

Evaluation of the Selectivity of the Epoxidation of *cis*- versus *trans*-Alkenes by Oxo[*meso*-tetrakis(2,6-dibromophenyl)porphinato]chromium(V). Dynamics, Products, and Van der Waals Energies

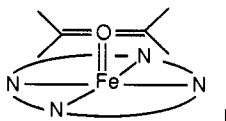
Gong-Xin He, Houg-Yau Mei, and Thomas C. Bruice*

Contribution from the Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106. Received November 19, 1990

Abstract: Studies of the reaction of oxo[*meso*-tetrakis(2,6-dibromophenyl)porphinato]chromium(V) [(Br₈TPP)Cr^V(O)(X)] with a number of *trans*-alkenes have been carried out with the objective of clarifying the nature of the reported stereoselectivity of the epoxidation of *cis*-alkenes as compared to *trans*-alkenes. The alkenes employed were *trans*-*p,p'*-dimethoxystilbene, *trans*-stilbene, *trans*- β -methylstyrene, *trans*-*p,p'*-dicyanostilbene, *trans*-2-pentene, *trans*-5-decene, *trans*-2-hexenyl acetate, (*E*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene, and also (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene. The influence of electronic and steric factors in determining the second-order rate constants (k_1) for the reactions of *trans*-alkenes with (Br₈TPP)Cr^V(O)(X) were separated by use of the linear free-energy relationship of log k_1 and the one-electron oxidation potentials ($E_{1/2}$) established by the reaction of a series of *cis*-alkenes with (Br₈TPP)Cr^V(O)(X). Quantification of the steric factors established that there is no appreciable steric retardation of the second-order rate constants for reaction of *trans*-*p,p'*-dimethoxystilbene, *trans*- β -methylstyrene, *trans*-2-pentene, *trans*-5-decene, and *trans*-2-hexenyl acetate with (Br₈TPP)Cr^V(O)(X). Steric hindrance is quite marked with *trans*-stilbene, *trans*-*p,p'*-dicyanostilbene, and (*E*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene. In comparison with *trans*-stilbene, the lack of a kinetic steric effect with *trans*-*p,p'*-dimethoxystilbene requires a change of mechanism. The standard free energy (ΔG°) for one-electron oxidation of *trans*-*p,p'*-dimethoxystilbene [(Br₈TPP)Cr^V(O)(X) + >C=C< \rightarrow (Br₈TPP)Cr^{IV}(O)(X) + >C[•]C<] is favored over the ΔG° values for *trans*-stilbene and *cis*-stilbene by 0.46 and 0.59 V, respectively. Thus, *trans*-*p,p'*-dimethoxystilbene but not *trans*-stilbene can undergo facile 1e⁻ oxidation by (Br₈TPP)Cr^V(O)(X). This can be shown to be allowed by comparison of ΔG° and ΔG^\ddagger values. One-electron transfer can take place at significantly longer distances than can covalent bond formation. Computer docking experiments have defined the stereochemistry associated with the closest approach of minimal van der Waals repulsive forces in the reaction of *trans*- and *cis*-stilbene. For *trans*-stilbene the closest approach is at a distance of 3.88 Å from directly above the Cr^V(O) while for *cis*-stilbene lowest energy closest approach is at 2.81 Å with the C=C bond: (i) lined parallel to opposite meso carbons; and (ii) above the Cr^V(O) oxygen with an offset (α) from the perpendicular Cr^V-O bond of $\alpha = 24^\circ$. Product yields are in accord with assigned steric effects and the nature of the products and mode of formation are discussed.

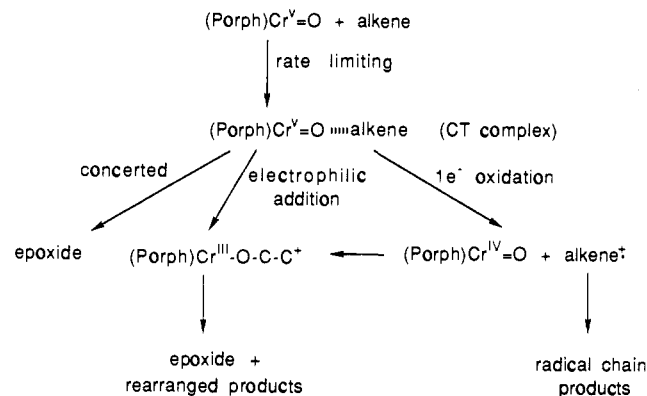
Introduction

To fully understand the mechanism of the epoxidation of alkenes by hypervalent metal-oxo porphyrin species it is important to know the stereochemistry of the transition state(s). Stereoselectivity has been reported for the epoxidation of alkenes catalyzed by metalloporphyrins.¹⁻³ In an early study Groves compared the products from competitive oxidation of *cis*- and *trans*-alkenes catalyzed by a series of iron porphyrins and sought to explain the selectivity by proposing a side-on approach of alkene (I) to the



Fe-O bond such that the alkene may interact with the d_{π^*} - p_{π^*} Fe-O antibonding orbitals.⁴ We subsequently pointed out that such a geometry of reactants is not required since the d_{π^*} - p_{π^*} Fe-O antibonding orbitals would not be parallel to the porphyrin ring and considerable electron density to the side of the oxygen distal to the porphyrin iron should be expected.⁵ An approach of the

Scheme I



>C=C< parallel to the porphyrin plane but above and to the side of the oxygen was suggested as more reasonable. This seems to be the case as shown by the following steric arguments. First, Traylor reported that an alkene which is incapable of a side approach to the Fe-O bond (substituted by two very bulky adamantyl groups) can be epoxidized by a variety of metalloporphyrins.⁶ Second, we established that high yields of epoxides were obtained when [*meso*-tetrakis(2,6-dibromophenyl)porphinato]iron(III) [(Br₈TPP)Fe^{III}(Cl)] was used as the catalyst. With (Br₈TPP)Fe^{III}(Cl) as the catalyst, the steric effect of the *o*-bromo substituents precludes approach of the C=C bond to the side of the Fe-O bond.⁵ In an ingenious approach, Groves has employed

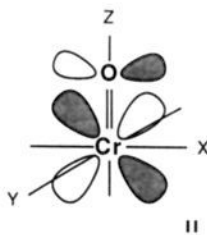
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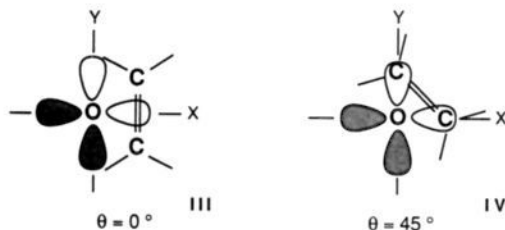
the X-ray structure of a complex composed of a ruthenium(III) porphyrin ligated to the oxygen of an epoxide to model the stereochemistry of the transition state for epoxidation.⁷ The angle defined by the epoxide ring and the porphyrin plane is 49° which is in the range that we had predicted.^{3,8}

To better understand *cis* vs *trans* stereoselectivity in alkene epoxidation we have compared the dynamics, products, and van der Waals closest approach minima in the reaction of oxo-*[meso-tetrakis(2,6-dibromophenyl)porphinato]chromium(V)* [(Br₈TPP)Cr^V(O)(X)] with a series of *cis*- and *trans*-alkenes. The results of this study are now reported. A unifying mechanism has been proposed for alkene epoxidation by hypervalent chromium-oxo and iron-oxo porphyrins in which the rate-limiting step is the formation of a charge-transfer (CT) complex (Scheme I).^{5,9} The steric requirements of the formation of the CT complex should be the origin of the stereoselectivity of the epoxidation reaction.

