

Is a Linear Relationship between the Free Energies of Activation and One-Electron Oxidation Potential Evidence for One-Electron Transfer Being Rate Determining?

Intermediates in the Epoxidation of Alkenes by Cytochrome P-450 Models. 4. Epoxidation of a Series of Alkenes by Oxo(*meso*-tetrakis(2,6-dibromophenyl)porphinato)-chromium(V)

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Abstract: The mechanism of reaction of (porphyrin)Cr^V(O)(X) with alkenes has been investigated by combining the electrochemical determinations of redox potentials with the tools of kinetics and product identification. Studies include the following: (i) the dynamics of the reaction of oxo(*meso*-tetrakis(2,6-dibromophenyl)porphinato)chromium(V) ((Br₈TPP)Cr^V(O)(X)) with 16 alkenes (1,4-diphenyl-1,3-butadiene, 4-methoxystyrene, 1,1-diphenylethylene, 4-methylstyrene, 2,3-dimethyl-2-butene, *cis*-stilbene, styrene, 4-acetoxystyrene, cyclohexene, norbornene, *cis*-cyclooctene, 4-cyanostyrene, *cis*-2-pentene, cyclopentene, 1-hexene, 1-octene); (ii) the dynamics of the reaction of norbornene with five (porphyrin)Cr^V(O)(X) species (oxo(*meso*-tetraphenylporphinato)chromium(V), oxo(*meso*-tetrakis(2,4,6-trimethylphenyl)porphinato)chromium(V), oxo(*meso*-tetrakis(2,6-dichlorophenyl)porphinato)chromium(V), oxo(*meso*-tetrakis(2,6-difluorophenyl)porphinato)chromium(V), and oxo(*meso*-tetrakis(2,6-dibromophenyl)porphinato)chromium(V)). Alkenes were selected on the basis of their 1e oxidation potential so as to cover the widest range of $E_{1/2}$ possible (1.14–2.80 V (SCE)), and the 1e oxidation potentials for the (porphyrin)Cr^V(O)(X) varied from 0.790 to 0.975 V (SCE). Standard solutions of (porphyrin)Cr^V(O)(X) were obtained by controlled-potential bulk electrolysis of the corresponding (porphyrin)Cr^{IV}(O) and used in the kinetic (CH₂Cl₂ solvent, 30 °C) and product studies. The time course for the change in concentration of (Br₈TPP)Cr^V(O)(X), (Br₈TPP)Cr^{IV}(O), and (Br₈TPP)Cr^{III}(X) was simulated for the reaction of (Br₈TPP)Cr^V(O)(X) with selected alkenes possessing "low, medium, and high" oxidation potentials. The time dependence of [(Br₈TPP)Cr^V(O)(X)], [(Br₈TPP)Cr^{IV}(O)], and [(Br₈TPP)Cr^{III}(X)] as well as the [alkene oxidation products] could be accurately fit to a scheme involving the following: (i) bimolecular reaction of alkene with (Br₈TPP)Cr^V(O)(X) to provide alkene oxidation product + (Br₈TPP)Cr^{III}(X); (ii) reversible comproportionation of (Br₈TPP)Cr^V(O)(X) + (Br₈TPP)Cr^{III}(X) to provide (Br₈TPP)Cr^{IV}(O) + (Br₈TPP)Cr^{IV}(X)₂; (iii) a spontaneous reversion (due to oxidation of solvent or solutes) of (Br₈TPP)Cr^V(O)(X) to (Br₈TPP)Cr^{IV}(O). The remainder of the alkene oxidations were followed by the more simplistic procedure of following the disappearance of (Br₈TPP)Cr^V(O)(X). The second-order rate constants (k_1) determined by either method were found to be in agreement. For about half the alkenes studied, the standard free energies for 1e oxidation by (Br₈TPP)Cr^V(O)(X), to provide alkene-derived π cation radicals (calculated from the potentials for 1e reduction of (Br₈TPP)Cr^V(O)(X) and 1e oxidation of the alkenes to π cation radicals), exceed the free energies of activation for epoxidation of alkenes by (Br₈TPP)Cr^V(O)(X). A unified mechanism of epoxidation involving rate-determining formation of alkene-derived π -cation-radical intermediate is deemed unlikely. The slopes of linear plots of log k_1 values vs $E_{1/2}$ when norbornene was the substrate with a series of (porphyrin)Cr^V(O)(X) oxidants (slope = 9.1 V⁻¹) and when (Br₈TPP)Cr^V(O)(X) was the oxidant with a series of alkenes (slope = -3 V⁻¹) are in accord with rate-determining formation of a charge-transfer (CT) complex. The CT complex may then break down in non-rate-determining steps to directly form epoxide + chromium(III) species, to yield a Cr^{III}-O-C-C⁺ carbocation or, for those alkenes with $E_{1/2}$ less positive than ca. 1.7 V (SCE), an alkene-derived π cation radical and a chromium(IV) species. For the epoxidations with (Br₈TPP)Cr^V(O)(X), there exists a linear free-energy relationship of log k_1 and σ^+ (i.e., $E_{1/2}$ is a linear function of σ^+). The value of ρ^+ for the epoxidation of substituted styrenes (-1.9) by (Br₈TPP)Cr^V(O)(X) when compared to literature values supports a transition state with little carbocation character, which is in accord with the developing charge transfer in the critical transition state.

The ability to determine the second-order rate constants for the epoxidation of alkenes by following the direct reaction of oxochromium(V) porphyrin and alkene along with the availability of the 1e redox potentials of reactants provides a unique opportunity to probe the mechanism of the epoxidation reaction.¹ In particular, one may decide if a discreet alkene-derived π cation radical may serve as an intermediate in a unifying mechanism for epoxidation. We have now determined the second-order rate constants for the following: (1) the reaction of oxo(*meso*-tetraphenylporphinato)chromium(V), oxo(*meso*-tetrakis(2,4,6-trimethylphenyl)porphinato)chromium(V), oxo(*meso*-tetrakis(2,6-dichlorophenyl)porphinato)chromium(V), oxo(*meso*-tetrakis(2,6-difluorophenyl)porphinato)chromium(V), and oxo(*meso*-tetrakis(2,6-dibromophenyl)porphinato)chromium(V) with norbornene; (2) the reaction of oxo(*meso*-tetrakis(2,6-dibromo-

phenyl)porphinato)chromium(V) with 1,4-diphenyl-1,3-butadiene, 4-methoxystyrene, 1,1-diphenylethylene, 4-methylstyrene, 2,3-dimethyl-2-butene, *cis*-stilbene, styrene, 4-acetoxystyrene, cyclohexene, norbornene, *cis*-cyclooctene, 4-cyanostyrene, *cis*-2-pentene, cyclopentene, 1-hexene, and 1-octene. The reversible 1e potentials for the couples (Porph)Cr^{IV}(O)/(Porph)Cr^V(O)(X) vary from 0.790 to 0.975 V (SCE) and the potentials for the couples alkene/alkene π cation radical range from 1.14 to 2.80 V (SCE). From kinetic and thermodynamic constants we conclude that the rate-determining step in alkene epoxidation by (Porph)Cr^V(O)(X) involves the formation of a complex of reactants with a small degree of charge transfer.

