl is an example of a previously unrecognized reactivity of metalloporphyrins. That the oxene complex, oxo-(TPP)Cr, is the probable reactive species for glycol cleavage in this model system extends the role of these metalloporphyrins as models for cytochrome P-450 monoxygenases to include those enzyme systems that catalyze the oxidative cleavage of vicinal diols. These studies are currently being expanded to include Fe^{III}- and Mn^{III}(TPP)Cl and a variety of aryl and alkyl diol substrates. Together with Cr(TPP)Cl, these porphyrins may well provide a simplified model system for studying the mechanism of cytochrome $P\text{-}450_{SCC}$ catalyzed conversion of cholesterol to pregnenolone.

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(13) Experimental section: (i) The reaction mixture for multiple turnover reactions consisted of Cr(TPP)Cl (100 μM), PED (30mM), and CN-DMANO (1.2 mM) in 300 μL of CH_3CN. Reactions were carried out at 23 °C under a nitrogen atmosphere. HPLC analyses were on a 30 cm × 4 mm MCH-10 (octadecylsilane, Varian) column eluted with a CH_3CN/H_2O gradient (10% initially, 15-min ramp to 45%, 10-min ramp to 100%; elution times, PED, 11.4 min; CN-DMANO, 17.4 min; Bzald, 22.6 min; CN-NMA, 23.6 min; CN-DMA, 25.4 min). Elution was monitored at 258 nm, and peak areas were calibrated with multiple runs of standards. No secondary oxidants (cyanoaniline, benzoic acid) were detected. (ii) The reaction mixture for spectral analysis of the oxo-(TPP)Cr intermediate consisted of Cr(TPP)Cl (8 μM) and CN-DMANO (8 μM) in 3 mL of CH_2Cl_2. The spectrum of the Cr(TPP)Cl solution was recorded after which reaction was initiated by addition of CN-DMANO in a minimum volume (2.4 μL). The solution was mixed by rapid inversion nd the spectrum was recorded at intervals (10 s for the first 10 min, 1 min thereafter) on a Hewlett-Packard Model 8450A diode-array spectrophotometer. When the oxo-(TPP)Cr concentration reached a maximum, the cleavage reaction was initiated by addition of PED (2.4 mM). Reaction progress was monitored spectrally during the 48 h required to complete the reaction. HPLC analyses were performed on aliquots of the reaction mixtures concentrated 30-fold under nitrogen.
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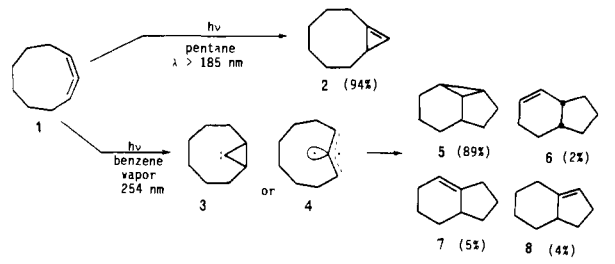
Cumulene Photochemistry: Evidence for *cis*- and *trans*-Cyclopropylidene Intermediates in Triplet Photoreactions of 1,2-Cyclodecadiene

John D. Price and Richard P. Johnson*

Department of Chemistry, Iowa State University
Ames, Iowa 50011
Received October 29, 1984

We have previously reported that direct irradiation of 1,2-cyclononadiene (**1**) affords predominantly cyclopropene **2**.[1] Independent generation of potential vinylcarbene intermediates led to arguments for a concerted $[_\sigma 2_a + _\pi 2_a]$ mechanism.[1] Vapor-phase triplet rearrangement of **1** to **5** was suggested by Ward and



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