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Kinetics and mechanisms of oxidation of organic and inorganic substrates by transition metal oxo complexes

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Kinetics and mechanisms of oxidation of organic and inorganic substrates by transition metal oxo complexes

by

Ahmad Mahmoud Al-Ajlouni

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Kinetics and mechanisms of oxidation of organic and inorganic substrates by transition metal oxo complexes

Ahmad Mahmoud Al-Ajlouni

Major Professor: James H. Espenson
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Epoxidation of olefins by H_2O_2 as catalyzed by methylrhenium trioxide, CH_3ReO_3, was investigated in semi-aqueous and organic solvents. Methylrhenium oxide activates H_2O_2 through formation of a mono-peroxo-Re(VII), **A**, and a bisperoxo-Re(VII), **B** ,species. Both species are active toward olefin epoxidation with very similar reactivities and are about 10^5 times more reactive than free H_2O_2. Epoxides, the initial products from these reactions, undergo ring-opening to the 1,2-diols. A concerted mechanism that involves external nucleophilic attack of the olefin on the peroxy oxygen has been proposed.

The kinetics and the mechanisms of oxidations of 1,2-diols, phenols and H_2O_2 by the pentaaquaoxochromium(IV) ion, CrO^{2+} were studied in aqueous acidic solutions. Oxidation of vicinal diols with CrO^{2+} involves a hydride abstraction from the α-position (primary and secondary 1,2-diols) or from the β-position (pinacol). Reactions of phenols with CrO^{2+} produce the corresponding phenoxyl radicals in a rate-determining-step. The phenoxyl radicals are further oxidized by the superoxochromiun(III), $CrOO^{2+}$, to produce quinones as final products. Oxidation of H_2O_2 with CrO^{2+} produces $CrOO^{2+}$ in the presence and in the absence of O_2.

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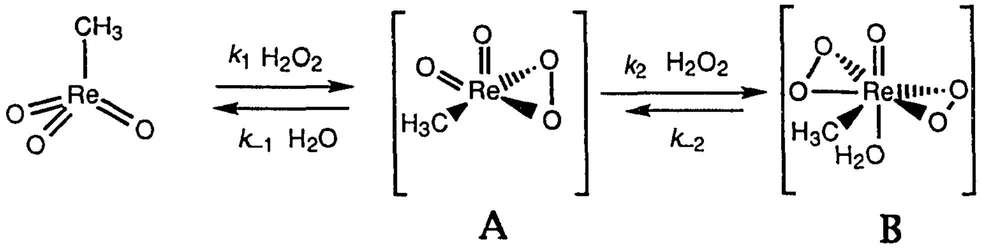
GENERAL INTRODUCTION

Epoxidation of olefins by hydrogen peroxide as catalyzed by methylrhenium trioxide. Oxidations of unsaturated hydrocarbons are very important processes in industry and organic synthesis. Many products, such as epoxides, diols, aldehydes, ketones, ethers, esters, ketoacids and carboxylic acids, can be obtained from these reactions. Of these products, epoxides are the most important for the chemical industry. Many oxidants, such as peracids, dioxiranes, and transition metal oxo and peroxo complexes under stoichiometric or catalytic conditions, have been used to oxidize olefins. In the case of transition metal catalysis the sources of oxygen are mainly O_2, H_2O_2, alkylperoxide, OX^- (X = Cl or I) and PhIO.

For many reasons, H_2O_2 is considered as the best source for an oxygen atom in epoxidation reactions. The amphoteric nature of H_2O_2 makes it more reactive and a better oxidant than O_2. It can be activated by basic and acidic catalysts, such as low-and high-valent transition metals. Heterolytic activation of H_2O_2 by transition metal salts and complexes to achieve selective oxygen-atom transfer and high activity has been studied extensively. With low valent late transition metal complexes (bases) H_2O_2 acts as an acid. Upon coordination, the nucleophilicity of the peroxo oxygens increases. Activation of H_2O_2 by high valent transition metal complexes increases the electrophilic character of the peroxo oxygens upon coordination.

Methylrhenium trioxide (MTO), CH_3ReO_3, has been found to activate H_2O_2 through formation of rhenium monoperoxide, **A**, and bisperoxide, **B**, having 1:1 and 2:1 ratios of peroxide to Re, respectively, eq 1.



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In this work kinetic and mechanistic studies on the epoxidation of styrenes and aliphatic olefins by H_2O_2 catalyzed by MTO were carried out in homogeneous semi-aqueous solutions at pH 1 and in organic solvents. Three different techniques (*NMR, Spectrophotometric and Thermometric methods*) and four methods of kinetic analysis have been used to obtain kinetic data and determine the rate law and the rate constants for epoxidation of more than 40 olefins by **A** and/or **B**. As shown in Chapter I, detailed kinetic studies on the epoxidation of styrenes were detected toward determining separately the activities and the relative reactivities of **A** and **B**. It was found that both **A** and **B** are active (with similar reactivities) toward styrene epoxidation. These results are not in agreement with previous conclusion made by Herrmann's group about the activities of **A** and **B**. They have stated that only **B** is reactive toward epoxidation of olefins. Kinetic studies on the epoxidation of alkyl-substituted alkenes were limited only to the diperoxorhenium(VII) complex, **B**, see Chapter II.

The initial products from these reaction are epoxides. In organic solvents, such as CD_3CN and CD_3OD, epoxides can be observed and isolated. The epoxide ring-opening to 1,2-diol is catalyzed by the CH_3ReO_3-H_2O_2 system. In 1:1 CH_3CN/H_2O at pH 1, the epoxide is rapidly hydrolyzed to 1,2-diol and cannot be observed. Its ring-opening is catalyzed by the acid.

Oxidation of 1,2-diols, phenols and hydrogen peroxide by pentaaquaoxochromium(IV) ion. The kinetics of the oxidation of organic and inorganic substrates by Cr(VI) have recently received the attention of chemists in an attempt to explain its carcinogenic properties. Two main mechanisms for reduction of Cr(VI) to Cr(III) by organic substrates have been suggested, eq 2 and 3.

$$\mathrm{Cr(VI)} \xrightarrow{\mathrm{RH}} \mathrm{Cr(IV)} \xrightarrow{\mathrm{Cr(VI)}} 2\,\mathrm{Cr(V)} \xrightarrow{\mathrm{RH}} 2\,\mathrm{Cr(III)} \qquad (2)$$

$$\begin{aligned} &\mathrm{Cr(VI)} \xrightarrow{\mathrm{RH}} \mathrm{Cr(IV)} \xrightarrow{\mathrm{RH}} \mathrm{Cr(II)} \xrightarrow{\mathrm{Cr(VI)}} \mathrm{Cr(III)} \\ &\qquad\qquad\qquad\qquad + \mathrm{Cr(V)} \xrightarrow{\mathrm{RH}} \mathrm{Cr(III)} \qquad (3) \end{aligned}$$

In both mechanisms, formation of Cr(IV) in the first step has been proposed. Cr(IV) has also been involved as an intermediate in many redox mechanisms, although it has not been directly observed. Recently, the Espenson group prepared the pentaaquaoxochromium(IV) ion, CrO^{2+} (here and elsewhere the coordinated water molecules are omitted), under aerobic conditions from reaction of Cr(II) ion with O_2, eq 4, and in the absence of O_2, from the reaction of $TlOH^{2+}$ with Cr(II) ion, eq 5.

$$\mathrm{Cr^{2+}} + \mathrm{O_2} \longrightarrow \mathrm{CrOO^{2+}} \xrightarrow{\mathrm{Cr^{2+}}} 2\mathrm{CrO^{2+}} \qquad (4)$$

$$\mathrm{Cr^{2+}} + \mathrm{TlOH^{2+}} \xrightarrow{-\,\mathrm{H^+}} \mathrm{CrO^{2+}} + \mathrm{Tl^+} \qquad (5)$$

The pentaaquaoxochromium(IV) ion, CrO^{2+}, is a strong oxidizing agent ($E_{1/2}$, Cr(IV)/Cr(III), > 1.5 V). It may be reduced by one or two electrons to Cr(III) or Cr(II). Under aerobic conditions Cr(II) reacts rapidly with O_2 and gives superoxochromium(III) ion, $CrOO^{2+}$. It has been found that CrO^{2+} oxidizes a variety of organic substrates, such as alcohols, aldehydes and carboxylates, by a two-electron or hydride transfer, mechanism. Oxidation of cyclobutanol was exceptional; it adopts a hydrogen atom abstraction pathway and produces an alkyl radical. CrO^{2+} also transfers an oxygen atom to PPh_3 to yield $OPPh_3$.

In this work kinetics and mechanistic studies on the oxidation of primary, secondary and tertiary 1,2-diols, a series of phenols and H_2O_2 by CrO^{2+} were investigated in aqueous acidic solutions. The results obtained for the oxidation of primary and secondary 1,2-diols are similar to those obtained previously for the oxidation of alcohols by CrO^{2+}. Oxidation of pinacol by CrO^{+2} adopts different mechanism in which a hydride is abstracted from the β-carbon.

Oxidation of phenols is an important process in organic synthesis and biological systems. Some enzymes catalyze oxidation of phenols to hydroquinones and benzoquinones. With labile transition metal oxidants, phenols have been oxidized either by a hydrogen-atom or a hydride transfer. Hydrogen atom abstraction from phenols gives phenoxyl radicals. The radicals are further oxidized to benzoquinones and/or dimerize (polymerize) to yield biphenoquinones. The results obtained from this study suggest that oxidation of phenols by CrO^{2+} involves hydrogen atom abstraction from the O-H group of the phenol by CrO^{2+} in a rate-determining step. Formation of a phenoxyl radical from reaction of a phenol with CrO^{2+} was directly observed. The final products are benzoquinones (major) and biphenols (minor).

It has been known that H_2O_2 reacts with $HCrO_4^-$ to give oxodiperoxochromium(VI), $Cr(O)(O_2)_2$ in acidic solutions, which then decomposes to Cr(III) and O_2 via a Cr(III)-superoxyl radical intermediate. This Cr(III)-superoxyl radical intermediate is the superoxochromium(III), $CrOO^{2+}$, which has been recently characterized. This study has shown that $CrOO^{2+}$ also forms from reaction of hydrogen peroxide with CrO^{2+} in the presence and in the absence of O_2.

Dissertation organization The dissertation consists of five chapters. The first two present the epoxidation of styrenes and alkyl-substituted alkenes by H_2O_2 catalyzed by CH_3ReO_3. Chapters I and II correspond to two manuscripts; one has been accepted by *J. Am. Chem. Soc.* and another submitted to *J. Am. Chem. Soc.* The last three chapters are on the oxidation of 1,2-diols, phenols and H_2O_2 by CrO^{2+}. Each chapter corresponds to a manuscript that has been published in *Inorg. Chem.* Each section is self-contained with its own equations, tables, figures and references. Following the last manuscript are general conclusions. All the work in this dissertation was performed by doctoral candidate.