Experimental Section

Materials. The solvent, CH₂Cl₂, was purified as described previously.¹ Tetrabutylammonium perchlorate (TBAP) and iodobenzene diacetate (IBDA) were purchased from Aldrich and used as received. (IBDA was stored at 4 °C.) All alkenes were purchased from commercial vendors.

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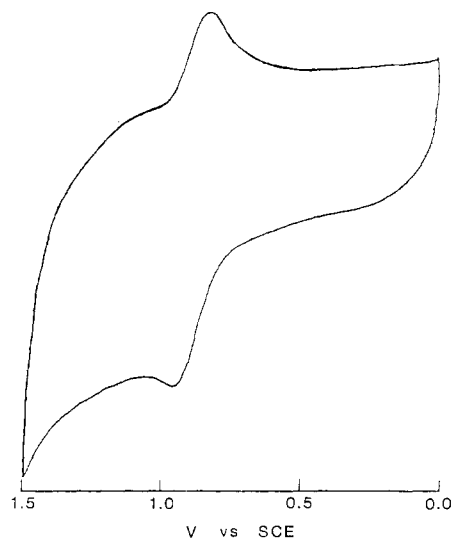


Figure 1. Cyclic voltammogram of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ (1.0×10^{-3} M) in CH_2Cl_2 at 25°C taken with a glassy-carbon electrode vs Ag/AgCl reference (0.0 V vs SCE) electrode. Conditions: 0.01 M TBAP; $\pm\text{Lim}$: 0.0–1.5 V; scan rate, 100 mV/s. $E_{1/2} = 0.880$ V.

Norbornene, *cis*-stilbene, cyclohexene, and *cis*-cyclooctene were purified as previously described.¹ All other alkenes and epoxide standards were purified by column chromatography and vacuum transfer or recrystallization. **meso-Tetrakis(2,6-dibromophenyl)porphine (1)** was synthesized as recently reported.² **Meso-(Tetrakis(2,6-dibromophenyl)porphinato)chromium(III) chloride (2)** was prepared by metalation of the free base (**1**) (100 mg, 0.08 mmol) with chromium(II) chloride (five 1-g portions) in a refluxing mixture of DMF/toluene (4/1). After addition of CrCl_2 , the solvent was slowly distilled off to near dryness. The resulting products were taken up in CH_2Cl_2 , the insoluble chromium salts were removed by filtration, and the mixture was column chromatographed on neutral alumina (activity $\text{III}^{1/2}$). The unreacted **1** was eluted first with CH_2Cl_2 followed by elution of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$ (**2**), as a green band, with CH_2Cl_2 /methanol (96/4). Purification of **2** was accomplished by oxidation with IBDA to give $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ (**3**), which was chromatographed (vide infra) and converted back to pure **2** by reaction with methanolic CH_2Cl_2 . Visible spectrum of **2** (CH_2Cl_2) [λ_{max} , nm (log ϵ): 366 (4.28), 393 (4.44), 449 (5.21), 564 (3.95), 599 (3.72)]. **Oxo(meso-tetrakis(2,6-dibromophenyl)porphinato)chromium(IV) (3)** was prepared by treatment of **2** 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 CH_2Cl_2 . $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ (**3**), which eluted as a red band, was collected, evaporated to dryness, and recrystallized from benzene/pentane to obtain deep purple crystals (21.3 mg; 20.2% yield based on **1**). Visible spectrum of **3** (CH_2Cl_2) [λ_{max} , nm (log ϵ): 375 (4.26), 431 (5.08), 549 (3.98), 582 (3.65)].

Instrumentation. UV-vis spectral measurements and repetitive scan experiments were carried out using the same equipment reported earlier.¹

Electrochemistry. Cyclic voltammetry and controlled-potential bulk electrolysis were carried out as previously reported¹ with $[(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})] = 1.0 \times 10^{-3}$ M; [TBAP] = 0.10 M; solvent, CH_2Cl_2 (25°C);

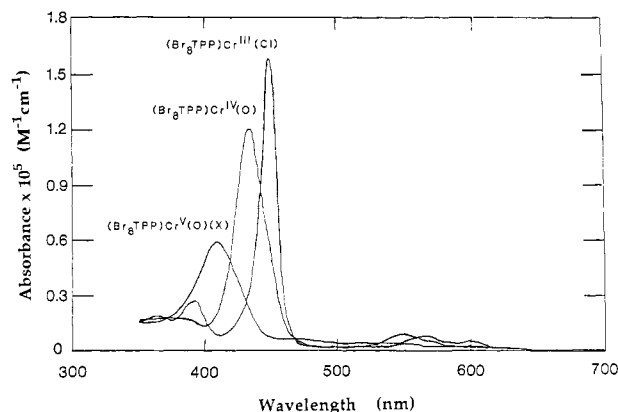


Figure 2. UV-vis spectra of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$, and $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$ (extinction coefficient vs nm).

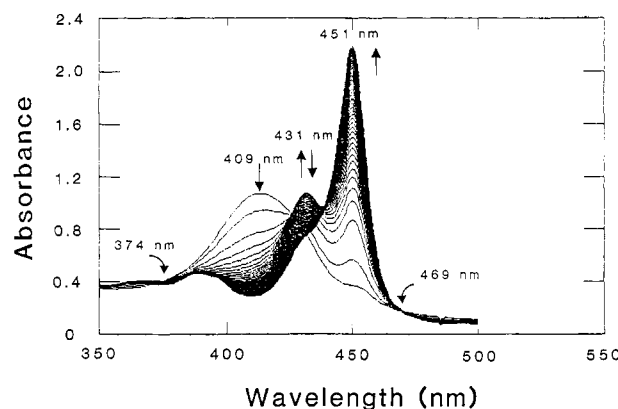


Figure 3. Repetitive scan of the reaction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ (1.15×10^{-5} M) with norbornene (6.0×10^{-2} M) at 30°C . Spectral changes of the $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ (409 nm), $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ (431 nm), and $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$ (451 nm) species are indicated. Isosbestic points are shown by curved arrows.

scan rate, 0.10 V/s. Cyclic voltammograms were obtained with a glassy-carbon electrode or a carbon microelectrode referenced to a Ag/AgCl electrode standardized to 0.00 V vs SCE. Controlled-potential bulk electrolysis of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ (**3**) was carried out using a platinum gauze electrode for a period of 1 h. The platinum gauze electrode and Ag/AgCl reference electrode were cleaned by scanning ($\pm\text{Lim} = 0.0$ –1.5 V) for 15 min in 10% $\text{HNO}_3(\text{aq})$ solution prior to each electrolytic preparation of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$.