For charge transfer to occur the HOMO of alkenes should be sufficiently close to the LUMO of the reactive center of the hypervalent oxometalporphyrin. For alkenes the HOMO is the π orbital of the double bond. For (Br₈TPP)Cr^V(O)(X), as suggested by several theoretical studies,¹⁰ the LUMO is the two empty Cr–O (d_x-p_x) antibonding orbitals ($1b_1$ and $1b_2$ in the *xz* and *yz* planes, respectively) and one of them ($1b_1$) is shown in II. With



the double bond parallel to the plane of the porphyrin ring, two angles (θ and α) will be employed to describe the approach of alkene to (Br₈TPP)Cr^V(O)(X). Looking down upon the reactive oxygen such that it covers the Cr^V, there are two approaches of the C=C bond that can be characterized by the angles $\theta = 0^\circ$ (III) and 45° (IV); both antibonding orbitals ($1b_1$ and $1b_2$) are drawn in III and IV. In III, the C=C bond is parallel with the N–Cr–N. In IV, the C=C bond is parallel with opposite meso carbons in the porphyrin ring. An additional angle α is defined



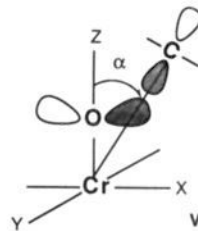
as in V. When $\alpha = 0$ the alkene approaches straight from the top of the oxygen in the oxometalporphyrin, while when $\alpha \rightarrow 90^\circ$ the situation is very close to the early side-on model (I).

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(8) In ref 7 Groves questions our modeling study of the trajectories for approach of alkene to iron(IV)-oxo porphyrin π -cation radical. We should like to clarify this misunderstanding: (i) We did not employ MM2 calculations; and (ii) the approach of alkene to the activated oxygen moiety was presented as above the oxygen with an angle α (see structure V, this paper) of 5 to 65° for norbornene, 30 to 45° for *cis*-stilbene, and 0° for *trans*-stilbene. The angle α reported by Groves from the X-ray structure of an Ru(II) porphyrin complex of styrene oxide is 41°. Thus, our structures are not in disagreement with that of Groves.

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Experimental Section

Instrumentation. Melting points were determined on a Bristoline hot-stage microscope without further correction. Infrared spectra were obtained in KBr on a Perkin-Elmer monochromator grating spectrometer (Model 1330). ¹H NMR spectra were obtained in CDCl₃ with Nicolet NT-300 and General Electric GN-500 spectrometers. UV–vis spectral measurements and repetitive scan experiments were carried out on a Cary-14 spectrophotometer (thermostated at 30 °C) interfaced to a Zenith computer equipped with OLIS data acquisition and processing software (On-Line Instruments, Inc.). High-pressure liquid chromatography (HPLC) was performed by using two Perkin-Elmer Series 10 pumps. For analytical HPLC, a Hewlett-Packard variable wavelength detector (Model HP1050) at 254 nm, an integrator (Model 3392A), and an Altex column (5 × 250 mm, 5 μ m RSil-CN eluted with a mixing solvent of hexane–CH₂Cl₂ (9:1) at 2 mL/min) were used. For semipreparative HPLC an ISCO variable wavelength absorbance detector (Model V⁴) at 254 nm, a fraction collector (Model Retriever II), and an Altex column (10 × 250 mm, 10 μ m RSil-CN eluted with a mixing solvent of hexane–CH₂Cl₂ (9:1) at 6 mL/min) were used.

Molecular modeling studies were performed on a Silicon Graphics Iris 4D/220 GTX computer with Polygen programs QUANTA (version 3.0) and CHARMM (version 21.2). The Cambridge Database (version 4.3) search was performed on a VAX 3100 workstation.

Materials. Methylene chloride was purified as described previously.¹¹ DMF was distilled over CaH₂ and stored in N₂. Toluene was refluxed over Na metal and distilled before use. Tetrabutylammonium perchlorate (TBAP) and iodobenzene diacetate (IBDA) were purchased from Aldrich and used as received (IBDA was stored at 4 °C). (*Z*- and (*E*)-1,2-bis(*trans*-2,3-diphenylcyclopropyl)ethene (*I-Z* and *I-E*, respectively) were synthesized as previously reported.¹² *p,p'*-Dicyanostilbene was prepared by Wittig condensation of *p*-cyanobenzyltriphenylphosphonium bromide and *p*-cyanobenzaldehyde in THF with lithium bis(trimethylsilyl)amide as base.¹³ The *cis* and *trans* isomer mixture obtained was irradiated by sunlight lamp in refluxing CCl₄ with small amounts of iodine for 24 h.¹⁴ After the mixture was cooled the precipitated *trans* isomer was collected by filtration and purified by recrystallization from CHCl₃–EtOH (8:2). The purity and structure of *trans-p,p'*-dicyanostilbene was confirmed by HPLC, mp 294–296 °C (lit.¹⁵ mp 278–280 °C), and IR and ¹H NMR spectra. All other alkenes were purchased from commercial vendors, and purified by distillation or recrystallization from suitable solvent. The possible products *trans*-2,3-diphenylcyclopropanecarboxaldehyde, *cis*- and *trans*-1,2-bis(*trans*-2,3-diphenylcyclopropyl)oxirane (*2-c* and *2-t*, respectively) were prepared according to published methods.¹² *trans-p,p'*-Dimethoxystilbene oxide and *trans*- β -methylstyrene oxide were synthesized from the corresponding alkenes with *m*-chloroperbenzoic acid and Na₂HPO₄ in CH₂Cl₂ and purified by semipreparative HPLC. Their structures were confirmed by IR and ¹H NMR spectra. Other standard samples for HPLC analysis were available commercially. *meso*-Tetrakis(2,6-dibromophenyl)porphyrin (**3**) was available from a previous study.⁵

Oxo(*meso*-tetrakis(2,6-dibromophenyl)porphinato)chromium(IV) (**5**) was prepared by the following improved method.⁹ The metalation of the free base (**3**) (100 mg, 0.08 mmol) with dry CrCl₂ (five 1-g portions) was carried out in a refluxing mixture of dry DMF–toluene (1:4). After addition of CrCl₂, the solvent was slowly distilled off to near dryness. During the distillation the color of the system changed gradually from purple to dark green. The resulting products were taken up in CH₂Cl₂, and the mixture was column chromatographed on neutral alumina (activity III). (Br₈TPP)Cr^{III}(Cl) (**4**) was eluted, as a large green band, with CH₂Cl₂ to CH₂Cl₂–methanol (96:4). The eluent was concentrated and pumped to remove trace DMF, and the green solid was column chro-