CHAPTER I. THE EPOXIDATION OF STYRENES BY HYDROGEN PEROXIDE AS CATALYZED BY METHYLRHENIUM TRIOXIDE

A paper accepted by the *Journal of the American Chemical Society*

Ahmad M. Al-Ajlouni and James Espenson

ABSTRACT

Methylrhenium trioxide, CH_3ReO_3, catalyzes the oxidation of styrenes by hydrogen peroxide. Kinetic studies by three methods were carried out in acidic CH_3CN/H_2O (1:1 v/v) solutions. The catalytically-active species are the mono-peroxide, $CH_3Re(O)_2(O_2)$, **A**, and the bis-peroxide, $CH_3Re(O)(O_2)_2$, **B**, which epoxidize a given styrene at a similar rate. The rate constants are relatively insensitive to steric hindrance, but increase with the nucleophilicity of the styrene, electron-donating groups on the olefinic carbons or on the aromatic ring enhancing the rate. The rate constants for meta- and para-substituted styrenes follow a linear Hammett relationship; correlation with σ^+ gave $\rho = -0.93 \pm 0.05$. In CD_3CN, epoxides were observed by ^1H NMR spectroscopy. *Cis*-β-methylstyrene and *trans*-β-methylstyrene led to the *cis* epoxide and the *trans* epoxide, respectively. In acidic CH_3CN/H_2O, the major products were 1,2-diols. In some cases C–C bond cleavage products were also observed, the extreme case being β-methoxystyrene where the C–C bond was completely cleaved to yield benzaldehyde, formaldehyde and methanol.

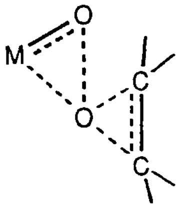
INTRODUCTION

The use of aqueous organometallic catalysts poses a challenge, since many are unstable to hydroxylic solvents. The research reported here utilizes the water-stable methylrhenium trioxide as an epoxidation catalyst. Epoxidations by peroxides are catalyzed by complexes of high-valent d^0 metals, such as Mo(VI), V(V) and Ti(IV),[1-3] which heterolyze the peroxides by way of an electron deficient peroxometal.[2c]

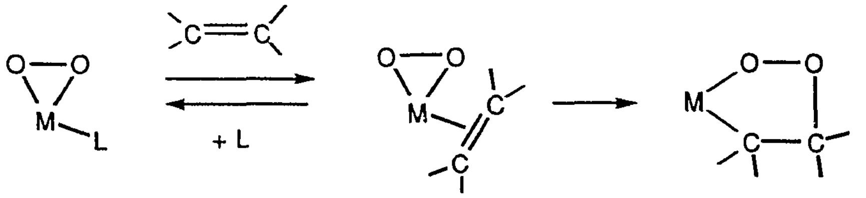
Nucleophilic olefins are the most reactive towards metal-peroxo complexes. The oxygen transferred to the olefin comes exclusively from the peroxo group,[1a,4] and epoxidation is mostly stereoselective.[5,6] In protic solvents 1,2-diols and β-methoxy alcohols are obtained.[7] Alkyl substituted styrenes are more prone to oxidative cleavage than are aliphatic olefins.[5]

The epoxidation mechanism remains controversial. Three proposals have been made for oxygen transfer from the peroxide, and plausibly each may be valid in certain circumstances. The mechanisms are these:

(1) External nucleophilic attack of the olefin on the electrophilic peroxy oxygen through a three-membered ring transition state:[2,12]



(2) Olefin binding, followed by insertion into the M-O bond to form a five-membered peroxometallacycle intermediate, eq 1:[1a]



(1)

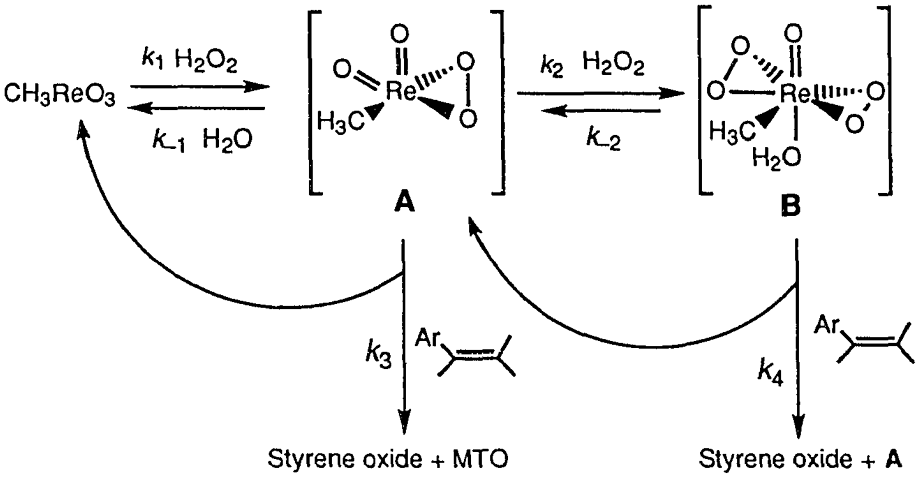
(3) Nucleophilic attack of one olefinic carbon (α or β) on the peroxy oxygen, followed by intramolecular attack of the same oxygen on the other carbon.[8]

External nucleophilic attack was preferred for Mo(VI)-peroxides.[2,9] The epoxide, while still complexed to the metal, is easily displaced by solvent or peroxide, although it may undergo further oxidation.[5,10] The second mechanism[1a,3] has been supported by the lack of reactivity of catalysts lacking an adjacent coordination site for a labile monodentate ligand.[5] The reactions are inhibited in the presence of basic ligands or solvent, such as water and alcohols.[1c] With no electrons available for back-bonding to the olefin, its nucleophilicity is lost upon coordination. The electron density on the peroxy oxygens increases and then nucleophilic attack of the peroxy oxygen on the metal-coordinated olefin leads to a peroxometallacycle intermediate, as isolated from reactions of Pt and Rh peroxo complexes with tetracyanoethene.[11] This mechanism has, however, not been found for d^0 metals.[12] A frontier orbital investigation[13] found the metal-bound olefin slipping toward the peroxy oxygen, with a three-membered, rather than five-membered, ring transition state.

Methylrhenium trioxide (MTO), CH_3ReO_3, activates hydrogen peroxide through the formation of mono- and bis-peroxides, **A** and **B**, as given in Scheme IV-1.[14-16] The crystal structure of **B** has been reported.[15] Both **A** and **B** are efficient oxygen donors, transferring oxygen to $ArNMe_2$,[17] Br^-,[18] PR_3,[19] and R_2S [20] at rates 10^4-10^6 times those of free hydrogen peroxide.

The catalytic epoxidation of olefins by hydrogen peroxide using CH_3ReO_3 as a catalyst in *tert*-butyl alcohol has been reported,[21] although no detailed kinetic studies were reported. Others have suggested that only **B** is active in the epoxidation of olefins.[15] In the oxidations of most other species, however, both **A** and **B** react, **A** usually somewhat faster.[16-20] Indeed, we have demonstrated that the same holds for styrenes.

Scheme I-1. Formation of $CH_3Re(O)_2(O_2)$, **A**, and $CH_3Re(O)(O_2)_2$, **B** and their reactions with a styrene.



A kinetic study of catalytic epoxidation of a series of styrenes by CH_3ReO_3–H_2O_2 has been carried out in acidic CH_3CN/H_2O to determine the reactivities of **A** and **B** and other features of the mechanism. The mixed solvent was chosen to promote solubility of the styrenes, and water and acidic conditions greatly increased catalyst stability in peroxide solutions. The major products were isolated and identified by ^{1}H-NMR experiments; some of these determinations were made in neat acetonitrile.

In this work detailed kinetic studies of the complicated catalytic system shown in Scheme I-1 have been conducted. It involves two active species, **A** and **B**, formed from H_2O_2 and MTO. These rhenium peroxides react independently with the styrene. Similar catalytic systems have been observed and studied before.[1d,3] Four different methods have been used to determine the rate constants k_3 and k_4 of Scheme I-1. In some cases the steady-state approximation was applied; in others, the equilibrium concentrations of **A** and **B** were applicable.

EXPERIMENTAL SECTION

Materials

Water was purified by a Millipore-Q water purification system. HPLC grade acetonitrile (Fisher) was used, and a low pH, usually 1, was maintained with perchloric acid to stabilize catalyst-peroxide solutions. The catalyst itself, however, was stable for long periods in the absence of hydrogen peroxide. Methylrhenium trioxide[14a] was purified first by sublimation, then by recrystallization from CH_2Cl_2/hexane and finally by a second sublimation. Solutions of CH_3ReO_3 in water or in CH_3CN were stored at 5 °C and used within 1–2 weeks. Concentrations were determined spectrophotometrically: 239 nm (ε 1900 L mol^{-1} cm^{-1}) or 270 nm (ε 1300 L mol^{-1} cm^{-1}).[16] Styrenes were purchased commercially from Aldrich, except *cis*-β-methylstyrene from TCI America. β-Methoxystyrene was purified by vacuum distillation. Other styrenes were used without further purification. Stock solutions of hydrogen peroxide were prepared by diluting 30% or 3% H_2O_2 (Fisher) and standardized daily by iodometric titration.

^1H NMR spectra were obtained with a Nicolet 300 MHz spectrometer referenced to $(CH_3)_4Si$. A Magnum GC/MS spectrometer was used for GC/MS results.

Kinetics

The kinetic studies were carried out in CH_3CN/H_2O (1:1 v/v) solutions at 25 °C. The concentration of perchloric acid and the ionic strength were maintained at 0.1 M unless specified otherwise. Quartz cuvettes with optical paths of 0.01–2 cm were used. The temperature was maintained at 25.0 °C, or another desired temperature, by immersing the reaction cell in a thermostated water-filled holder positioned in the light beam of the spectrophotometer throughout the experiment. Air (oxygen) had no effect on the reactions and was not excluded. The kinetic data were obtained by following the loss of styrene absorption in the region 265-300 nm using a Shimadzu UV-visible spectrometer.

Reaction mixtures were prepared in a spectrophotometric cell with the last reagent added being H_2O_2 (Method I) or the styrene (Methods II and III) to optimize the kinetic conditions as explained later. Initial rate and pseudo-first-order conditions applied in different protocols; in the latter case the pseudo-first-order rate constants were evaluated by nonlinear least-squares fitting of the absorbance-time curves to a single exponential function, eq 2.

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + (\mathrm{Abs}_0 - \mathrm{Abs}_\infty)e^{-k_\psi t} \qquad (2)$$

Products

Epoxides were formed in CD_3CN without added acid or water. To an NMR tube containing the styrene (0.2 M) and CH_3ReO_3 (0.01 M), 0.25 M H_2O_2 was added as a 30% stock solution. The ^{1}H–NMR spectra were recorded intermittently over 12 h.