Kinetic Studies. Solutions of **4** used in the kinetic studies were prepared by dissolving TBAP (0.10 M) and the porphyrin (1.15×10^{-4} M) in 3.0 mL of CH_2Cl_2 . After controlled-potential bulk electrolysis, a 200- μL 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 . A known concentration of alkene (300–2800-fold molar excess) was then added and the ensuing reaction monitored with time by repetitive scanning (500–350 nm) or by change in absorbance vs time at the λ_{max} (409 nm) of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$.

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] (same molar ratio range as kinetic studies) in 1.0-mm cuvettes and monitored by repetitive spectral scanning (500–350 nm) to completion of the reaction. Product yields were determined by using the spent reaction solutions. The methods for GC and HPLC product analysis have been described previously.¹

Results

All kinetic (30°C) and electrochemical (25°C) studies were carried out in CH_2Cl_2 . The cyclic voltammogram (Figure 1) of oxo(*meso*-tetrakis(2,6-dibromophenyl)porphinato)chromium(V) ($(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$; $\text{X}^- = \text{ClO}_4^-$) shows chemical and electrochemical reversibility for the couple $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})/(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ with $E_{1/2}$ (SCE) of 0.880 V with a glassy-carbon electrode (scan rate 100 mV/s) and 0.850 V by use of a carbon microelectrode (scan rate 20 mV/s). For bulk electrolytic controlled-potential oxidation of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$, to prepare

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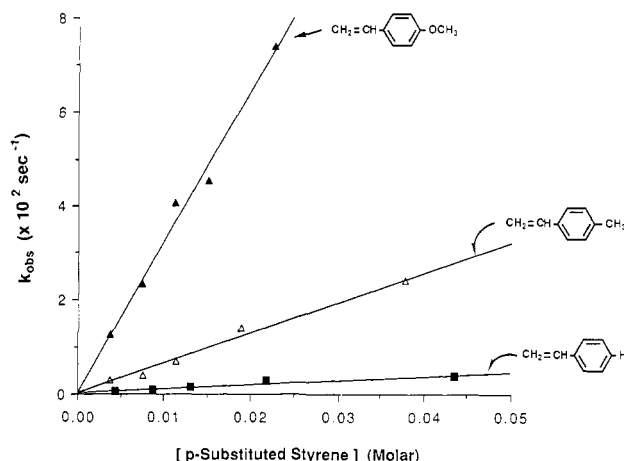


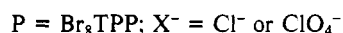
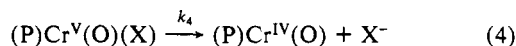
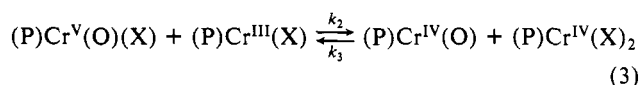
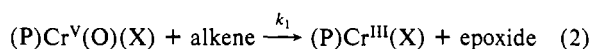
Figure 4. Plot of the observed pseudo-first-order rate constant [$k_{\text{obsd}} (\times 10^{-2} \text{ s}^{-1})$] for the disappearance of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ vs the concentrations of styrene, 4-methylstyrene, and 4-methoxystyrene (30 °C).

$(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, the potential was set at 1.04 V (vs SCE) (eq 1). The visible spectra of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ ($\xrightarrow{-1e}$) $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ (1)

$\text{Cr}^{\text{IV}}(\text{O})$, and $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$ are shown in Figure 2. The Soret peaks are characterized as follows: $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ (λ_{max} 409 nm; $\epsilon = 5.98 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ (λ_{max} 431 nm; $\epsilon = 1.2 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), and $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$ (λ_{max} 449 nm; $\epsilon = 1.62 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$).

Reactions of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with 1,4-Diphenyl-1,3-Butadiene, 4-Methoxystyrene, 1,1-Diphenylethylene, 4-Methylstyrene, 2,3-Dimethyl-2-butene, *cis*-Stilbene, Styrene, 4-Acetoxy-styrene, Cyclohexene, Norbornene, *cis*-Cyclooctene, 4-Cyanostyrene, *cis*-2-Pentene, Cyclopentene, 1-Hexene, and 1-Octene. Addition of norbornene ($6.0 \times 10^{-2} \text{ M}$) to a solution of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ ($1.15 \times 10^{-5} \text{ M}$) is followed (Figure 3) by a continual decrease in the Soret absorbance of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ (409 nm), which gives way to the Soret absorbances of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ (431 nm) and $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$ (451 nm) with isosbestic points at 374 and 469 nm. Formation of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{X})$ occurs on reaction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with alkene and $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ arises on comproportionation of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$ with remaining $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ (Scheme I). Similar spectral changes are seen in the reaction of other alkenes with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$. As expected, with the more reactive alkenes there is formed less $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ and more $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{X})$.

Scheme I



The disappearance of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with time followed the first-order rate law under the pseudo-first-order conditions of $[\text{alkene}] (3.0 \times 10^{-3} \text{--} 6.0 \times 10^{-2} \text{ M}) \gg [(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})] (1.15 \times 10^{-5} \text{ M})$. Plots of k_{obsd} vs $[\text{alkene}]$ for the reaction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with seven different alkenes are shown in Figures 4 and 5. Examination of the plots shows that k_{obsd} is linearly dependent upon $[\text{alkene}]$. The slopes of such plots are equal to the second-order rate constants (k_1) for reaction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with alkene. There was never observed a saturation of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ by alkene. Values of k_1 , so determined, are as follows: $1.34 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for 4-cyanostyrene; $2.32 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for *cis*-cyclooctene; $4.63 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for 4-acetoxystyrene; $7.83 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for cyclohexene; $8.57 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for styrene; $6.38 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for 4-methylstyrene; 3.52

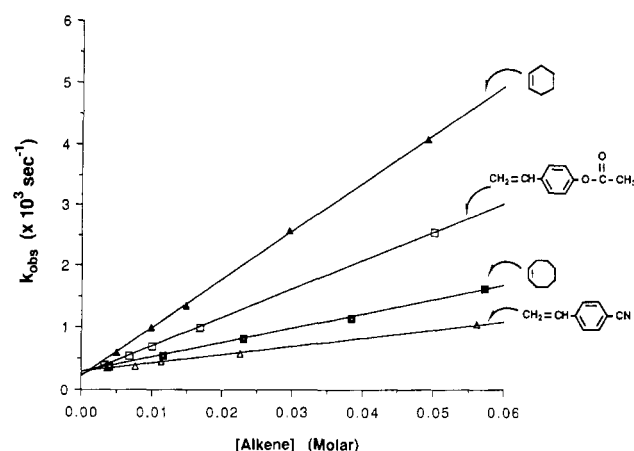


Figure 5. Plot of the observed pseudo-first-order rate constant [$k_{\text{obsd}} (\times 10^{-3} \text{ s}^{-1})$] for the disappearance of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ vs the concentrations of 4-cyanostyrene, *cis*-cyclooctene, 4-acetoxystyrene, and cyclohexene (30 °C).