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Table I. Second-Order Rate Constants (k_1) for the Oxidation of Alkenes with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ and the $E_{1/2}$ (V, SCE) of the Alkenes in CH_3CN

no.	alkenes	$E_{1/2}$	k_1	$\log k_1$	$k_{1,\text{cal}}/k_1^a$
1	<i>trans-p,p'</i> -dimethoxystilbene	1.05	4.5	0.65	1.6
2	1- <i>E</i> ^b	1.22	0.098	-1.01	23
3	1- <i>Z</i> ^c	1.47	0.18	-0.75	2.3
4	<i>trans</i> -stilbene	1.51	0.00067	-3.17	461
5	<i>trans-β</i> -methylstyrene	1.69	0.048	-1.32	1.9
6	<i>trans-p,p'</i> -cyanostilbene	1.89	<0.00004	<-4.40	>560
7	<i>trans</i> -2-pentene	2.14	0.0011	-2.95	3.6
8	<i>trans</i> -5-decene	2.14	0.0069	-2.16	0.6
9	<i>trans</i> -2-hexenyl acetate	2.25	0.00052	-3.29	3.6

^a The $k_{1,\text{cal}}$ was calculated from the plot of the log of the second-order rate constant for reaction of a series of 16 alkenes with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ vs the $E_{1/2}$ for $1e^-$ oxidation of the alkenes. See text. ^b (*E*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene. ^c (*Z*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene.

matographed again as before. A narrow green band was obtained with CH_2Cl_2 -MeOH (96:4). The effluent was diluted with CH_2Cl_2 and stirred with 10% aqueous hydrochloric acid overnight at room temperature. The organic phase was separated and dried by filtration through NaCl, and the solvent was removed to yield (*meso*-tetrakis-(2,6-dibromophenyl)porphinato)chromium(III) chloride (**4**) as a green solid (90 mg). Oxo(*meso*-tetrakis(2,6-dibromophenyl)porphinato)chromium(IV) (**5**) was prepared by treatment of **4** with IBDA (3-fold excess) in reagent grade CH_2Cl_2 (5–10 mL). After a 15-min period, the solution was chromatographed on basic alumina (activity V) with purified CH_2Cl_2 . $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ (**5**), which eluted as a red band, was collected, evaporated to dryness, and recrystallized from benzene-pentane to obtain purple crystals (52 mg; 50% yield based on **3**). Visible spectra of **4** and **5** in CH_2Cl_2 were found to be identical with those previously reported.⁹

Electrochemistry. Cyclic voltammetry and controlled-potential bulk electrolysis (CPBE) were carried out as previously reported.^{9,11,16} The potentiostats used were a Bioanalytical Systems Model CV-27 voltgraph (West Lafayette, IN) or a Cypress Systems Model CYSY-1 computer-controlled electroanalysis system (Lawrence, KS). A Pt flag electrode separated from the analyte compartment by a medium porosity frit was used as the auxiliary electrode. An Ag/AgCl electrode standardized to 0.00 V vs SCE was used as the reference electrode. The potentials ($E_{1/2}$) for one-electron oxidation of (*Z*)- and (*E*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (1-*Z* and 1-*E*, respectively) were obtained with a Pt disk electrode (1 mm diameter, Cypress Systems) at [alkene] = 5.0×10^{-3} M, [TBAP] = 0.10 M, solvent CH_3CN (25 °C), and scan rate 0.5 V/s. The $E_{1/2}$ values for other alkenes were measured with a carbon microelectrode (7- μm diameter, Bioanalytical Systems) at 0.2 V/s. Controlled-potential bulk electrolytic oxidation of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ (**5**) \rightarrow $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ (**6**) was carried out with use of a platinum gauze electrode (20 \times 30 mm, 100 mesh, Aldrich) for 10 min at 1.06 V, and completion of the oxidation was confirmed by coulomb counting. The platinum gauze electrode and Ag/AgCl reference electrode were cleaned by scanning (\pm lim = 0.0–1.5 V) for 15 min in 10% HNO_3 (aq) solution prior to each electrolytic preparation of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$.

Kinetic Studies. Solutions of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ (**6**) used in the kinetic studies were prepared by dissolving TBAP (0.10 M) and **5** (1.15×10^{-4} M) in 3.0 mL of CH_2Cl_2 . After controlled-potential bulk electrolysis under Ar blowing, a 0.2-mL aliquot of the resultant $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ solution was placed in a 1.0-cm cuvette and diluted with 1.8 mL of CH_2Cl_2 . The alkene (200–5000-fold molar excess) was then added as a solid or liquid and the ensuing disappearance of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ monitored with time by repetitive scanning (500–350 nm) at 30 °C.

Reactions for product analysis were carried out at higher [$(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$] (1.15×10^{-4} M) and higher [alkene] with the same molar ratio range as employed in the kinetic studies. To a vial containing an alkene was added 2 mL of the $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ solution obtained from CPBE. The reaction vial was sealed and stirred at room temperature in the dark for 24 h. After the electrolyte and chromium porphyrin species were precipitated by the addition of 15 mL of hexane, the precipitate was removed by filtration and the filtrate concentrated at room temperature. The residue so obtained was analyzed by HPLC. Structural assignments were based on co-elution with authentic standards. The product quantitation by HPLC analysis involved integration of peaks after determining response factors with authentic standards.

Molecular Modeling Studies. Interactions of *cis*- and *trans*-alkene isomers with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ were modeled by using computer