1,2-Diols. The styrene (10 mmol in 5 mL CH_3CN) was added dropwise to a flask containing CH_3ReO_3 (0.1–1 mmol) and H_2O_2 (12 mmol) in 1:1 CH_3CN/H_2O containing 0.1 M $HClO_4$. The reactions were protected from light and stirred for 1-4 h at room temperature. The acetonitrile was removed under low pressure at 40-50 °C and the products, after extraction into CH_2Cl_2, were dried over $MgSO_4$, and crystallized from CH_2Cl_2/hexane. The percentage yields were then calculated based on styrene, the limiting reactant. The major products, 1,2-diols, were characterized by their ^{1}H–NMR spectra, GC-MS, and melting point. Under these conditions epoxides form , then undergo rapid ring-opening, catalyzed by the acid, to 1,2-diols.

RESULTS

The uncatalyzed versus the catalyzed reactions

The reactions of β-methoxystyrene with H_2O_2 in the presence and in the absence of CH_3ReO_3 showed that the uncatalyzed reaction is relatively so slow (Figure I-1) that it was not necessary to correct for the uncatalyzed process.

Formation of the peroxo-rhenium(VII) species, A and B

The equilibrium and rate constants of Scheme I-1 are given in Table I-1.[19] The catalytic system involves two reactive species, **A** and **B**. By themselves they are in equilibrium with the catalyst, but during the catalytic cycle either the steady-state approximation (Method Ia and Ib) or the equilibrium condition (Methods II and III) defines their concentrations.

Table I-1. Rate constants and equilibrium constants for the reactions of CH_3ReO_3 with hydrogen peroxide, Scheme I-1[a]

Forward Rate Constants ($L\ mol^{-1}\ s^{-1}$)	Reverse Rate Constants (s^{-1})	Equilibrium Constants ($L\ mol^{-1}$)
$k_1 = 32.5^b$	$k_{-1} = 3.0^b$	$K_1 = 10.8^b$
$k_2 = 1.05^c$	$k_{-2} = 0.008^c$	$K_2 = 136^b$

[a] In 0.1 M $HClO_4$, CH_3CN/H_2O (1:1 v/v) at 25 °C. [b] ref. 19. [c] this work.

The rate law

The rate of epoxidation resulting according to Scheme I-1 is expressed by eq 3, in which it is assumed that both **A** and **B** react independently with the styrene.

$$v = -\frac{d[\text{Styrene}]}{dt} = (k_3[\mathbf{A}] + k_4[\mathbf{B}])\ [\text{Styrene}] \tag{3}$$

The rate equation was derived by means of the steady-state approximation for [**A**] and [**B**]. With the mass balance expression, $[\text{Re}]_T = [CH_3ReO_3] + [\mathbf{A}] + [\mathbf{B}]$, the rate of the reaction can be expressed as follows (see Appendix, page 49, for the complete derivation) :

$$v = \frac{k_1[\text{Re}]_T[\text{Styrene}][H_2O_2]\left\{k_3 + \frac{K_2k_4[H_2O_2]}{1+(k_4/k_{-2})[\text{Styrene}]}\right\}}{k_{-1} + k_3[\text{Styrene}] + k_1[H_2O_2] + \left\{\frac{k_1K_2[H_2O_2]^2}{1+(k_4/k_{-2})[\text{Styrene}]}\right\}} \tag{4}$$

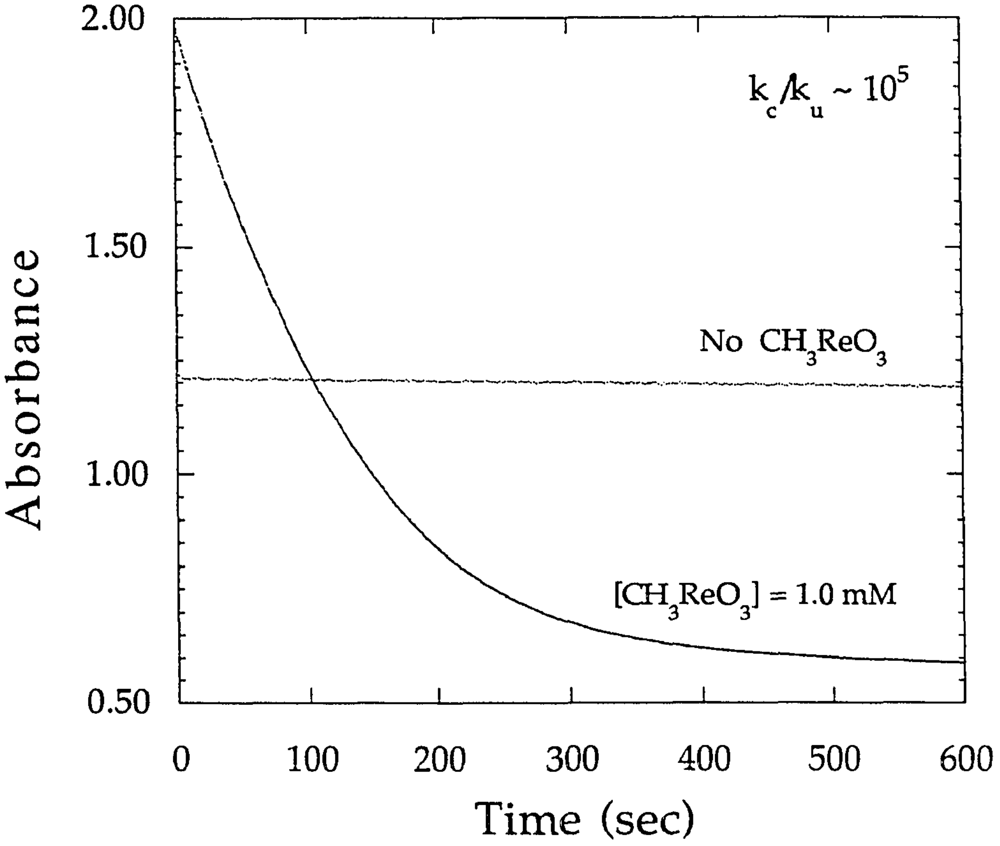


Figure I-1. Typical absorbance-time data at 295 nm for β-methoxystyrene (2.0 mM) with H_2O_2 (50 mM) at 25 °C in 0.1 M $HClO_4$, CH_3CN/H_2O (1:1 v/v), in the presence and absence of CH_3ReO_3.

Under conditions in which [A] is much greater than [B] ($[H_2O_2] \le 2.0$ mM) eq 4 simplifies to eq 5. Actually the determinant is k_3[A] versus k_4[B], but the use of concentrations is not incorrect since the values of k_3 and k_4 are quite close.

$$v = \frac{k_1 k_3 [\mathrm{Re}]_T [\mathrm{Styrene}][\mathrm{H_2O_2}]}{k_{-1} + k_3[\mathrm{Styrene}] + k_1[\mathrm{H_2O_2}]} \tag{5}$$

Kinetics with variable $[\mathrm{Re}]_T$

Values of the initial rate (v_i) were calculated from experiments in which $[\mathrm{Re}]_T$ varied over a range of 0.05–1.0 mM. Hydrogen peroxide and β-methoxystyrene were held constant at 50 mM and 4.0 mM, respectively. As shown in Figure I-2, the initial rates showed a linear dependence on $[\mathrm{Re}]_T$ as expected from eq 4 and 5.

The rate constants for the reaction of the styrenes with **A** and **B**, k_3 and k_4, respectively, were determined by four different methods:

Initial Rates with involvement of A only, Method Ia

The reaction of β-methoxystyrene was studied at constant concentrations of CH_3ReO_3 and β-methoxystyrene of 2.0 and 3.0 mM, respectively. To minimize [**B**], the variable concentration of hydrogen peroxide was kept ≤ 2.0 mM , and it was added last to minimize [B] in the pre-reaction period.

The initial rate at each $[H_2O_2]$ was calculated from the initial rate of absorbance change from the loss of styrene in the region 265-300 nm:

$$v_i = \frac{1}{b\Delta\varepsilon_\lambda} \times \frac{\Delta Abs}{\Delta t} \tag{6}$$

where $\Delta\varepsilon$ is the difference in the molar absorptivities of the reactants and the products at wavelength λ, and b the optical path length. The dependence of v_i on $[H_2O_2]$, shown in Figure I-3, was fit to eq 5 giving $k_3 = 14.6 \pm 0.4$ L mol^{-1} s^{-1}, the other quantities being fixed at the specified values.

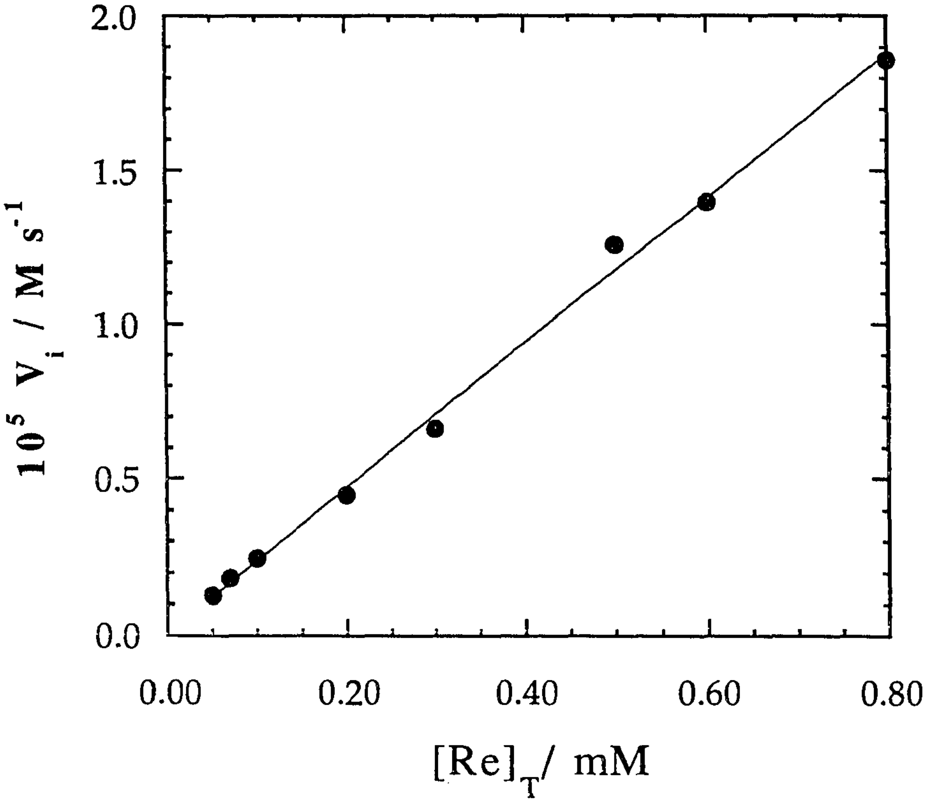


Figure I-2. The initial rate of oxidation of β-methoxystyrene (4.0 mM) by $[H_2O_2]$ (50 mM) varies linearly with $[Re]_T$ in 0.1 M $HClO_4$,CH_3CN/H_2O (1:1 v/v) at 25 °C.