$\text{M}^{-1} \text{ s}^{-1}$ for 4-methoxystyrene. The spontaneous rate of disappearance of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ to give $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$, in the absence of alkene, was independently monitored at 409 nm and found to be $2.4 \times 10^{-4} \text{ s}^{-1}$. This value is, within the experimental error, equal to the intercepts of the lines of Figures 4 and 5 at $[\text{alkene}] = 0.0 \text{ M}$.

In selected cases, the reactions were followed by repetitive spectral scanning (500–350 nm) and the time courses for the reactions computer simulated to Scheme I by monitoring the time-dependent changes in absorbance at the Soret maxima of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$, and $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$. In the simulations the following considerations hold. The value of k_1 is dependent upon the alkene. The values of k_2 and k_3 are the minimal values that provide good computer fits. The ratio k_2/k_3 is critical, but the true rate constants may be much greater than the minimal values employed. Thus, though the spectral data shown in Figure 6 were simulated with $k_2 = 5.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $k_3 = 50 \text{ M}^{-1} \text{ s}^{-1}$, a change in these constants to $k_2 = 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_3 = 10^7 \text{ M}^{-1} \text{ s}^{-1}$ provides an equally good fit and results in only a 2.8% increase in the predicted yield of epoxide. The rate constant k_4 pertains to the decomposition of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ in the absence of alkene, and its value has been determined independently ($2.4 \times 10^{-4} \text{ s}^{-1}$). It has been shown in this and a previous investigation¹ that the second-order rate constants for the reaction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with alkenes, calculated from the rate of disappearance of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ and by simulation of the time dependence of the absorbances of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$, and $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{X})$, are, within experimental error, the same.

In Figure 6 are shown the spectral changes that accompany the reaction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ ($1.15 \times 10^{-5} \text{ M}$) with 1,1-diphenylethylene ($2.24 \times 10^{-3} \text{ M}$). The points of Figure 6 are experimental and the lines have been computer simulated to Scheme I by use of the following constants: $k_1 = 1.2 \text{ M}^{-1} \text{ s}^{-1}$; $k_2 = 5.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$; $k_3 = 5.0 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$; $k_4 = 2.3 \times 10^{-4} \text{ s}^{-1}$. Product analysis (HPLC) indicated the presence of 1,1-diphenyl-1,2-epoxyethane in 19% and 1,1-diphenylacetaldehyde in 47% yield based on $[(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})]$ employed (total product yield of 66%). The yield of products predicted by computer simulation was 63%.

Kinetic analysis of the reaction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ ($1.15 \times 10^{-5} \text{ M}$) with 1-octene ($4.2 \times 10^{-3} \text{ M}$) was carried out in 1.0-mm cuvettes and monitored by repetitive scanning (500–350 nm). Computer simulation of the time dependence of absorbances at the position of the Soret maxima of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$, and $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$ according to Scheme I are shown in Figure 7. Fits to the kinetic points were obtained when $k_1 = 3.2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, $k_2 = 5.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, $k_3 = 5.0 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$, and $k_4 = 2.2 \times 10^{-4} \text{ s}^{-1}$. The rate constants are much the same when determined by simulation using a 10-fold lower concentration of both $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ and 1-octene (i.e., k_1

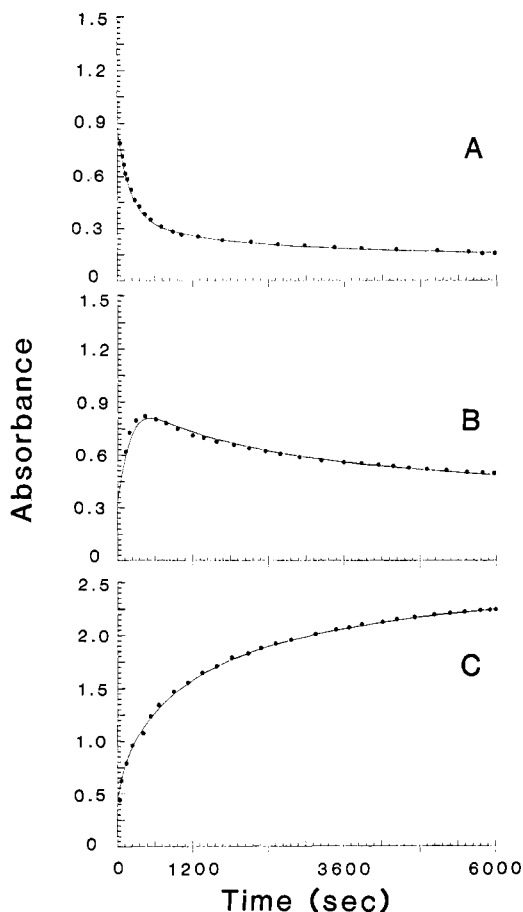


Figure 6. Computer simulation of the reaction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with 1,1-diphenylethylene at 30 °C. (A) Absorbance at the λ_{max} (409 nm) of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$; (B) absorbance at the λ_{max} (431 nm) of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$; (C) absorbance at the λ_{max} (451 nm) of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$. The points are experimental and the lines are computer generated. For computer simulation account was taken of the extinction coefficients of the species $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$, and $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$ at each wavelength. The spectrum of the species $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ was taken prior to the addition of the alkene to assure the absence of more than a few percent of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$.

$= 3.2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$). Product analysis (GC) indicated only the presence of 1,2-epoxyoctane in 3.3% yield based on $[(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})]$ employed. The yield of 1,2-epoxyoctane predicted by the computer simulation of the absorbance data was 2.8%.

Simulations of the time courses to Scheme I for the reaction of norbornene, styrene, and *cis*-stilbene were also carried out under conditions as those described for 1,1-diphenylethylene and 1-octene. Values of k_1 were determined as $7.0 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for norbornene, $8.9 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for styrene, and $3.98 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for *cis*-stilbene. By simulation, the products of reaction of norbornene with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ are predicted at 64% yield. By GC, *exo*-norbornene oxide is obtained in 63% yield. No endo isomer was detected. With styrene the product yield is predicted to be 61%. There was obtained (HPLC) 59% styrene oxide and 6% phenylacetaldehyde (65% total product yield). With *cis*-stilbene the product yield is predicted to be 68%. There was obtained (HPLC) 21% *cis*-stilbene oxide and 52% 1,1-diphenylacetaldehyde (73% total product yield). Control experiments established that in the presence of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ the epoxide of *cis*-stilbene provides 1,1-diphenylacetaldehyde. Such a rearrangement has been seen (and discussed¹) in the reaction of *cis*-stilbene oxide with oxo(*meso*-tetrakis(2,4,6-trimethylphenyl)porphinato)chromium(V).