graphics.⁵ Construction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ was based upon the X-ray coordinates of oxo(*meso*-tetra-*p*-tolylporphinato)chromium(IV), $(\text{TTP})\text{Cr}^{\text{IV}}(\text{O})$.¹⁷ The bond length of $\text{O}=\text{Cr}^{\text{V}}$ was assumed to be 1.55 Å taken from the average of two X-ray crystal structures of *N,N'*-ethylenebis(salicylidineaminato)oxochromium(V) complex, with and without axial pyridine *N*-oxide, 1.554 and 1.545 Å, respectively.¹⁸ This is very close to the $\text{O}=\text{Cr}^{\text{IV}}$ bond length in $(\text{TTP})\text{Cr}^{\text{IV}}(\text{O})$, 1.572 Å. The porphyrin ring for $(\text{TTP})\text{Cr}^{\text{IV}}(\text{O})$ is nonplanar and the Cr atom is displaced 0.469 Å above the mean plane of the four pyrrole nitrogens. Such a saddle-shaped structure of the porphyrin is very similar to that of the nitrido(porphyrinato)chromium(V) complex, in which the Cr atom is 0.42 Å above the mean plane.¹⁹ Prior to docking, the following changes were made in the template. *p*-Methyl groups on the phenyl rings in $(\text{TTP})\text{Cr}^{\text{IV}}(\text{O})$ were changed to hydrogens with C–H bond length of 1.09 Å, and *o*-bromo substituents were appended to the phenyl rings with a C–Br bond length of 1.85 Å. No axial ligand (X) was added for the model. The structure of *cis*-stilbene was taken from the X-ray structure of *cis*-dichlorostilbene (from Cambridge Database, refcod GANLAI) by replacing the two chloro substituents with two hydrogens (with a C–H bond length of 1.09 Å). Coordinates for *trans*-stilbene were obtained from the Cambridge Database (Refcod TSTILB01). *trans-β*-Methylstyrene was created by use of the program QUANTA (Polygen Corp.). All alkene structures used in docking experiments were energy minimized before use. Because the exact charge distribution in the $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ molecule is unavailable only the van der Waals energy (6–12 Lenard-Jones potential) was considered throughout the study. Due to the steric interaction of bromine atoms with pyrrole carbons, each phenyl group was rotated to a dihedral angle of about 70° with respect to the plane of the porphyrin ring to provide a minimum energy structure. Two orientations of alkene with respect to the $\text{Cr}^{\text{V}}(\text{O})$ porphyrin plane were investigated. For the first one, alkenes were positioned so that the C=C bond was parallel to the linear N–Cr–N fragment of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ ($\theta = 0^\circ$ in III). Rotation along the C=C bond was also performed to ensure a minimal steric interaction of alkene with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ before any translation. From this starting position, alkene was moved along an axis defined by the center of the C=C bond and the chromium metal ion. Interaction energies were calculated continuously with CHARMM (Polygen Corp.). The second orientation was obtained by rotating alkene 45° according to the *z* axis such that the C=C bond is parallel with the opposite meso carbons on the porphyrin plane ($\theta = 45^\circ$ in IV).

Results

The Dynamics and Products of the Reaction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with Alkenes. To obtain reproducible kinetic results $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ should be very carefully purified to remove $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$ and other impurities (Experimental Section). The CH_2Cl_2 solvent employed in bulk controlled-potential oxidation of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O}) \rightarrow (\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ must be purified according to the published method to remove trace alcohol and acid.¹¹ The second-order rate constants (k_1) for the reaction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with alkenes were determined by following the disappearance of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ at its λ_{max} of 409 nm. The change in A_{409} was found to follow the first-order rate law under the pseudo-first-order conditions of [alkene] (2.0×10^{-3}

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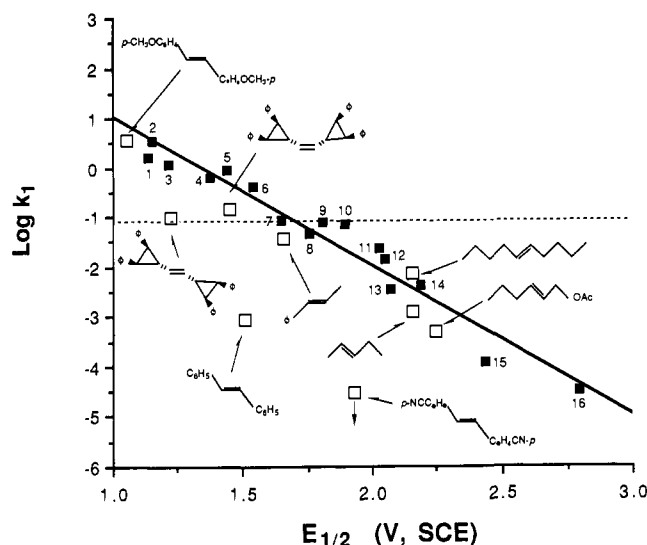


Figure 1. Plot of the log of the second-order rate constant (k_1) for reaction of a series of alkenes with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ vs the $E_{1/2}$ for $1e^-$ oxidation of the alkenes. The results as shown in open squares are from the present study. Solid squares represent the results from the previous paper.⁹ They are (1) 1,4-diphenyl-1,3-butadiene, (2) 4-methoxystyrene, (3) 1,1-diphenylethylene, (4) 4-methylstyrene, (5) 2,3-dimethyl-2-butene, (6) *cis*-stilbene, (7) styrene, (8) 4-acetoxystyrene, (9) cyclohexene, (10) norbornene, (11) *cis*-cyclooctene, (12) 4-cyanostyrene, (13) *cis*-2-pentene, (14) cyclopentene, (15) 1-hexene, and (16) 1-octene. On the intersection of the dashed line and the solid line (linear free energy line) the standard free energy (ΔG°) is equal to the free energy of activation (ΔG^\ddagger) for the reaction.⁹

to $6.3 \times 10^{-2} \text{ M}$ \gg $[(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})]$ ($1.15 \times 10^{-5} \text{ M}$) as previously reported.⁹ Determined values of k_1 are shown in Table I along with the $E_{1/2}$ values for $1e^-$ oxidation of the given alkenes. In a previous study,⁹ a linear relationship (Figure 1) was established between the log of the second-order rate constant (k_1) for alkene oxidation by $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})$ and $E_{1/2}$ for electrochemical $1e^-$ oxidation of alkenes (eq 1). The values of second-order rate constants calculated by use of eq 1 are referred to as $k_{1,\text{cal}}$. Values

$$\log k_1 = -3E_{1/2} + 4.02 \quad (1)$$

of $k_{1,\text{cal}}/k_1$ are included in Table I. The relationship of eq 1 was obtained by use of 16 *cis* or terminal alkenes (the one exception being 1,4-diphenyl-1,3-butadiene).⁹ The data points for these 16 alkenes are shown in Figure 1 as solid squares. The results from the present study for *trans*-alkenes are shown in Figure 1 as open squares. *trans-p,p'*-Dicyanostilbene exhibited no reactivity with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$. The data point for this alkene in Figure 1 indicates that the value of k_1 is less than $4 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$.

Product analysis was carried out for the reactions of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with *trans-p,p'*-dimethoxystilbene, *trans*-stilbene, and *trans-β*-methylstyrene, as well as (*Z*)- and (*E*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene. The results are shown in Table II. It was found that authentic *trans-p,p'*-dimethoxystilbene oxide decomposed in part to bis(*p*-methoxyphenyl)acetaldehyde under the HPLC conditions used.