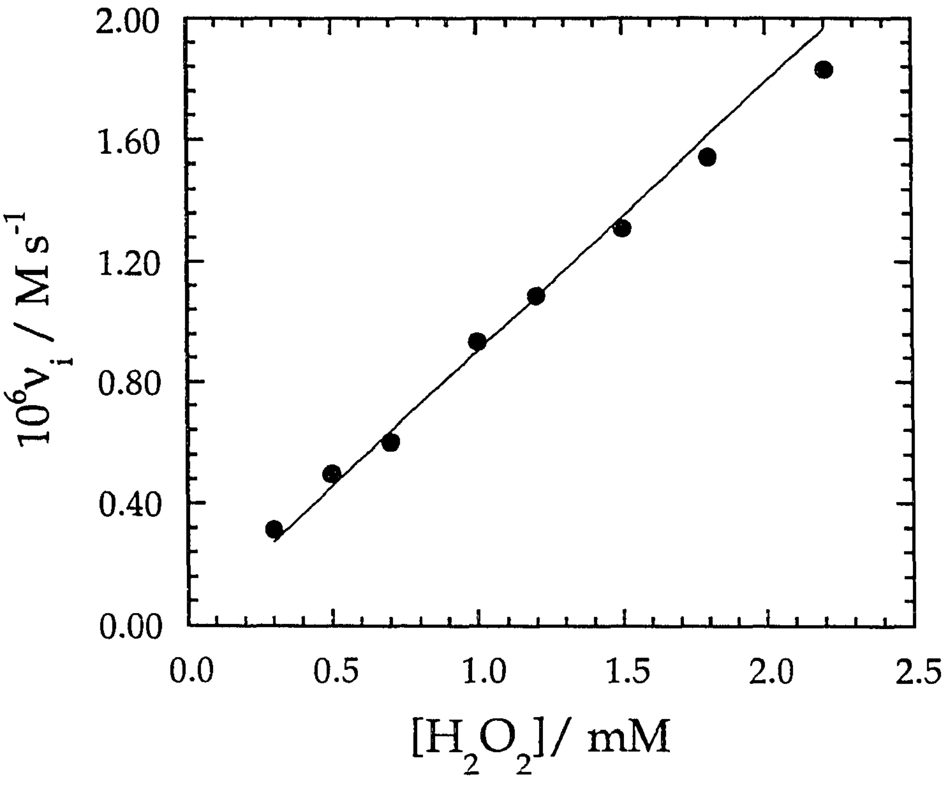


Figure I-3. The initial rate of oxidation of β-methoxystyrene (3.0 mM) with [H_2O_2] fits eq 5 at low [H_2O_2] (involving only **A**) at $[Re]_T$ = 2.0 mM.

Initial rates with involvement of A and B, Method Ib

Kinetic measurements were carried out with a constant $[Re]_T$ of 1.0 mM and a constant concentration of β-methoxystyrene of 2.0 mM. The concentration of H_2O_2 was varied in the range 1–200 mM. The nineteen values (see Figure I-4) were fit to eq 4 and yielded values for the unknown rate constants:

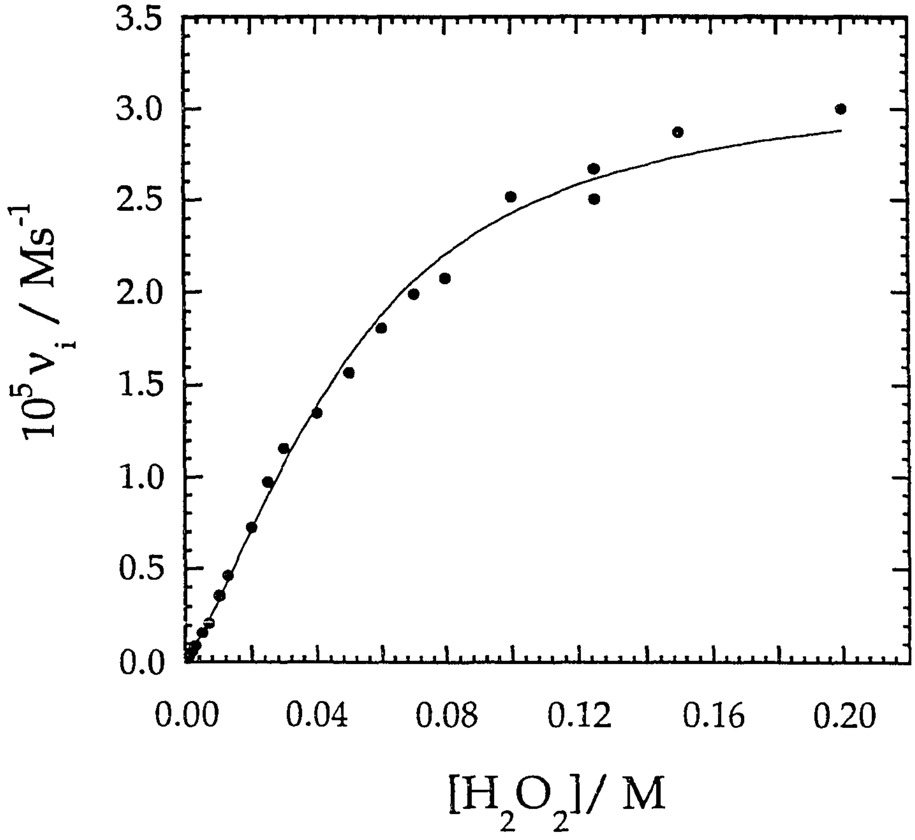


Figure I-4. Variation of the initial rate of oxidation of β-methoxystyrene (2.0 mM) with $[H_2O_2]$ fits eq 7 under conditions involving both **A** and **B**, at $[Re]_T$ = 1.0 mM.

k_3 = 14.2 ± 0.5 L mol^{-1} s^{-1}, k_4 = 15.7 ± 0.75 L mol^{-1} s^{-1}, and k_{-2} = 0.008 ± 0.001 s^{-1}. From K_2 and k_{-2}, we obtained k_2 = 1.05 L mol^{-1} s^{-1}. Fitting of k_2 was needed, as it was previously unknown in this medium.

The reactions of *trans*-4-propenylanisole and *trans*-2-methyl-3-phenyl-2-propen-1-ol were studied similarly. With k_{-2} fixed at 0.008 s^{-1}, the kinetic data were fitted to eq 4. The values of k_3 and k_4 are summarized in Table I-2.

Table I-2. Rate constants for the reactions of styrenes with **A** [= $CH_3Re(O)_2(O_2)$, k_3] and **B** [= $CH_3Re(O)(O_2)_2(H_2O)$, k_4] [a] by various methods [b]

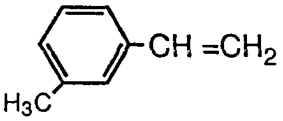
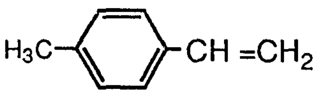
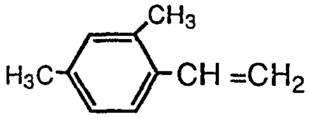
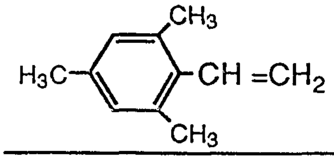
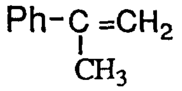
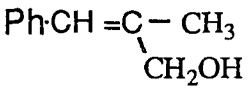
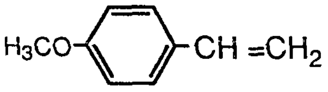
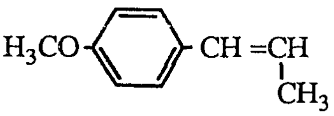
Styrene	k_3 / M^{-1} s^{-1}	k_4 / M^{-1} s^{-1}
Ph·CH =CH_2	——	0.11 ± 0.02(II)
	——	0.12 ± 0.01(II)
	0.38 ± 0.06(III)	0.16 ± 0.01(II) 0.19 ± 0.01(III)
	——	0.38 ± 0.02(II)
	0.13 ± 0.05(III)	0.12 ± 0.01(III)

Table I-2. Continued.

Styrene	k_3 / M^{-1} s^{-1} (Method)	k_4 / M^{-1} s^{-1} (Method)
 $Ph-C(CH_3)=CH_2$	——	0.47 ± 0.02(II)
trans-Ph-CH=CH(CH_3)	0.51 ± 0.07(III)	0.22 ± 0.02(III)
cis-Ph-CH=CH(CH_3)	0.74 ± 0.08(III)	0.28 ± 0.01(III)
Ph·CH =C$(CH_3)_2$	1.00 ± 0.17 (III)	0.70 ± 0.04 (III)
Ph·CH =CH-CH_2OH	——	0.14 ± 0.01(II)
trans-  $Ph\cdot CH=C(CH_3)CH_2OH$	0.73 ± 0.07(Ib)	0.40 ± 0.03(Ib) 0.45 ± 0.03(II)
	0.67 ± 0.12(III)	0.63 ± 0.01(II) 0.57 ± 0.04(III)
trans- 	2.79 ± 0.05(Ib) 2.80 ± 0.11(III)	0.80 ± 0.03(Ib) 1.20 ± 0.03(II) 0.92 ± 0.03(III)
Ph·CH =CH(OCH_3)	14.2 ± 0.5(Ib)	15.7 ± 0.8(Ib) 18.0 ± 0.7(II)

[a] In CH_3CN /H_2O (1:1 v/v), 0.1 M $HClO_4$ at 25 °C; [b] The methods are given by the roman numerals (see text).

First order kinetics involving **B** only, Method II

In the epoxidation of the styrenes with $[H_2O_2] > 0.5$ M, the absorbance-time values followed first-order kinetics. Indeed, at high $[H_2O_2]$, the amount of **A** present is negligible, and the formation of **B** during the reaction is much faster than the reaction of **B** with styrene; i.e. $k_2[H_2O_2] >> k_4[\text{Styrene}]$. The concentration of **B** was constant during the reaction and essentially equal to $[\text{Re}]_T$. Under these conditions the rate of the reaction becomes:

$$v = k_4[\mathbf{B}][\text{Styrene}] = k_4[\text{Re}]_T[\mathit{Styrene}] = k_\psi[\text{Styrene}] \qquad (7)$$

A series of experiments was done with constant $[H_2O_2] = 0.5$–1 M and [Styrene] = 2–5 mM, with $[\text{Re}]_T$ varied from 0.3–3 mM. The solutions of CH_3ReO_3 and H_2O_2 were allowed to equilibrate with **B** for 3–5 min. before adding the styrene. The rate constants k_ψ from eq 2 varied linearly with $[\mathbf{B}] = [\text{Re}]_T$ at each $[\text{Re}]_T$, Figure I-5. The value of k_4 is given by the slope of the line. Their values are summarized in Table I-2.