Other second-order rate constants for $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ epoxidations (k_1) obtained by simulations of the time dependence of the concentrations of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$, $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$ are as follows: $1.2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ for 1-hexene; $3.98 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for cyclopentene; $3.55 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for

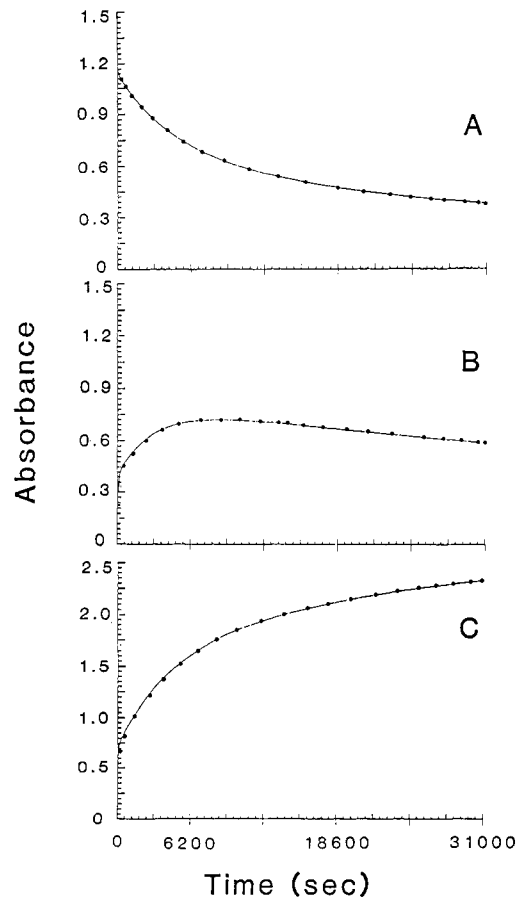


Figure 7. Computer simulation of the reaction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with 1-octene at 30 °C. (A) Absorbance at the λ_{max} (409 nm) of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$; (B) absorbance at the λ_{max} (431 nm) of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$; (C) absorbance at the λ_{max} (451 nm) of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$. The points are experimental and the lines are computer generated. For computer simulation account was taken of the extinction coefficients of the species $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$, and $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{Cl})$ at each wavelength. The spectrum of the species $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ was taken prior to the addition of the alkene to assure the absence of more than a few percent of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$.

cis-2-pentene; $2.1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for *cis*-cyclooctene (compared to $2.32 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ obtained by fitting the first-order rate law to the disappearance of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$); $9.5 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for 2,3-dimethyl-2-butene; and $1.7 \text{ M}^{-1} \text{ s}^{-1}$ for 1,4-diphenyl-1,3-butadiene.

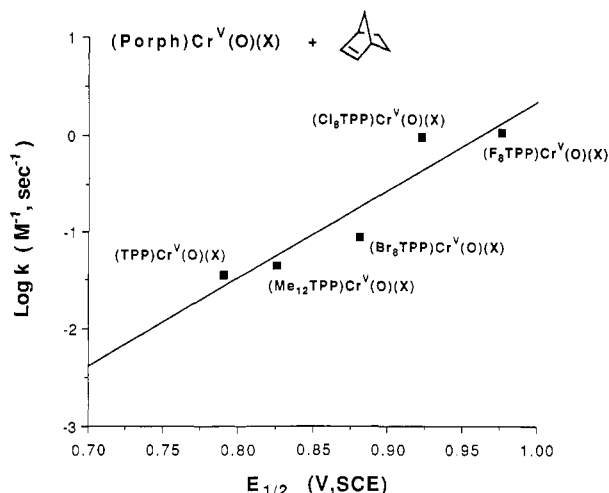
Discussion

The second-order rate constants for the epoxidation of 16 alkenes by oxo(*meso*-tetrakis(2,6-dibromophenyl)porphinato)chromium(V) ($(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$) (eq 2) have been determined under stoichiometric conditions (see Results). The $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ reagent was prepared by electrochemical oxidation of the stable $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ (eq 1). The electrochemical potential for the couple $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})/(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})$ has been determined by two methods to be $0.865 \pm 0.015 \text{ V}$ (SCE). In a previous study the electrochemical potentials for the following couples were determined: oxo(*meso*-tetraphenylporphinato)chromium(V)/oxo(*meso*-tetraphenylporphinato)chromium(IV), $((\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})/(\text{TPP})\text{Cr}^{\text{IV}}(\text{O}))$; oxo(*meso*-tetrakis(2,4,6-trimethylphenyl)porphinato)chromium(V)/oxo(*meso*-tetrakis(2,4,6-trimethylphenyl)porphinato)chromium(IV), $((\text{Me}_6\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})/(\text{Me}_6\text{TPP})\text{Cr}^{\text{IV}}(\text{O}))$; oxo(*meso*-tetrakis(2,6-dichlorophenyl)porphinato)chromium(V)/oxo(*meso*-tetrakis(2,6-dichlorophenyl)porphinato)chromium(IV), $((\text{Cl}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})/(\text{Cl}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O}))$; oxo(*meso*-tetrakis(2,6-difluorophenyl)porphinato)chromium(V)/oxo(*meso*-tetrakis(2,6-difluorophenyl)porphinato)chromium(IV), $((\text{F}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})/(\text{F}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O}))$. In Table I are listed literature values for the

Table I. Literature Values of the $E_{1/2}$ (V, SCE) for One-Electron Oxidation of Alkenes^a

alkene	$E_{1/2}$	method	ref
1,4-diphenyl-1,3-butadiene	1.14	*	5
4-methoxystyrene	1.15	*	6
1,1-diphenylethylene	1.22	+	7
4-methylstyrene	1.38	*	6
2,3-dimethyl-2-butene	1.44	+	8
<i>cis</i> -stilbene	1.54	*	9
styrene	1.65	+	4
4-acetoxystyrene	1.76	*	6
cyclohexene	1.81	+	10
norbornene	1.90	+	11
<i>cis</i> -cyclooctene	2.03	+	12
4-cyanostyrene	2.05	*	6
<i>cis</i> -2-pentene	2.07	+	8
cyclopentene	2.19	+	13
1-hexene	2.44	+	8
1-octene	2.80	*	14

^a Carried out in acetonitrile (*),³ extrapolated from gas-phase ionization potentials to acetonitrile (+) by the general method of ref 4.