Van der Waals Minimal Energies in the Approach of *cis*- and *trans*-Stilbenes to the Cr=O Moiety of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$. Shown in Figure 2 are the results of docking experiments in which the approach of the alkene to the reactive oxygen of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ is restricted to being directly above with the angles α equal to zero and the C=C bond aligned with the N-Cr-N fragment ($\theta = 0^\circ$). The plots in Figure 2 are of the total van der Waals energy (kcal/mol) vs the distance between the center of the C=C bond and the Cr moiety. Such van der Waals energy (6–12 Lenard-Jones potential) curves were obtained for each alkene. *cis*-Stilbene, being the smallest in dimension, can be docked closest to the active center of the oxochromium porphyrin. In comparison, *trans*-stilbene, due to the full expansion of the two phenyl rings and accompanying steric hindrance, is forced to be

Table II. Product Yields for the Oxidation of Alkenes with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$

alkenes	products (yields, %) ^a
<i>trans-p,p'</i> -dimethoxystilbene	<i>p</i> -anisaldehyde (8) bis(<i>p</i> -methoxyphenyl)acetaldehyde (65) ^b
(<i>Z</i>)-1,2-bis(<i>trans</i> -2, <i>trans</i> -3-diphenylcyclopropyl)ethene	<i>trans</i> -2, <i>trans</i> -3-diphenylcyclopropanecarboxaldehyde (50) ^c
(<i>E</i>)-1,2-bis(<i>trans</i> -2, <i>trans</i> -3-diphenylcyclopropyl)ethene	<i>trans</i> -2, <i>trans</i> -3-diphenylcyclopropanecarboxaldehyde (7) ^c
<i>trans</i> -stilbene	no oxidation product
<i>trans-β</i> -methylstyrene	benzaldehyde (20) <i>trans-β</i> -methylstyrene oxide (63)

^a Yields are based on the oxidant. ^b It was found that authentic *trans-p,p'*-dimethoxystilbene oxide decomposes in part to bis(*p*-methoxyphenyl)acetaldehyde under the HPLC conditions used. ^c Several very nonpolar products (total yields $\sim 30\%$) have been found from HPLC.

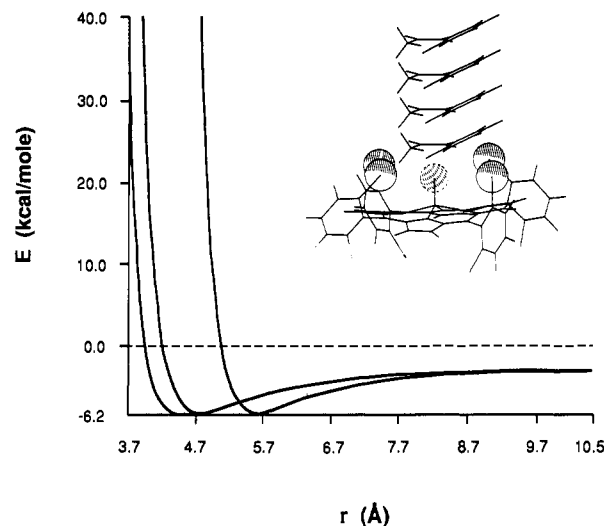


Figure 2. Energy plots of docking of alkenes onto $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$. Lennard-Jones type potential curves were obtained by plotting E , van der Waals energy, against r , the distance between the center of the C=C bond and the chromium center. Upon approaching substituted tetraphenylporphyrin, *cis*-stilbene (left curve) shows the least steric hindrance with an r_{min} of 4.55 Å (the distance between the C=C bond and the oxygen, l_{min} , is 2.98 Å). To reach an energy minimum, *trans*-stilbene (right), on the other hand, has a much larger r_{min} of 5.45 Å ($l_{\text{min}} = 3.88$ Å). *trans-β*-Methylstyrene (center), with an r_{min} of 4.70 Å ($l_{\text{min}} = 3.13$ Å), shows only slightly increased hindrance compared to that of *cis*-stilbene. The hypothetical model shows continuous motion of *trans-β*-methylstyrene approaching stationary oxochromium porphyrin (with the upper four bromine substituents as half solid spheres and the oxygen as a dashed sphere).

~ 1 Å further away from the oxygen. *trans-β*-Methylstyrene exhibits steric hindrance similar to that of *cis*-stilbene when docking to the same porphyrin.

Steric hindrance by the large bulky *o*-bromo substituents of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ plays an important role in determining the optimal angles for approach of the C=C bond to the $\text{Cr}^{\text{V}}(\text{O})$ moiety. To determine the energy minima for approach of alkenes to $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ without any restraints, detailed docking studies were carried out in which both the docking distance r and angle α were varied. For a given angle θ , the center of the C=C bond was allowed to progress along a curved trajectory drawn with a radius r with the double bond always tangent to the curvature, where r is the distance between the center of the C=C bond and the chromium. For each chosen value of α between 0° and 39° , the distance r varied from 3.5 to 9.35 Å (VI). Interaction energies, for alkenes at various distances from the Cr^{V} moiety, were computed at intervals of 1° . Forty different docking modes for stilbene were used, and the three-dimensional energy contours thus generated are shown in Figure 3. The calculated distances between the C=C bond and the oxygen at the lowest energy minima

Table III. The Distance and Angles for the Lowest Energy Minima Position from the Docking of the Alkenes on $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})^{\text{a}}$

alkenes	θ , deg	α , deg	r_{min} , Å	l_{min} , Å	$E_{\text{min}}^{\text{b}}$, kcal/mol
<i>cis</i> -stilbene	0	0	4.55	2.98	-6.50
	45	24	4.10	2.81	-7.63
<i>trans</i> -stilbene	0	0	5.45	3.88	-6.34
	45	6	5.60	4.05	-6.33
<i>trans</i> - β -methylstyrene ^c	0	0	4.70	3.13	-6.00
	45	0	4.80	3.23	-5.95

^a For the definition of the distance and angles, see text. ^b Only van der Waals energy was considered in the calculation. ^c For *trans*- β -methylstyrene no effort has been made to search the optimum α .

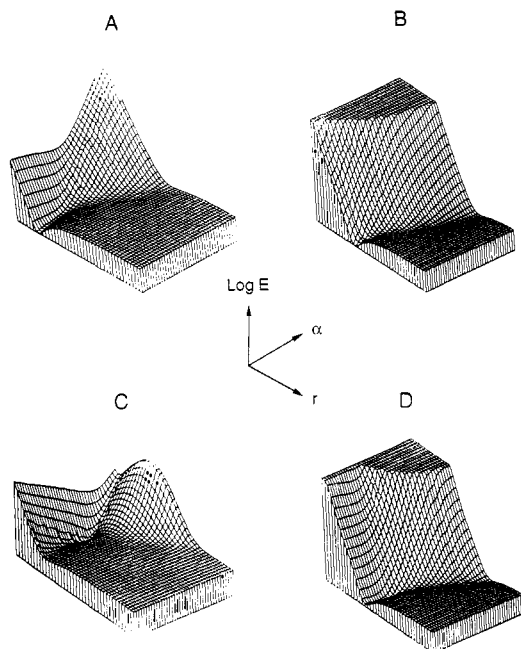


Figure 3. Three-dimensional energy plots of *cis*- and *trans*-stilbene docking onto $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$. For clarity, $\log E$ is plotted against r , α , the maximum energy cutoff, is 100 000 kcal/mol, and the minimum energies in all cases are around -7 kcal/mol. The distance r spans between 3.5 and 9.35 Å with intervals of 0.15 Å, and the center of the C=C bond was allowed to progress along a curved trajectory, with the C=C bond tangent to the curvature of 0° to 39° with the intervals of 1° . (A) 3-D energy surface of *cis*-stilbene with $\theta = 0^\circ$ relative to the porphyrin. (B) Similar energy surface obtained with *trans*-stilbene with $\theta = 0^\circ$. In both cases, the energy minima are found when $\alpha = 0^\circ$ but r_{min} is ~ 1 Å apart as described in Figure 2. After a 45° rotation of angle θ , the energy surface of *cis*-stilbene, shown in C, shows a deep valley around $\alpha = 24^\circ$ and the r_{min} is 4.10 Å ($l_{\text{min}} = 2.81$ Å). For *trans*-stilbene (D) the energy minimum shifts only a little to $\alpha = 6^\circ$ and $r_{\text{min}} = 5.60$ Å ($l_{\text{min}} = 4.05$ Å).