At high $[H_2O_2]$, with essentially only **B** present, the rate law simply reduces to eq 7. Method II is easily applied and is the most accurate one. The assumption $[\mathbf{B}] \approx [\text{Re}]_T$ is valid throughout the reaction. The values of K_1 and K_2 are such that when $[H_2O_2] > 0.5$ M, $[CH_3ReO_3]_{eq}$ and $[\mathbf{A}]_{eq}$ are less than 2% of $[\mathbf{B}]_{eq}$ (i.e., $[\mathbf{B}]_{eq} \sim [\text{Re}]_T$). To ensure that $[H_2O_2]$ and $[\mathbf{B}]_{eq}$ remain essentially constant during the reaction, styrenes were used at ~2–5 mM, very low relative to $[H_2O_2]$. Furthermore the experimental observation of pseudo-first-order kinetics under these conditions was confirmed by kinetic simulations using KINSIM.[24]

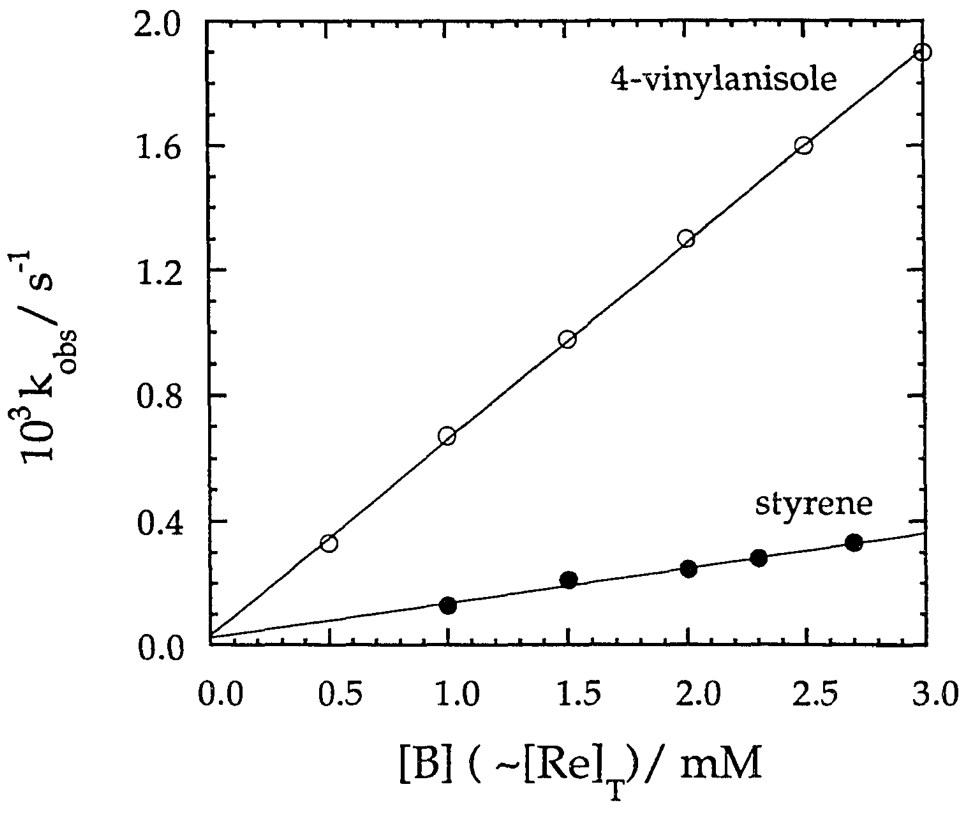


Figure I-5. The pseudo-first-order rate constants for the oxidation of 5.0 mM styrene and 4-vinylstyrene with $[H_2O_2]$ (0.8 M) vary with **B** (≅ $[Re]_T$) are fitted by eq 8, $k_\psi = k_4[B]$.

The values of k_4 obtained by methods I and II are in a good agreement, Table I-2, except for *trans*-4-propenylanisole, 0.80 ± 0.03 (I) and 1.20 ± 0.03 (II) L $mol^{-1}s^{-1}$. This is more likely due to systematic errors in the experiments rather than differences in the chemistry under the two sets of conditions.

First order kinetics with A and B, Method III

Inspection of Scheme I-1 reveals that the equilibrium concentrations of **A** and **B** will not change during the reaction if the following conditions are maintained throughout the reaction time:

$$k_1[H_2O_2]+k_{-1} >> k_3[\text{Styrene}] \quad \text{and} \quad k_2[H_2O_2]+k_{-2} >> k_4[\text{Styrene}] \qquad (8)$$

Helping to attain this condition, for all except β-methoxystyrene, is the finding $k_1 >> k_3$ and $k_2 > k_4$. In addition to that, $[H_2O_2]$ was at least ten times more than [Styrene]. A wide set of concentrations could be found for the styrenes where the inequalities in expression 8 were fully satisfied. Under these conditions the rate law can be written as:

$$v=(k_3[\mathbf{A}]_{eq}+k_4[\mathbf{B}]_{eq})\ [\mathbf{Styrene}]=k_\psi[\mathbf{Styrene}] \qquad (9)$$

The validity of eq 9 in which $[\mathbf{A}]_{eq}$ and $[\mathbf{B}]_{eq}$ remain constants under these conditions was confirmed by kinetic simulations using KINSIM, Figure I-6.[24]

In this method, kinetic measurements were carried out with constant $[Re]_T$ of 1–2 mM and constant [Styrene] of 1–3 mM, different values being used for different styrenes. To ensure a significant contribution from **A**, $[H_2O_2]$ was not used in very large excess. The concentration of $[H_2O_2]$ was varied between 15–60 mM, at least ten times more than [Styrene]. As in Method II, the solutions of CH_3ReO_3 and H_2O_2 were allowed to equilibrate with **A** and **B** for 3–5 min. before adding the styrene.

The experimental observation of pseudo-first-order kinetic traces also confirms the validity of eq 9. The traces fit very well to the first-order exponential equation, eq 2, yielding $k_\psi = k_3[\mathbf{A}]_{eq} + k_4[\mathbf{B}]_{eq}$. In some cases, where the reactions were relatively slow, the initial reaction rates were calculated from the initial stage only.

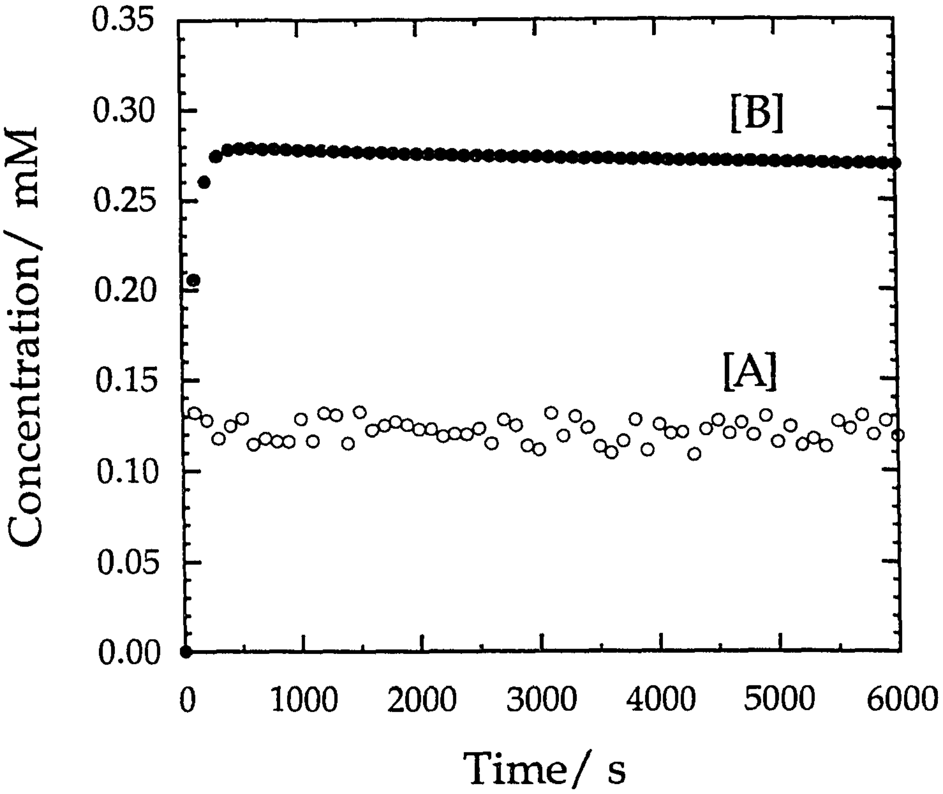


Figure I-6. The calculated concentrations of A and B, from the simulation program KINSIM,[24] based on Scheme IV-1 with $K_1 = 10.8$ and $K_2 = 136$ L mol^{-1}. The rate constants $k_3 = k_4 = 0.5$ L mol^{-1} s^{-1} and the concentrations are 2.0 mM styrene, 20 mM H_2O_2 and 1.0 mM CH_3ReO_3.

The observed rate constants, k_ψ, were then calculated from the initial rates, $k_\psi = v_i$ /[Styrene]. The concentrations of $[A]_{eq}$ and $[B]_{eq}$ for each $[H_2O_2]$ and $[Re]_T$ were calculated from the equilibrium constants, $K_1 = 10.8$ L mol^{-1} and $K_2 = 136$ L mol^{-1}. The values of k_3 and k_4, Table I-2, were calculated using the nonlinear least-squares program GraFit, which allowed the simultaneous use of two independent variables, $[\mathbf{A}]_{eq}$ and $[\mathbf{B}]_{eq}$. An equation with single independent variable can also be used by dividing k_ψ by $[\mathbf{A}]_{eq}$ (eq 10) or $[\mathbf{B}]_{eq}$.

$$\frac{k_\psi}{[\mathbf{A}]_{eq}} = k_3 + k_4 \frac{[\mathbf{B}]_{eq}}{[\mathbf{A}]_{eq}} \tag{10}$$

Plots of $k_\psi/[\mathbf{A}]_{eq}$ against $[\mathbf{B}]_{eq}/[\mathbf{A}]_{eq}$ give straight lines with slopes of k_4 and intercepts of k_3, Figure I-7. The values of k_3 and k_4 obtained by both types of fits are very similar, but those from the dual variable treatment are sounder statistically and are the ones tabulated.

The use of different methods for the kinetics under which different solutions to the rate laws applied allowed the various constants to be determined and to be checked independently. The initial rate method allowed the rate constant for **A** to be determined at low $[H_2O_2]$ ($\leq$ 2 mM). Variation of the initial rates with $[H_2O_2]$ over a wide range of $[H_2O_2]$, Figure I-4, allowed us to determine both k_3 and k_4. The values for the reactions of β-methoxystyrene with **A** obtained under these two conditions agreed, $k_3 = 14.6 \pm 0.4$ and 14.2 ± 0.5 L mol^{-1} s^{-1}.

Method III applies only to substrates that react relatively slowly with **A** and **B**. This method could not be used for the reactions of PR_3 [19] or R_2S [20]. Method III is permissible especially when $k_3 < k_1$ and $k_4 < k_2$, and $[H_2O_2] >> [\text{Styrene}]$, which is true except for β-methoxystyrene.