**Figure 8.** Plot of the log of the second-order rate constant (k_1) for reaction of a series of five $(\text{Porph})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ species with norbornene vs the $E_{1/2}$ for the couple $(\text{Porph})\text{Cr}^{\text{V}}(\text{O})(\text{X})/(\text{Porph})\text{Cr}^{\text{IV}}(\text{O})$.

1e oxidation potentials (eq 7b) for the alkenes employed in this study.

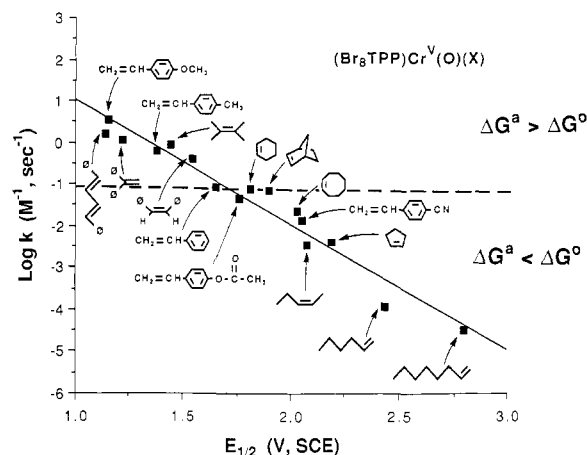
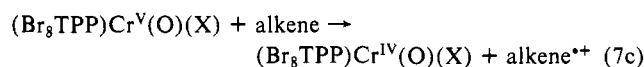
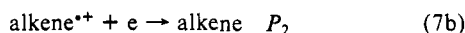
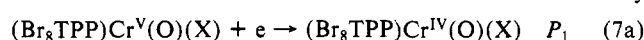
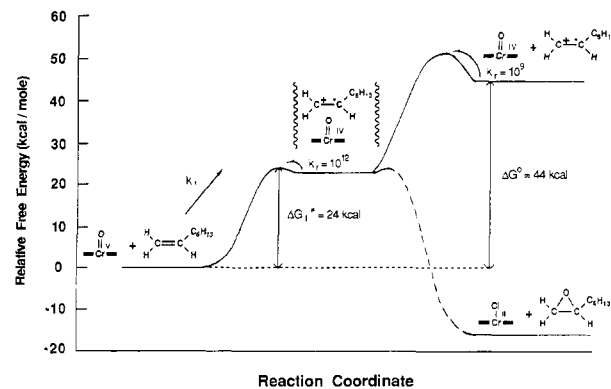
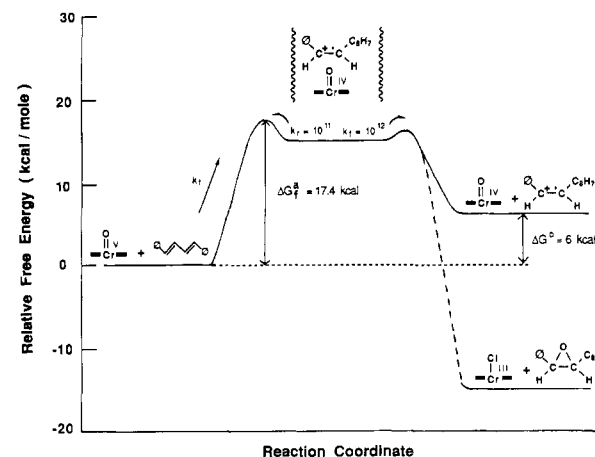
For the epoxidation of norbornene, the $\log k_1$ and $E_{1/2}$ values of Figure 8 include the constants determined in this study with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ as well as constants determined in a previous study¹ using $(\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, $(\text{Me}_{12}\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, $(\text{Cl}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$, and $(\text{F}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$. The linear correlation line of Figure 8 is given by eq 5. A linear correlation

$$\log k_1 = 9.08E_{1/2} - 8.76 \quad (5)$$

between the log of the second-order rate constant (k_1) for the reaction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with the various alkenes and the alkene $E_{1/2}$ values is shown in Figure 9. The values of k_1 range from $3.2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ to $3.5 \text{ M}^{-1} \text{ s}^{-1}$, while the alkene $E_{1/2}$ values range from 1.14 to 2.80 V. The correlation line of Figure 9 is given by eq 6.

$$\log k_1 = -2.99E_{1/2} + 4.02 \quad (6)$$

The interpretation of the linear free-energy correlations of $\log k_1$ to $E_{1/2}$ values (eq 5 and 6) as evidence for the intermediacy of $(\text{Porph})\text{Cr}^{\text{IV}}(\text{O})$ + alkene-derived π cation radical leads to eq 7. The emf values for 1e oxidations of various alkenes by

**Figure 9.** Plot of the log of the second-order rate constant (k_1) 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.**Figure 10.** A cartoon of the reaction coordinate for the hypothetical 1e oxidation of 1-octene by $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$. The picture shows that the experimentally determined standard free energy (ΔG^o) for the formation of alkene-derived π cation radical + chromium(IV)-oxo porphyrin exceeds the free energy of formation of the transition state (ΔG^a) by ca. 21 kcal/mol.**Figure 11.** A cartoon of the reaction coordinate for the hypothetical 1e oxidation of 1,4-diphenyl-1,3-butadiene by $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$. The picture shows that the experimentally determined standard free energy (ΔG^o) for the formation of alkene-derived π cation radical + chromium(IV)-oxo porphyrin is less than the free energy of formation of the transition state (ΔG^a) by ca. 11 kcal/mol.

$(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ (eq 7c) are given as $\text{emf} = P_1 - P_2$ (eq 7a,b) and the standard free energies (ΔG^o) for the 1e-transfer reaction (eq 7c) were calculated from the relationship $\Delta G^o = (n = 1) \cdot (F)(\text{emf})$. The free energies of activation for epoxidation of alkenes by $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ were calculated by use of the Eyring equation¹⁵ (at 30 °C, $\Delta G^a = -17.74 + 1.386(\log k_1)$). The dashed