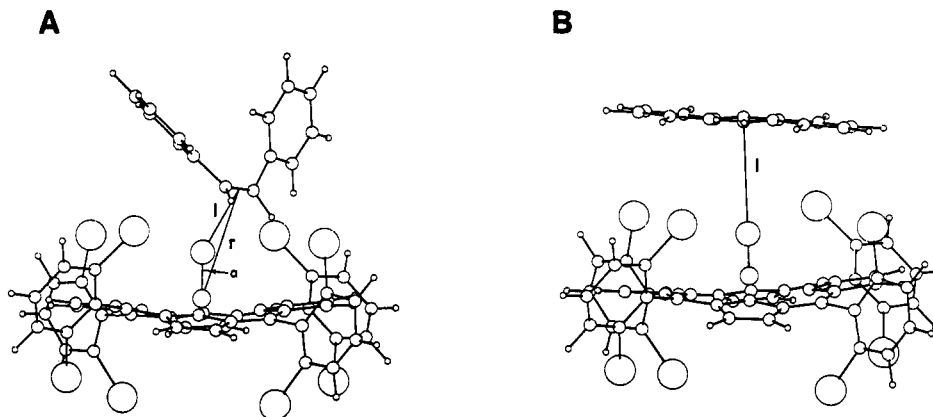
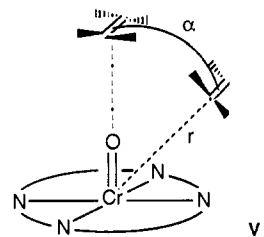


Figure 4. The lowest energy minima positions from the docking experiments: (A) *cis*-stilbene on $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with $\theta = 45^\circ$, $\alpha = 24^\circ$, $r_{\text{min}} = 4.10$ Å, and $l_{\text{min}} = 2.81$ Å; (B) *trans*-stilbene on $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with $\theta = 0^\circ$, $\alpha = 0^\circ$, $r_{\text{min}} = 5.45$ Å, and $l_{\text{min}} = 3.88$ Å.



positions (l_{min}) are given in Table III and Figures 2 and 3. Plots A and B in Figure 3 show *cis*- and *trans*-stilbene, with the C=C bond parallel with the N-Cr-N fragment ($\theta = 0^\circ$), docking to oxochromium porphyrin with varying angle α , respectively. In Figure 3A, the minimum in potential energy, -6.50 kcal/mol, occurs when *cis*-stilbene lies 2.98 Å away from the oxygen (l_{min}) with $\alpha = 0^\circ$. Any deviations in distance or angle resulted in higher van der Waals energy. For *trans*-stilbene, the minimum steric hindrance is also obtained with $\alpha = 0^\circ$ but at a distance 0.90 Å further from the oxygen than with *cis*-stilbene. The minimal van der Waals energy for the *trans* isomer is 0.16 kcal/mol greater than that of the *cis* isomer. No slight changes in angle α are allowed for *trans*-stilbene without serious steric clashes with the *o*-bromo substituents of the tetraphenylporphyrin. Similar dockings were performed with the C=C bond aligned at a bisect of the 90° angle formed between Cr^V and adjacent pyrrole nitrogens ($\theta = 45^\circ$). The results are shown in Figure 3, C and D. A comparison of plot C with plot A in Figure 3 shows that when $\theta = 45^\circ$ the energy minimum for *cis*-stilbene falls at $l_{\text{min}} = 2.81$ Å away from the oxygen with $\alpha = 24^\circ$. At this position, *cis*-stilbene has a -7.63 kcal/mol interaction energy with the oxometalloporphyrin. For *trans*-stilbene (Figure 3D), a shallow energy valley occurs around $\alpha = 6^\circ$ and at a distance $l_{\text{min}} = 4.05$ Å. The minimum energy of -6.33 kcal/mol is comparable with that determined (Figure 3B) when the *trans*-stilbene double bond is parallel to the line between N-Cr-N. In all cases, an angle $\alpha > 39^\circ$ seems to be energetically improbable. In summary, the lowest energy minima for the docking of *cis*- and *trans*-stilbene are those shown in Figure 4, A and B, respectively. The distance and angles for the various energy minima are summarized in Table III.

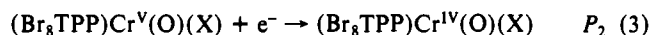
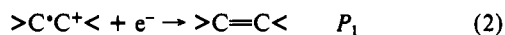
Discussion

In the present study we have determined the second-order rate constants and the products formed in the reactions of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with a number of *trans*-alkenes (dry CH_2Cl_2). These results have been combined with computer graphics determination of the trajectories for approach of alkene to the oxygen of the Cr^V(O) moiety on the basis of van der Waals interactions. Our objective has been to further the knowledge of the reaction mechanisms involved and to determine the importance of the various factors which control the magnitude of the rate constants for *trans*-alkene oxidation (see Introduction).

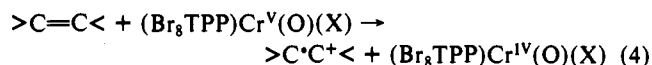
Dynamics for and Products from the Reactions of *trans*-Alkenes with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$. Of considerable assistance to this study is the previous finding that the log of the second-order rate constants (k_1) for *cis*-alkene oxidation by $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ is a linear function of the alkene $1e^-$ oxidation potential (Figure 1).⁹ The use of this linear free-energy relationship allows the quantification of steric factors brought about by a trans disposition of substituent groups through comparison of determined values of k_1 and values ($k_{1,\text{cal}}$) calculated from eq 1.