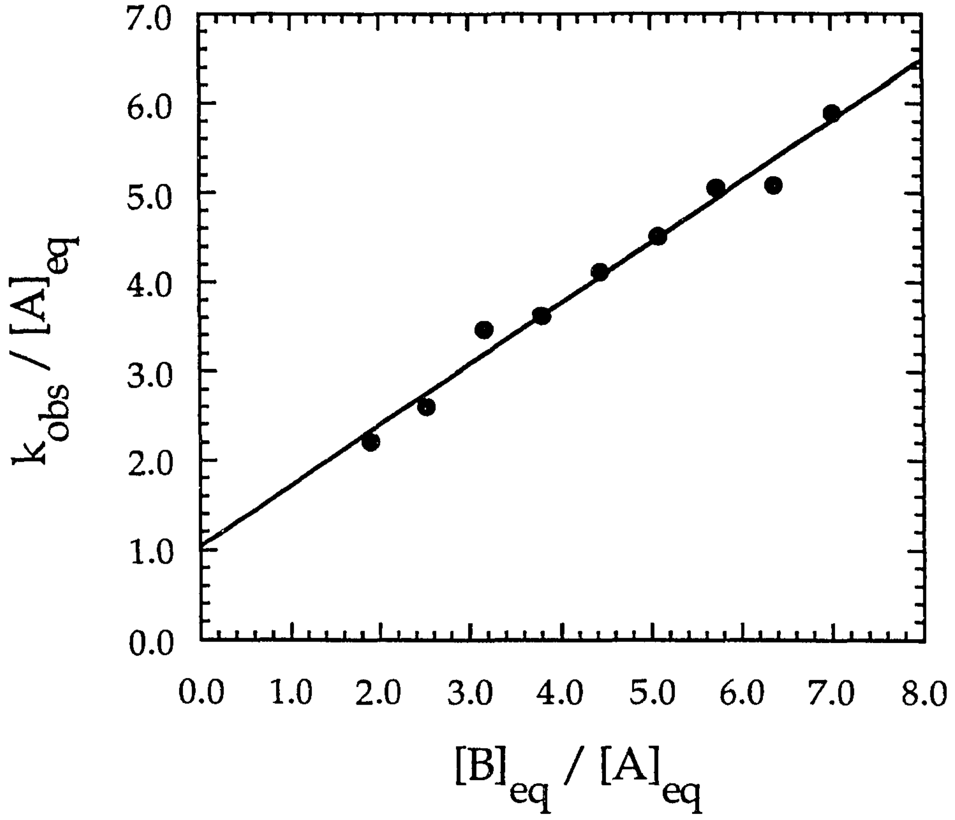


Figure I-7. A plot of $k_\psi/[\mathbf{A}]_{eq}$ against $[\mathbf{B}]_{eq}/[\mathbf{A}]_{eq}$ for the oxidation of 2-methyl-1-phenyl-1-propene (1.0 mM) by **A** and **B** at $[Re]_T = 1.0$ mM, and $[H_2O_2]$ 15–60 mM. The fit to eq 13 gave $k_3 = 1.03 \pm 0.17$ L mol^{-1} s^{-1} and $k_4 = 0.68 \pm 0.04$ L mol^{-1} s^{-1}. Fitting the same data to two independent variables, $[\mathbf{A}]_{eq}$ and $[\mathbf{B}]_{eq}$, gave $k_3 = 1.00 \pm 0.17$ and $k_4 = 0.70 \pm 0.04$ L mol^{-1} s^{-1}.

Activation parameters

Only k_4 for 4-methoxystyrene was studied in this respect. These are the data:

T/°C	3.3	8.0	14.5	20.0	25.0	30.0	37.5
k_4/L mol^{-1} s^{-1}	0.133	0.195	0.273	0.398	0.626	0.75	1.18

Analysis by the TST equation $k_4 = (RT/Nh) \times \exp(\Delta S^{\ddagger}/R) \times \exp(-\Delta H^{\ddagger}/RT)$ gave $\Delta H^{\ddagger} = 42.8 \pm 1.5$ kJ mol^{-1} and $\Delta S^{\ddagger} = -106 \pm 5$ J mol^{-1} K^{-1}.

Products

In CH_3CN/H_2O acidic solutions. The reactions of β-methoxystyrene and *trans*-4-propenylanisole with CH_3ReO_3–H_2O_2 in CH_3CN/H_2O at 0.1M $HClO_4$ showed that epoxidation of 1.0 equivalent of styrene required 1.0-1.2 equivalents of H_2O_2. This slight mismatch is consistent with the known slow decomposition of the catalytic system, CH_3ReO_3-H_2O_2, to $HReO_4$, CH_3OH and oxygen.[22]

^{1}H–NMR experiments showed that the initial product from reaction of the styrenes with CH_3ReO_3–H_2O_2 was the styrene oxide. In the presence of aqueous acid, the epoxide ring opened, yielding 1,2-diol and other minor products. In CH_3CN/H_2O, the final product was the 1,2-diol. The catalytic reactions of 0.5 M styrene, 4-methoxystyrene and *trans*-4-propenylanisole with H_2O_2 (0.6 M) in the presence of 2–20 mM CH_3ReO_3 yielded the corresponding 1,2–diol with isolated yields of 55%, 43% and 35%, respectively. Other products, such as aldehydes, ketones or alcohols, were detected by GC-MS with relatively low yields depending on the nature of the styrene.

C-C bond cleavage. Electron-donating groups on the aromatic ring or on the olefinic carbons enhance the C–C bond cleavage. For example, no C–C bond cleavage was observed from reaction of styrene, whereas *trans*-4-propenylanisole produced 4-methoxybenzaldehyde and 4-methoxybenzyl alcohol in 10-15% yield. Epoxidation of β-methoxystyrene, on the other hand, involved complete C-C bond cleavage. The products were benzaldehyde, identified by ^{1}H–NMR and GC–MS, and formaldehyde, characterized by chromotropic acid analysis.[23] ^{1}H NMR experiments showed that the same products also resulted from the reaction of β-methoxystyrene with *m*-chloroperoxybenzoic acid in CD_3CN/D_2O (1:1 v/v) containing 0.1 M $HClO_4$.

In CD_3CN. The stereochemistry of these reactions was studied in CD_3CN in the absence of acid. The difference in the coupling constants in the ^{1}H NMR spectra of the cis protons, J_{AB} (cis) = 4.2 Hz, and the trans protons, J_{AB} (trans) = 2.0 Hz, was used to distinguish between the products. Epoxidation of *cis*-β-methylstyrene with the CH_3ReO_3-H_2O_2 system gives the cis epoxide; likewise, trans-β-methylstyrene is converted to the trans epoxide, Figure I-8.

Epoxide ring opening

In CD_3CN, in the absence of acid, styrene oxide reacts with CH_3ReO_3 in both the presence *and absence* of H_2O_2 to yield a Re(VII) compound with a bound diol, eq 11. Its ^{1}H–NMR spectrum in CD_3CN showed six signals: δ 2.45 ppm (s, 3H, Re-CH_3), 4.78 ppm (dd, 1H, H_a), 5.23 ppm (t, 1H, H_b), at 5.54 ppm (dd, 1H, H_c), 7.32 ppm (m, 3H, p- and m-Ph) and 7.47 ppm (m, 2H, o-Ph). The coupling constants for the protons H_a, H_b and H_c are: $J_{cb} \sim J_{ab} = 9.6$ Hz and $J_{ac} = 8.3$ Hz. Reaction 11 occurs only when water is absent. In the presence of water (~ 1 M), the Re-diol adduct hydrolzed slowly to CH_3ReO_3 and the 1,2-diol.

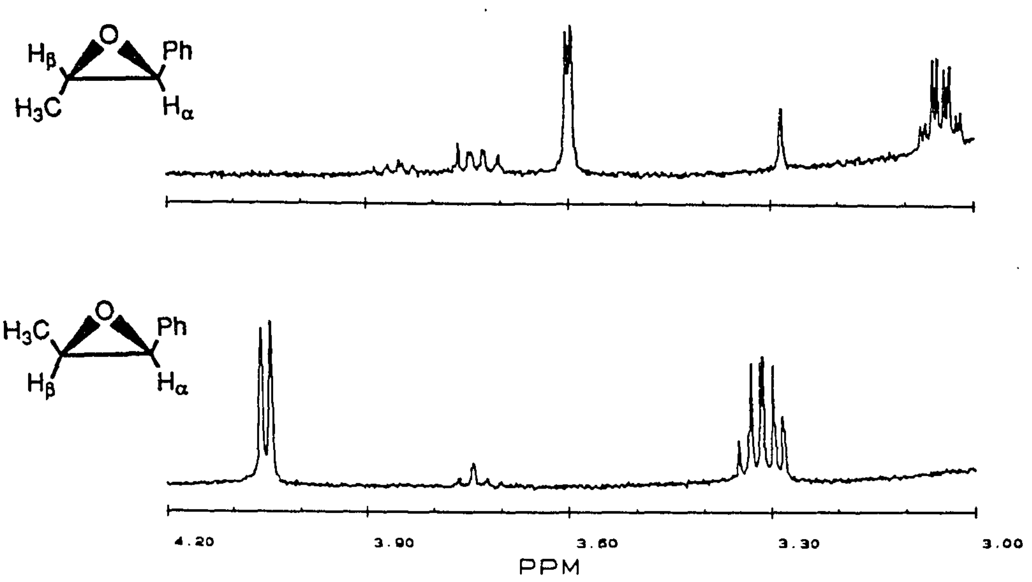
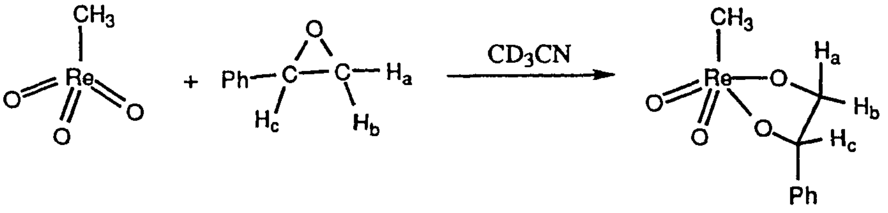


Figure I-8. ^1H NMR spectra, in CD_3CN, of *cis*- and *trans*-β-methylstyrene epoxide formed from reactions of *cis*- and *trans*-β-methylstyrene, respectively, with H_2O_2/CH_3ReO_3 catalytic system. The scale in the bottom is for both ^1H NMR spectra.



(11)

In addition to the bound diol, free phenyl-1,2-ethanediol was also formed. The rhenium diolate adduct in eq 11 forms from the reaction of styrene epoxide with CH_3ReO_3 and not from reaction of phenyl-1,2-ethanediol with CH_3ReO_3. Under the same conditions, phenyl-1,2-ethanediol (0.10 M) and CH_3ReO_3 (0.05 M) in CD_3CN did not yield any Re-diol adduct even after two days. In CH_3CN/H_2O (1:1 v/v), 0.10 M $HClO_4$, addition of CH_3ReO_3 did not enhance the rate of formation of phenyl-1,2-ethanediol from styrene oxide. The epoxide-ring-opening in the presence of 0.1 M $HClO_4$ is much faster than in the presence of 1-5 mM CH_3ReO_3.