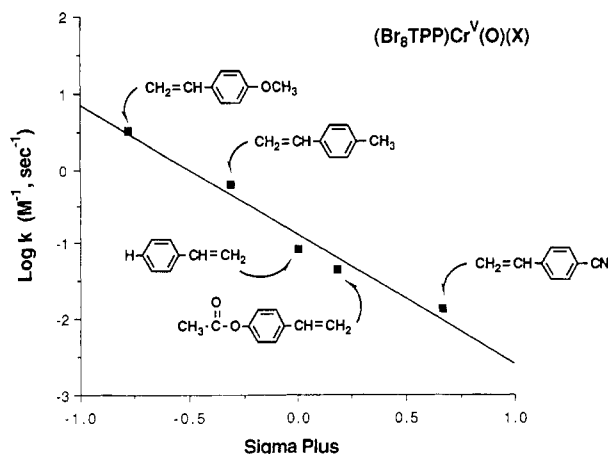


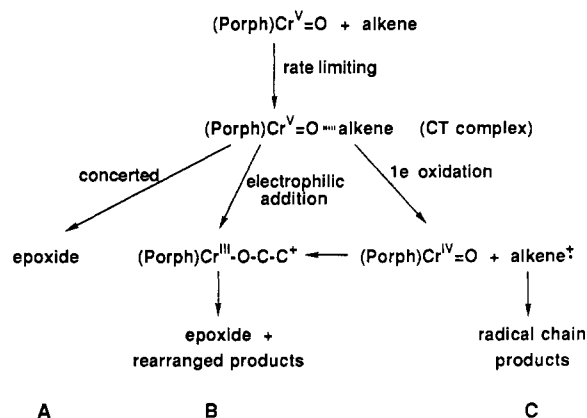
Figure 12. Plot of the log of the second-order rate constants (k_1) for reaction of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ with a series of five substituted styrenes vs the substituent constants σ^+ (30 °C).

line of Figure 9 separates those alkenes for which $\Delta G^{\text{a}} < \Delta G^{\circ}$ and those for which $\Delta G^{\text{a}} > \Delta G^{\circ}$. The standard free energy for the formation of the putative $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O}) + \text{alkene } \pi\text{-cation-radical}$ intermediates is greater than the free energy of activation for epoxidation for about half of the alkenes investigated. Cartoons of the reaction coordinates for epoxidation of 1-octene ($\Delta G^{\text{a}} < \Delta G^{\circ}$) and 1,4-diphenyl-1,3-butadiene ($\Delta G^{\text{a}} > \Delta G^{\circ}$) are shown in Figures 10 and 11, respectively. In the construction of the reaction coordinate cartoons a solvent-caged pair of the species $/(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})(\text{X}) + \text{alkene } \pi\text{-cation radical}/$ is drawn as though it were intermediate to epoxidation and at a free-energy content approaching the transition state for the rate-determining step. Figure 10 represents an extreme example for which ΔG° exceeds ΔG^{a} by 20.7 kcal/mol. An immediate concern is the plausibility of an intermediate solvent-caged $/(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})(\text{X}) + \text{alkene } \pi\text{-cation radical}/$ species, which must be stabilized, relative to the solvent-separated pair, by up to 21 + Y kcal/mol (where Y = ΔG^{a} for reversion of solvent-caged intermediates to solvent-separated alkene + $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})$). The possibility of a change in mechanism for the epoxidation from one involving intermediate formation of solvent-caged $/(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})(\text{X}) + \text{alkene } \pi\text{-cation radical}/$ pair (when $\Delta G^{\text{a}} > \Delta G^{\circ}$) to a concerted reaction or one involving the intermediacy of a covalent species (when $\Delta G^{\text{a}} < \Delta G^{\circ}$) does not seem likely since there is no break in the plot of $\log k_1$ vs $E_{1/2}$. It is concluded that a mechanism involving the formation of an alkene-derived π cation radical can not be correct.

In the interpretation of linear free energy plots of $\log k_1$ vs $E_{1/2}$ one might assume that the relationship is direct or, alternatively, that $E_{1/2}$ and $\log k_1$ are a function of a common parameter. Figure 12 shows that there is a linear free-energy relationship of $\log k_1$ and σ^+ for the epoxidation of the substituted styrenes with $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$. It is known¹⁶ that $E_{1/2}$ for 1e oxidations and σ^+ are linearly related to the vertical ionization potential (IP). There are two possibilities: (i) all electrophilic reactions that correlate with σ^+ are in fact rate-controlled 1e-transfer reactions; or (ii) both σ^+ and IP (or $E_{1/2}$) are dependent upon a third parameter, which is electron availability of the substrate and ability to stabilize a positive charge in the transition state.

For a reaction that proceeds via an initial electron transfer three situations are possible: (i) at one extreme the diffusion together of the reactants is rate limiting and $\log k_1$ for 1e transfer shows no dependence on $\Delta E_{1/2}$ (slope = 0); (ii) in the other extreme 1e transfer is so endothermic that $\log k_1$ is directly proportional to the $\Delta E_{1/2}$ for the overall 1e transfer (slope = -16.6 V^{-1}); and (iii) the intermediate region where $\log k_1$ for rate-limiting 1e transfer is dependent on $\Delta E_{1/2}$ with the slope dependent upon the degree

Scheme II



of electron transfer in the transition state, changing from zero to -16.6 V^{-1} .¹⁷ When our data are plotted in the form of a modified Brønsted plot (eq 6), a slope of -2.99 V^{-1} is obtained. In a conventional Brønsted plot ($\log k_1$ vs $\log K_{\text{eq}}$), this corresponds to Brønsted $\alpha = 0.18$. If 1e transfer is involved in the reaction of $(\text{Porph})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ species with alkenes, the transition state must be early such that the electron has undergone only a partial transfer. Such a situation would be equivalent to rate-determining formation of a charge-transfer complex. Only a late transition state would be in accord with the formation of a solvent-caged $/(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})(\text{X}) + \text{alkene } \pi\text{-cation radical}/$ pair. Again, a single consistent mechanism involving a caged $/(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})(\text{X}) + \text{alkene } \pi\text{-cation radical}/$ pair may be dismissed. In contrast, the rate-limiting formation of a complex with a small degree of charge transfer would appear to be feasible.

The difference in slopes of the linear free-energy relationships of $\log k_1$ vs $\log K_{\text{eq}}$ when $(\text{Porph})\text{Cr}^{\text{V}}(\text{O})(\text{X})$ is varied (eq 5), and when alkene is varied (eq 6), indicates the presence of perpendicular (Thornton) contribution to the overall slope. In the first approximation^{18a} the overall slope (α) is given by eq 8, where the

$$\alpha = \chi \pm 0.5(\tau - 1) \quad (8)$$

first term (χ) incorporates the parallel (Leffler-Hammond^{18b,c}) contribution, and the second term ($0.5(\tau - 1)$) is the perpendicular (Thornton^{18d}) contribution. The term χ represents the progress of the reaction along the reaction coordinate and τ is the measure of the "tightness" of the transition state. The χ term has a positive sign when the (electron) acceptor is varied and a negative sign when the (electron) donor is varied in a homologous series of reactions. The full physical significance of these terms is discussed elsewhere.^{18a} With two slopes available, $\alpha = 0.18$ when the alkene (donor) is varied, and $\alpha = 0.55$ when porphyrin (acceptor) is varied, two equations for α with two unknowns (χ and τ) were solved. The values obtained were $\chi = 0.37$ and $\tau = 0.63$. Presuming a 1e-transfer mechanism and the validity of eq 8 for such purpose, the transition state is located ca. 37% along the reaction coordinate for the formation of $(\text{Br}_8\text{TPP})\text{Cr}^{\text{IV}}(\text{O})(\text{X}) + \text{alkene } \pi\text{-cation radical}$, and it is moderately "loose". This approximation of the structure of the transition state is not consistent with a full electron transfer but is reasonable for rate-limiting formation of a charge-transfer complex between alkene and $(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})$. An initially formed charge-transfer complex could collapse to give epoxide + $(\text{Br}_8\text{TPP})\text{Cr}^{\text{III}}(\text{X})$ in one or more rapid sequential or parallel steps (Scheme II; where Porph = porphyrin). Pathway C can only be of importance for the alkenes of low oxidation potentials (alkenes above the dashed line in Figure 9).