A finding of considerable interest is that *trans*-alkenes do not generally react with the sterically restricted $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with second-order rate constants (k_1) that are appreciably less than those predicted from electronic effects ($k_{1,\text{cal}}$). Thus (Table I and Figure 1), values of k_1 for the oxidation of *trans*-*p,p'*-dimethoxystilbene, *trans*- β -methylstyrene, *trans*-2-pentene, *trans*-5-decene, and *trans*-2-hexenyl acetate are very close to the values of $k_{1,\text{cal}}$ anticipated (eq 1) from their electron availability. Therefore, there can be little or no steric hindrance for these alkenes in the rate-limiting step. A significant steric effect is found only for *trans*-stilbene, *trans*-*p,p'*-dicyanostilbene, and (*E*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (1-*E*). The influence of this steric effect is discernable not only in $k_{1,\text{cal}}/k_1$ (Table I and Figure 1) but also from product analysis (Table II). Especially, for *trans*-stilbene no oxidation products could be detected. The value of $\log k_1$ plotted in Figure 1 for *trans*-stilbene can be considered as a maximum value because, under the conditions employed, the pseudo-first-order rate of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ disappearance was not greatly different in the presence and absence (spontaneous disappearance of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ to give $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$) of *trans*-stilbene.⁹ The fact that *trans*-stilbene cannot be epoxidized was also found when using $(\text{Br}_8\text{TPP})\text{Fe}^{\text{III}}(\text{Cl})$ and perfluoroiodosylbenzene.⁵

The lack of a steric effect (dynamics and products) in the epoxidation of *trans*-*p,p'*-dimethoxystilbene with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ deserves comment because the X-ray structures of *trans*-*p,p'*-dimethoxystilbene²⁰ and *trans*-stilbene²¹ are comparable. They have a similar planar structure and the same C=C bond length in the solid state (1.316 and 1.313 Å for *trans*-*p,p'*-dimethoxystilbene and *trans*-stilbene, respectively). The potentials P_1 of eq 2 are provided in Figure 1 while the potential P_2 (eq 3) is equal to 0.88 V (SCE).⁹ The value of the standard free energy



(ΔG°) for the reaction of eq 4 is equal to unity when $P_1 = 0.88$ V. Thus the $1e^-$ oxidations of the alkenes of Figure 1 (eq 4) are all endergonic. For *cis*-stilbene and *trans*-stilbene the oxidation



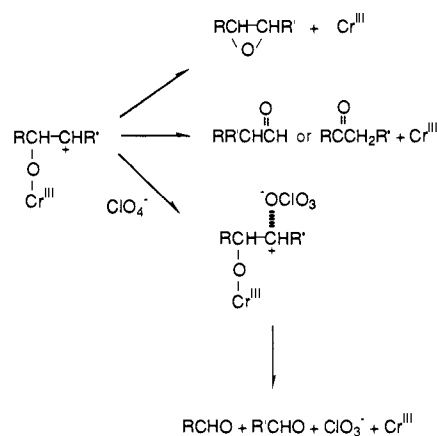
by $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ is endergonic by 0.76 and 0.63 V, respectively.²² For *trans*-*p,p'*-dimethoxystilbene the $1e^-$ oxidation in eq 4 is endergonic by only 0.17 V. We have proposed the mechanism of Scheme I to explain the formation of epoxide and other products.⁹ In Scheme I the formation of a CT complex between alkenes and $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ is rate-limiting. In Figure 1, for those alkenes whose values of P_1 are to the left of the intersection of the dashed line and linear free energy line $\Delta G^\circ < \Delta G^\circ$ so that $1e^-$ transfer (eq 4) is allowed along the reaction path to products. For alkenes whose P_1 values are to the right of this intersection $\Delta G^\circ > \Delta G^\circ$ and $1e^-$ transfer along the reaction path is not allowed.⁹ Therefore, $1e^-$ transfer (eq 4) along the

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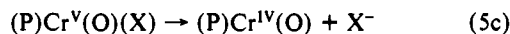
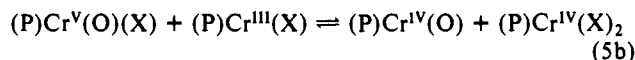
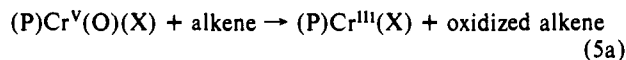
(22) In a previous paper, ref 9, we used $E_{1/2} = 1.54$ V (SCE) for *cis*-stilbene from the literature (Catalan, C. E.; Ortíz de Montellano, P. R. *Biochemistry* **1987**, 26, 8373.), in which, however, the experimental conditions have not been given for the measurement. In this study we measured $E_{1/2}$ for *cis*-stilbene under the conditions shown in the experimental section is 1.64 V (SCE).

Scheme II



reaction coordinate is allowed with *cis*- and *trans*-stilbene and particularly *trans*-*p,p'*-dimethoxystilbene. The distance of approach of reactants is of importance to an electron-transfer reaction. The calculated van der Waals energy minimum for approach of *trans*-stilbene to $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ occurs (Figure 4B) at a distance of the center of the C=C bond to the oxygen in the $\text{Cr}^{\text{V}}\text{O}$ moiety of 3.98 Å which is well within the distance for an electron transfer.^{23,24} Since the potential P_1 for *trans*-*p,p'*-dimethoxystilbene is favorable for an electron transfer this may be the mode of its reaction with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$. Another mode of reaction which should be considered would involve the docking of a *p*-methoxybenzene ring of the alkene to $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ in rate-limiting CT complex formation. (In separate experiments, anisole does not react with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$.) *p*-Anisaldehyde and bis(*p*-methoxyphenyl)acetaldehyde are the isolatable products of *trans*-*p,p'*-dimethoxystilbene oxidation (Table II) and epoxide is not produced. According to our unified mechanism (Scheme I) both *p*-anisaldehyde and bis(*p*-methoxyphenyl)acetaldehyde arise by the coupling of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})(\text{X}) + >\text{C}^*\text{C}^* <$ to form a cationic intermediate followed by a mechanism as shown in Scheme II (vide infra). A similar lack of a trans steric effect, which may be attributed to a very favorable electron transfer from alkene to $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, is apparent in the comparison of k_1 and $k_{1,\text{cal}}$ for 1,4-diphenyl-1,3-butadiene (Figure 1).⁹

The reactions of eq 5 are known to be involved in the reaction of an alkene with a $(\text{Porph})\text{Cr}^{\text{V}}(\text{O})$ species in CH_2Cl_2 .^{9,11} The rate-limiting step is (5a) while the disproportionation reaction (5b) is very rapid. The spontaneous decomposition (solvent



oxidation, etc.) of (5c) is only important in determining product yields for those alkenes with $E_{1/2} > +2.0$ V. One can compute the theoretical yield of "oxidized alkene" products by computer simulation of the time course for disappearance and appearance of the Cr^{V} , Cr^{IV} , and Cr^{III} species. The calculated and experimentally determined total yields of "oxidized alkene" products are in reasonable agreement {1,1-diphenylethylene, 19% epoxide + 47% diphenylacetaldehyde (calc 63%); *cis*-stilbene, 21% epoxide + 52% diphenylacetaldehyde (calc 68%); styrene, 59% epoxide + 6% phenylacetaldehyde (calc 61%); norbornene, 63% exo epoxide (calc 64%); 1-octene, 3.3% 1,2-epoxyoctene (calc 2.8%)}.⁹ From these findings, the expected percentage yield of "oxidized alkene" products from the alkenes of this study is ($64 \pm 4\%$). *trans*-*p,p'*-Dicyanostilbene does not react with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, *trans*-stilbene provides no detectable "oxidized alkene"

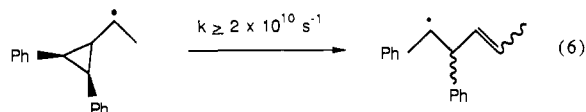
(23) Shimada, K.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, 97, 3313.

(24) Shimada, K.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, 97, 3321.