DISCUSSION

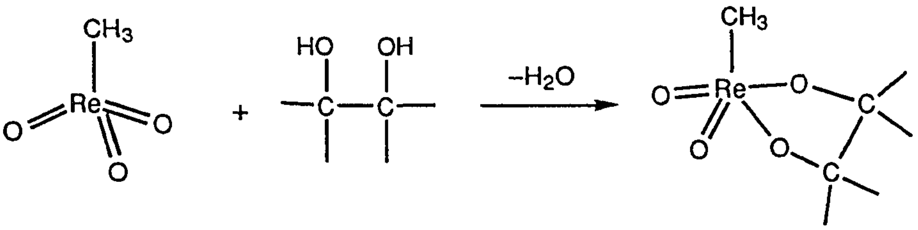
Epoxidation in semi-aqueous solutions

In organic solvents, the rhenium–catalyzed reactions of hydrogen peroxide and styrenes do yield epoxides, as established in our research and in work reported in the literature.[22] For the study of the quantitative kinetics, however, a semi-aqueous medium was employed since the rate and equilibrium constants of the initial steps, formation and dissociation of the rhenium peroxides, has been quantitatively established from earlier work and improved by subsequent experiments carried out in the course of this work. Once the activity of water is this high, acid must be added to stabilize the rhenium peroxides, even though CH_3ReO_3

itself is stable toward water. In aqueous acid, of course, the first-formed epoxide product undergoes "instant" ring opening to the diol, which is thus the identified product in the aqueous, acidic medium.

Formation of bis(alkoxy)rhenium(VII) complexes

During olefin epoxidation by CH_3ReO_3-H_2O_2 in *tert*-butyl alcohol catalytic ring opening of epoxides to 1,2-diols also occurs.[21] In dry organic solvents, such as CH_2Cl_2 and THF, 1,2-diols react with CH_3ReO_3 to form Re-diol chelate complexes, eq 12.[25]



(12)

Formation of the diolate may reduce the catalytic turnover. Epoxides bind more strongly to Mo^{VI}-peroxo complexes than the corresponding olefins do,[26] inhibiting epoxidation and leading to further oxidation of the metal-coordinated epoxide.[5,10] Formation of rhenium epoxide adducts was not observed. The coupling patterns of the aliphatic protons, H_a, H_b and H_c, in free styrene oxide, eq 11 and in rhenium bound styrene oxide are expected to be very similar. Free styrene oxide gives three doublet-of-doublets signals at 2.77 ppm (H_a, J_{ac} = 2.7 and J_{ab} = 5.4 Hz), 3.07 ppm (H_b, J_{bc} = 4.2) and 3.82 ppm (H_c). The chemical shifts and the coupling constants obtained by ^1H-NMR from the reaction of styrene oxide with CH_3ReO_3 suggest formation of the Re-diol adduct rather than a Re-epoxide adduct. Here the Re-diol chelate complex was observed only in CD_3CN in the absence of acid. Under the conditions for the kinetics, CH_3CN/H_2O, 0.1 M $HClO_4$, CH_3ReO_3 did not react with phenyl-1,2-ethanediol or styrene oxide, nor did it enhance the opening of the styrene oxide ring. Also, addition of 1,2-diols did not alter the rate of epoxidation of styrene by CH_3ReO_3-H_2O_2. The epoxide ring-opening is catalyzed by the acid (0.10 M $HClO_4$) rather than by CH_3ReO_3. The reaction of 1,2-diols with Re(VII) is inhibited by water since d^0 early transition metals (Lewis acids) have high affinity for bases such as water, present in high concentration relative to the 1,2-diols.

Effect of the solvent on the reactivity

The rate of reaction of β-methoxystyrene with CH_3ReO_3-H_2O_2 increases with the amount of water in the solution, consistent with the higher values of k_1, k_{-1}, k_2 and k_{-2}, in H_2O.[16,19] There is also an effect on the catalytic steps: the rate constants for *trans*-4-propenylanisole are k_4 = 1.1 L mol^{-1} s^{-1} in 1:1 CH_3CN/H_2O, and 0.45 L mol^{-1} s^{-1} in a 4:1 solvent mixture. Another examination of solvent effects was carried out for styrene. The value of k_4 is 0.021 L mol^{-1} s^{-1} in methanol, compared to 0.11 in 1:1 CH_3CN/H_2O. Note that the results cited refer to the reactions of **B** only, and do not reflect any effect of water on the rates or equilibria of the peroxide-binding steps. Again, the catalytic step of this reaction is accelerated in the presence of water.

The realtive reactivities of the monoperoxo-Re(VII), A, and the diperoxo-Re(VII), B

Clearly **A** and **B** epoxidize styrenes at similar rates. What differences exist between the two depend upon the kind of styrene being used. A recent study[17] of the oxidation of anilines by the CH_3ReO_3/H_2O_2 system in methanol has shown that **A** is more active than **B**. These results do not agree with the findings for alkenes reported recently, from studies carried out in *tert*-butanol,[21] from which it was concluded that **B** but not **A** epoxidizes olefins. Since both **A** and **B** are neutral molecules in which Re^{VII} binds to CH_3, oxo, and peroxo ligands, the medium should not greatly effect their relative reactivities. The absolute activities of **A** and **B** are, however, media dependent. In general, the relative activity of the diperoxo to the monoperoxo metal complexes depends greatly on the size of the metal and the reaction mechanism. Competitive studies of olefin epoxidation by $M(O)(O_2)_2HMPT$ (HMPT = hexamethylphosphoric triamide; M = Mo and W) have shown that the diperoxo is more reactive than the monoperoxo when M = W. In the case of Mo it is the opposite, the monoperoxo being more reactive.[3] We have found that **A** is less sensitive to steric factors than **B**. For example, the rate constant for the reaction of *trans*-4-propenylanisole with **A** is about three times larger than that from the same reaction with **B** ($k_3/k_4 = 3.4$), whereas for the less sterically hindered 4-vinylanisole, $k_3/k_4 = 1.3$.

It is pertinent to this research to comment upon the very similar reactivities of **A** and **B**, not only toward styrenes, but also with respect to several of the species cited earlier: Br^-, $ArNMe_2$, R_2S, and Ar_3P, for example. This might at first seem surprising, in that CH_3ReO_3 is the product of **A**, whereas **A** itself is formed when **B** reacts; clearly the two products, CH_3ReO_3 and **A**, are quite different. Nonetheless, the cause seems to be that these two hardly differ in free energy with respect to the extra molecule of H_2O_2/H_2O by which they differ; that is, K_1 is only 10.6 L mol^{-1}, or $\Delta G_1^\circ = -6$ kJ mol^{-1}. Both **A** and **B** contain $Re(\eta^2\text{-}O_2^{2-})$, and it this chemical unit that is the reactive one.

Effect of the styrene nucleophilicity

In both cases the rate constants increase with the presence of electron donating groups, whether on the olefinic carbons or on the aromatic ring. For methyl substituted styrenes the following reactivity trend was observed: Styrene < trans-β-methylstyrene ~ cis-β-methylstyrene < α-methylstyrene < β-dimethylstyrene.

Steric factors have little effect. The ratio of the rate constants (k_4) for epoxidation of *cis-* and *trans*-β-methylstyrene is 1.3. Addition of one methyl group to the olefinic carbon increases the rate constant by a factor of 3–4. A large effect was observed when the substituent on an olefinic carbon donates electrons through resonance. The rate constant of β-methoxystyrene is ~150 times greater than that of styrene. Donation of electrons from the OCH_3 group through resonance enhances greatly the nucleophilicity because it develops negative charge on the olefinic carbons. Electron-donating substituents on the aromatic ring in ortho and para positions increase the rate through resonance;[27] thus 4-methylstyrene and 2,4-dimethylstyrene have rate constants 2–5 times greater than that of styrene. On the other hand, the rate constants for styrene and 3-methylstyrene are almost the same, as given in Table I-2.

The rate of epoxidation of 2,4,6-trimethylstyrene is almost equal to that of styrene and 3-4 times less than that of 2,4-dimethylstyrene. Steric factors resulting from the presence of methyl groups in both ortho positions lower the reactivity of 2,4,6-trimethylstyrene. Sterically, these substituents affect the attack of the olefinic carbons on the peroxy oxygen of **B.** They also disturb the delocalization of electrons between the aromatic and the olefinic systems. In 2,4,6-trimethylstyrene the β-carbon lies out of the plane that contains the aromatic carbons and the α-carbon. This, of course, reduces the donation of electrons from the methyl groups to the olefinic system through resonance, probably the most important path for donation of electrons in this case.

Hammett correlation

Further evidence for the importance of electron donation through resonance was obtained from a correlation of substituent effects by the Hammett equation. The rate constants for styrene, 3-methylstyrene, 4-methylstyrene and 4-methoxystyrene were correlated by the Hammett linear free-energy relationship, σ^+ (but not σ) gave a good correlation, Figure I-9, with $\rho = -0.93 \pm 0.05$. The correlation with σ^+ implies a