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Cationic intermediates ($M-O-C-C^+$) have been proposed, on numerous occasions,¹⁹ in the epoxidation of alkenes by hypervalent oxo-metallo porphyrins in order to explain the presence of rearranged products. By use of radical-trapping experiments²⁰ it was established that intermediates with radical character are unlikely. The proposition has been made that the most likely candidate is a $M-O-C-C^+$ species with the positive charge partially stabilized by interaction with the electron cloud on porphyrin nitrogens.¹⁹ Consider the linear free-energy relationship of $\log k_1$ with σ^+ . From Figure 12 the value of ρ^+ for the epoxidation of the substituted styrenes by $(Br_8TPP)Cr^V(O)(X)$ is -1.9 . However, the reported ρ^+ values for electrophilic additions to substituted styrenes, which involve the formation of carbocation intermediates are much greater (i.e., -3.58 (hydration),²¹ and -4.8 (bromination)²²). This indicates that if an electrophilic mechanism were operative, an early transition state is necessary to accommodate the observed slope.

A third mechanism that should be considered is a concerted insertion of oxygen into the alkene double bond. A plot of the log of the second-order rate constants for the epoxidation of 15 alkenes by *meta*-chloroperbenzoic acid vs $E_{1/2}$ for the alkenes possesses a slope of $-2.4 V^{-1}$.²³ (Figure not shown but available on request.) This value may be compared to the slope ($-3 V^{-1}$) of the plot of $\log k_1$ vs $E_{1/2}$ for the epoxidation of alkenes by $(Br_8TPP)Cr^V(O)(X)$. It is obvious that epoxidation of alkenes by both *meta*-chloroperbenzoic acid and $(Br_8TPP)Cr^V(O)(X)$ is equally dependent upon the electron availability of the alkene. A non-symmetrical transition state for peracid epoxidations and carbene insertion into C-C double bonds has been proposed wherein one carbon carries a partial positive charge.²⁴ To continue, the following values of ρ^+ have been published for electrophilic reactions which are believed not to involve carbocationic intermediates: -0.62 ($:CCl_2$ insertion into the double bond of substituted styrenes),²⁵ -1.61 ($:CH_2$ insertion into the double bond of substituted styrenes using $C_2H_5ZnCH_2I$),²⁶ and -1.2 (epoxidation of substituted stilbenes with perbenzoic acid).²⁷ These values may be compared to the ρ^+ value (-1.9) for epoxidation of substituted styrenes by $(Br_8TPP)Cr^V(O)(X)$. The only other ρ^+ reported for epoxidation of substituted styrenes, determined by bimolecular reaction of a hypervalent metallo-oxo porphyrin species with alkene, is that for the reaction of substituted styrenes with oxo(*meso*-tetrakis(2,4,6-trimethylphenyl)porphinato- π -cation-radical)iron(IV). The reported ρ^+ is -1.9 .²⁸ Kochi and

co-workers²⁹ have reported the second-order rate constants for epoxidation of a number of alkenes using substituted oxo(salen)chromium(V) complexes as catalysts. By use of Kochi's data for reaction of bis(5,5'-dichloro)-(8,8,8',8'-tetramethylsalen)-chromium(V)oxo with alkenes it is found that a plot of $\log k_1$ vs $E_{1/2}$ of alkenes gives a good linear free-energy relationship with slope of $-1.83 V^{-1}$. Using the data for a series of substituted styrenes $\rho^+ = -1.44$. The similarity in the values of ρ^+ for chromium(V)-oxo species epoxidations and known concerted reactions should be noted.

If such a concerted mechanism were operative, it would be required that rearrangement products attributable to the formation of cation intermediates etc. arise from reactions that are parallel to and competitive with epoxidation.

The rate constant k_1 pertains to the second-order reaction of $(Br_8TPP)Cr^V(O)(X)$ with alkene. The second-order rate constant for epoxidation of alkene (k_{ep}) is equal to k_1 for the majority of alkenes investigated which do not provide appreciable yields of rearranged etc. products. For the alkenes that provide considerable yields of rearranged products (styrene, *cis*-stilbene, and 1,1-diphenylethylene) $k_1 = k_{ep} + k_{re}$. Thus, it is required for the linear relationship of $\log k_1$ and $E_{1/2}$ (Figure 9) that the rate constants of epoxidation, and reactions to give rearrangement, exhibit the same dependency upon $E_{1/2}$. The ρ^+ values (-3.6 to -4.8) for reactions that provide carbocation in the rate-limiting step differ greatly from the ρ^+ value derived from k_1 values. It would appear unlikely, therefore, that the reaction of $(Br_8TPP)Cr^V(O)(X)$ with alkenes can be characterized as rate-limiting oxygen insertion, to provide epoxide, in competition with carbocation intermediate formation. Thus, Scheme II would appear to represent the most logical mechanism. It should be understood that these conclusions have been reached from experiments carried out with $(Me_8TPP)Cr^V(O)(X)$ and $(Br_8TPP)Cr^V(O)(X)$; however, the similarities of ρ^+ values obtained in this study and those reported for hypervalent oxo-manganese³⁰ and oxo-iron^{28,31} porphyrins suggest that they may share a common mechanism. The mechanism of Scheme II provides a suitable rationalization of the experimental results of Traylor and co-workers.³² They proposed epoxidation with $(^+Porph)Fe^{IV}(O)(X)$ to proceed via rate-determining formation of iron(IV)-oxo porphyrin + alkene-derived π cation radical. Thus, the observed rearrangements of hexamethyl Dewar benzene and 1,4,4a,5,8,8a-hexahydro-1,4,5,8-endo,endo-dimethanonaphthalene are adequately explained by reaction path C of Scheme II as is their purported linear dependence of $\log k_{rate}$ on $E_{1/2}$.

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