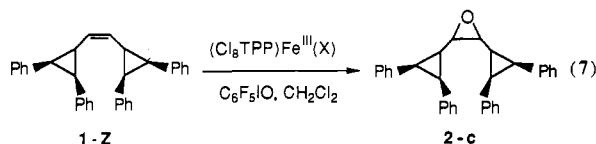
products, while *trans-p,p'*-dimethoxystilbene provides 73% "oxidized alkene" products.

Comparison of $k_{1,cat}/k_1$ values and products as well as trajectories for *trans*-stilbene, *trans-p,p'*-dicyanostilbene, and *trans-p,p'*-dimethoxystilbene substantiate our previous conclusion⁹ that the oxidation (epoxidation) of alkenes by $(Br_8TPP)Cr^V(O)(X)$ can involve $1e^-$ transfer for only those alkenes of low potential (above the dashed line of Figure 1). Also, as previously discussed, the slope of the linear free-energy plot of Figure 1 is much smaller than expected for a rate-limiting $1e^-$ transfer but reasonable for rate-limiting CT complex formation. The latter conclusion, as previously explained,^{5,9} also holds for alkene oxidation by hypervalent iron-oxo porphyrin.

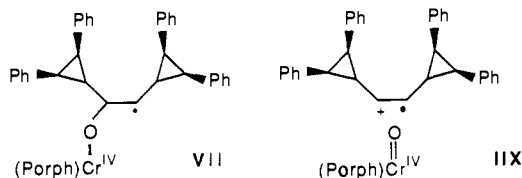
Both (*E*)- and (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1-E** and **1-Z**, respectively) were designed to be (and are) very efficient radical traps via the cyclopropylcarbinyl to homoallylcarbinyl rearrangement (eq 6).¹² It has been found that (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene can



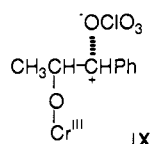
be oxidized by C_6F_5IO and iron porphyrins to *cis*-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)oxirane (**2-c**) in a quantitative yield (eq 7), and this result excludes a radical mechanism for epoxidation in this system.¹² On the other hand, a radical mechanism



of the epoxidation of alkenes with *t*-BuOOH in the presence of iron porphyrins has been established by a study using such a radical trap since a ring-opened product, which arises from the cyclopropylcarbinyl to homoallylcarbinyl rearrangement, was found as a major product from the reaction.²⁵ Oxidation of (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene provided *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde in 50% yield which may be compared to the ~64% anticipated yield. No epoxide was obtained. Thus, the major reaction of **1-Z** does not involve radical VII and, most likely not, radical carbocation VIII intermediates.²⁶ The oxidation of **1-E** exhibits a marked kinetic *trans* steric effect which is reflected in the isolation of only 7% of *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde as a



product. Several very nonpolar compounds (unknown structures) were also found from HPLC analysis. Similar nonpolar compounds were obtained as minor products in oxidations by perfluoriodosylbenzene with iron(III) and manganese(III) porphyrins as catalysts.¹² Formation of *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde may be explained by the mechanism shown in Scheme II which involves nucleophilic attack of ClO_4^- on carbocation intermediate. A similar oxidation producing



benzaldehyde (Table II) occurs with *trans*- β -methylstyrene. Benzaldehyde is the expected product since the intermediate carbocation would be created at the benzylic carbon (IX). The involvement of ClO_4^- as an oxidant in the formation of aldehyde by oxidative cleavage of the C-C bond has been established from the observation that replacement of tetrabutylammonium perchlorate by tetrabutylammonium tetrafluoroborate greatly reduces the yield of aldehyde product.²⁶

Van der Waals Minimal Energy Calculations for the Approach of Alkene to the $Cr^V(O)$ Moiety of $(Br_8TPP)Cr^V(O)(X)$. In previous studies⁵ we have employed computer docking experiments with an iron-oxo porphyrin π -cation radical [$(^+Br_8TPP)Fe^{IV}(O)(X)$] and *cis*-stilbene, 2,3-dimethyl-2-butene, norbornene, and 1-hexene (i) to assess the proposed formation of metallaoxetane intermediates on the path to epoxide formation and (ii) to obtain preferred trajectories of approach of the C=C bond to the oxygen of the $Fe^{IV}(O)$ moiety. Metallaoxetane intermediates were excluded on the basis that high yields of epoxide were obtained though the bulky *o*-bromo substituents would require metallaoxetane bond lengths for Fe-O and Fe-C to be about 3 Å. Also, we showed that the sterically allowed trajectories for epoxidation required approach of the alkene $>C=C<$ to the oxygen of the $Fe^{IV}(O)$ moiety with a moderate optimum angle α , as shown in V. The angle α may change for different alkenes, but the alkenes could not approach the Fe-O bond as in the side-on model I.

In the molecular modeling studies described in this report, *trans*-stilbene was found to have a much larger steric hindrance than both *cis*-stilbene and *trans*- β -methylstyrene, shown in Figure 2, with docking of these alkenes directly on the top of the activated oxygen ($\theta = 0^\circ$ and $\alpha = 0^\circ$). The closest distance that the nucleophilic C=C bond of *trans*-stilbene can approach the electrophilic oxygen of $(Br_8TPP)Cr^V(O)(X)$ is 0.90 Å longer than that for the *cis*-stilbene. This steric difference is even more enhanced when α varies away from 0° (Figure 3, A and B). When $\theta = 45^\circ$, *cis*-stilbene can be docked to the porphyrin from a range of angle α with less steric hindrance while docking of *trans*-stilbene is still restricted at $\alpha = 0^\circ$ with higher van der Waals energy. The stereoselectivity of *cis*- over *trans*-stilbene can be considered to be understood.

Interestingly, *trans*- β -methylstyrene shows a steric effect similar to that of *cis*-stilbene (l_{min} of 3.13 versus 2.98 Å) rather than *trans*-stilbene ($l_{min} = 3.88$ Å). This finding is consistent with the results from the kinetic study (Figure 1) and strongly suggests that both configuration and substituent size of the alkenes are important in determining the steric hindrance of the epoxidation reaction. The docking results presented here also support previous studies which show a much larger steric effect of *trans*-stilbene than other *trans*-alkenes in the epoxidation catalyzed by iron porphyrin.¹

The formation of a charge-transfer complex usually requires only a moderate separation of the two interacting moieties. The critical distance for CT complex to occur was reported to be 3.5 Å or less,²⁴ while electron-transfer reaction can proceed at a relatively long distance, ca. 7–9 Å or more.²³ As shown in Figures 2 and 3, the closest distance between *cis*-stilbene and the oxygen in porphyrin (l_{min}) is less than 3 Å, and for *trans*-stilbene it is ~4 Å. From the product analysis, *cis*-stilbene is quantitatively oxidized but *trans*-stilbene is not oxidized. These results are in accord with a mechanism involving rate-limiting formation of a CT complex. The mechanism of Scheme I is also applicable to alkene epoxidation catalyzed by iron porphyrins since similar stereoselectivity is found in both iron and chromium systems.

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