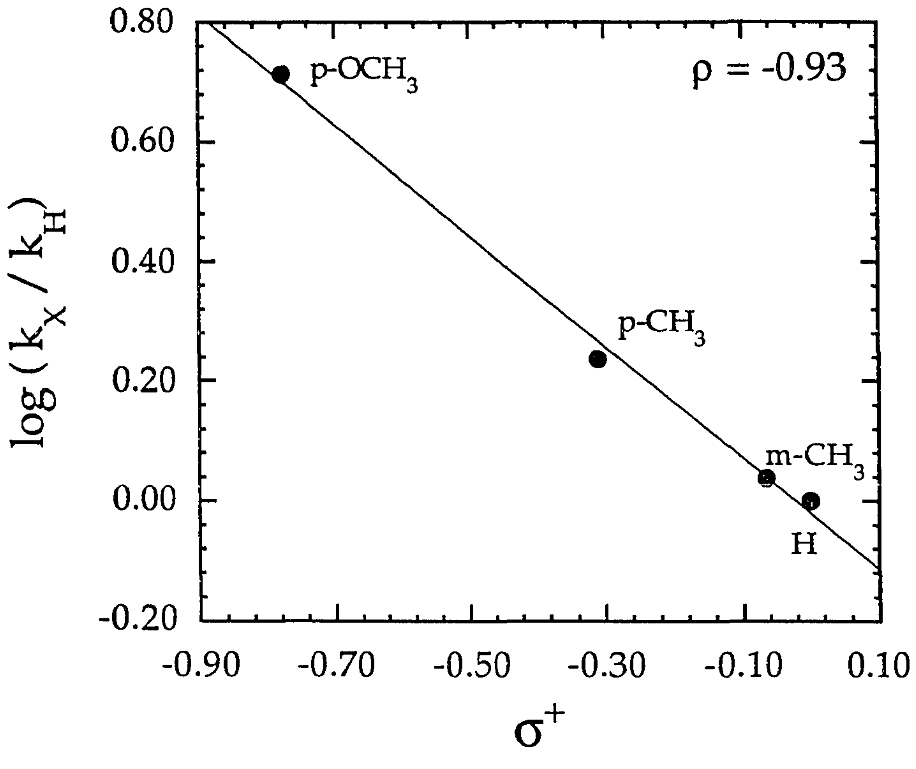


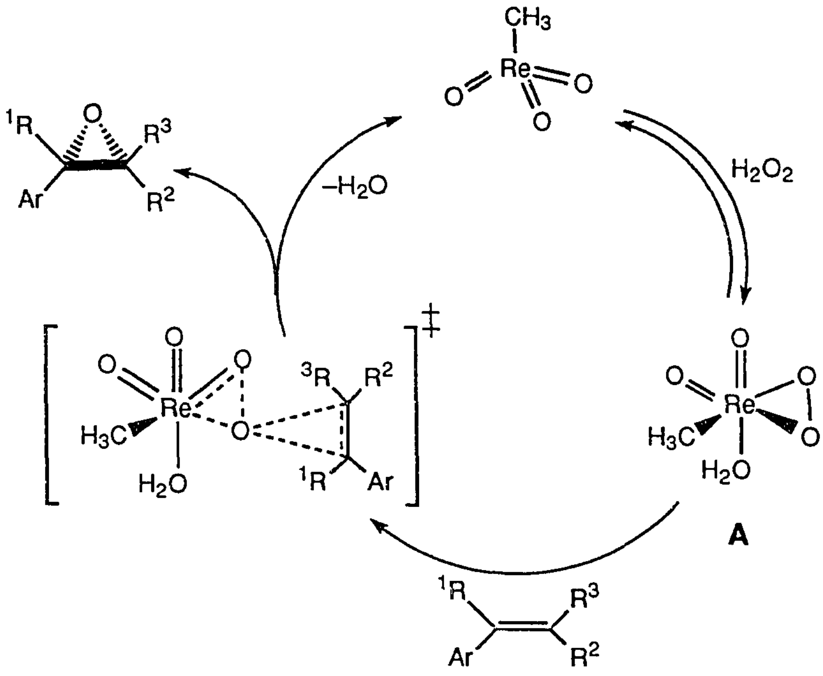
Figure I-9. The Hammett correlation of k_4 for the oxidation of styrenes by **B** against σ^+. The reaction constant is $\rho = -0.93$.

direct interaction through resonance between the substituent and the reaction site. The relatively small negative value of ρ indicates the buildup of partial positive charge on the olefinic carbons in the transition state. Compare the epoxidation of styrenes with dimethyl dioxirane ($\rho = -0.90$)[28] and by peracetic acid ($\rho = -1.3$)[8]. In both studies the rate constants correlated well with σ^+. The latter study proposed nucleophilic attack of one of the olefinic carbons (α or β) on the peroxy oxygen followed by intramolecular attack of the same oxygen on the other olefinic carbon.

The suggested mechanism

For the epoxidation of styrenes by CH_3ReO_3-H_2O_2 we propose for **A** the mechanism diagrammed in Scheme I-2.

Scheme I-2. Proposed mechanism for epoxidation of a styrene by **A**.



Reactions of B should adopt the same mechanism. It involves external nucleophilic attack of the π-system of the olefin on the electrophilic peroxide oxygen. This leads to the formation of a three-membered ring transition state. This proposed mechanism is consistent with the slight effect of steric factors on the rate constant since such attack is insensitive to steric hindrance.

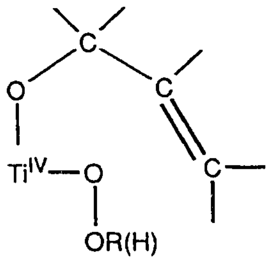
Mechanistic considerations

A similar three-membered ring transition state has been proposed for the epoxidation of olefins by Mo(VI)–peroxo complexes.[2] Theoretical studies of epoxidations by M(VI)–peroxo complexes (M = Cr, Mo, W) show that three-membered ring transition states are more favorable than five-membered rings which including both peroxy oxygens and the metal.[13]

The activation parameters for k_4 support this model. Bimolecular reactions will nearly always have a negative value for $\Delta S^{\ddagger}$, but the value of -106 J mol^{-1} K^{-1} is so negative as to suggest specific orientational features in the transition state formed from two uncharged species. The value of $\Delta H^{\ddagger}$ of 42.8 kJ mol^{-1} is substantial and must surely reflect a composite of bond breaking (Re–O, O–O) and bond making (C–O); without such compensation the reaction would be extraordinarily slow: witness the very slow uncatalyzed reaction between hydrogen peroxide and styrenes.

Epoxidation of allyl alcohols

Allyl alcohols are epoxidized more readily than normal olefins by d^0-peroxides of early transition metals, such as Ti(IV) and V(V).[12] An allyl alcohol binds the metal through its OH group, 5, before oxygen transfer. In addition, this binding leads to selective epoxidations.



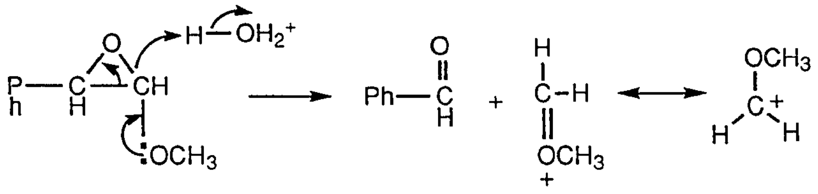
5

Our results for cinnamyl alcohol and *trans*-3-methyl-2-phenyl-2-propen-1-ol show that such binding to Re(VII) is not likely. The rate constants for cinnamyl alcohol and *trans*-3-methyl-2-phenyl-2-propen-1-ol are less than those of β-methylstyrene and β-dimethylstyrene, respectively, Table I-2. The slight changes in reactivity of allyl alcohols relative to methyl–substituted styrenes follow the trend for other alkyl-substituted styrenes; the CH_3 group is simply better electron donor than CH_2OH. This finding confirms the observation that aqueous Re(VII)–peroxo complexes do not bind to OH groups of diols and allyl alcohols. Indirectly, it further suggests that olefins do not bind to **A** or **B** prior to the oxygen-transfer step since high oxidation state d^0 early transition metals are known to have a much higher affinity for hard ligands, such as ones with OH groups, than for π-acid ligands, such as olefins. This result suggests that the alternative mechanism, eq 1,[1a] which involves binding of the olefin to Re^{VII} before the oxygen atom transfer takes place is not possible under these conditions. Furthermore, reactions that involve this mechanism are inhibited by basic solvents, such as water or alcohols. In the case of CH_3ReO_3/H_2O_2, however, the reactivity increases with the $[H_2O]$ present in the solutions.

The substituents effects on the C-C bond cleavge

Expoxides are the initial products from these reactions. Epoxides react rapidly with acids to yield carbocation intermediates that react immediately with nucleophiles, such as H_2O, to yield 1,2-diols or other organic products. The extent of carbon–carbon bond cleavage depends on the styrene and on the experimental conditions. The amount of cleavage increased with acidity but decreased with the amount of H_2O. Electron-donating groups, especially on the olefinic carbons, enhance the C–C bond cleavage in this order: styrene < cis-β-methylstyrene ≤ trans-β-methylstyrene < *trans*-4-propenylanisole << β–methoxystyrene.

β-Methoxystyrene undergoes complete C–C bond cleavage and produces benzaldehyde, formaldehyde and methanol, assisted by the strong electron-donating group, OCH_3. Formation of the same products from oxidation of β-methoxystyrene by *m*-chloroperoxybenzoic acid under the same conditions suggested that the C-C bond cleavage is catalyzed by acid, eq 13:



(13)

The carbocation shown as the product of eq 13 then rapidly hydrolyzes to formaldehyde, methanol and acid.

Epoxides formation and stereochemistry

In aqueous acid the epoxide forms slowly and reacts rapidly, and could not be observed. Although the epoxide ring-opening in organic solvent, such as alcohols, is catalyzed by CH_3ReO_3, the epoxide can be observed and isolated.[21] In the presence of basic ligands, such as pyridines, only the epoxide is formed at 25 °C in almost quantitative yield.[22] In the absence of acid, using only CD_3CN as solvent, the epoxide was detected by ^1H NMR. It reacted slowly with the water introduced with the 30% H_2O_2 and produced by the overall reaction. Under these conditions the epoxidation reactions are stereospecific. Epoxidation of *cis*-β-methylstyrene led to the *cis* epoxide, whereas epoxidation of *trans*-β-methylstyrene gave exclusively the *trans* epoxide. These results are consistent with the proposed mechanism of concerted oxygen transfer through a three-membered ring transition state. Rotation of the C–C bond is not possible and so the reactions are completely stereospecific. Reactions that adopt radical mechanisms[1c, 29] or proceed by nucleophilic attack of one of the olefinic carbon atoms on the peroxo oxygen, as in the third mechanism,[8] are partially or completely nonstereospecific. The radical mechanism has been proposed for epoxidation of allyl alcohols by $V(O)(O_2)(pic)(H_2O)_2$.[1b]

CONCLUSION

Epoxidation rates catalyzed by d^0 early transition element peroxo complexes increase in the following, Ti(IV) < V(V) < Mo(VI).[2] Tungsten(VI) complexes are the best, but water or a polar solvent retards the reaction.[2c] Rhenium(VII) may be the most active catalyst among these d^0 early transition metals. Herrmann et al[22] have claimed that CH_3ReO_3 is the best catalyst for epoxidation of olefins by H_2O_2; they state: "Among the epoxidation catalysts, only Groves' manganese/porphyrin systems can successfully compete with CH_3ReO_3 in terms of yields and turnover numbers (TON)." [22] The sources of oxygen in these reactions, however, are PhIO, $KHSO_5$ or very high $[H_2O_2]$ (> 30%). The efficiency and selectivity of the catalyst for oxygen transfer is very important since a less effective epoxidation catalyst, such as

Ti(IV), leads to free-radical formation and catalytic decomposition of the peroxide.[2] Furthermore, non-selective catalysts, such as (Por)M=O; M = Fe [3,30] or Mn,[2,31] lead to further oxidation of the epoxides by C–C bond cleavage and hydride or hydrogen atom abstraction pathways. Although the CH_3ReO_3–H_2O_2 catalyst decomposes slowly under certain conditions,[32] CH_3ReO_3 is a good catalyst for epoxidation of olefins. It is easy to prepare and handle, soluble and active in H_2O and most organic solvents. Methylrhenium trioxide activates H_2O_2 heterolytically and achieves high reactivity ($k_{cat}/k_{uncat} \sim 10^5$) and selectivity. It does not catalyze hydride or hydrogen atom abstraction reactions, or involve radical pathways. Unlike other transition metal peroxo complexes, the reactivities of the monoperoxo-Re, **A**, and diperoxo-Re, **B**, species are not inhibited by the presence of basic ligands or solvents, such as alcohols or water. The epoxidation reactions are stereospecific. Finally, CH_3ReO_3 can be used, efficiently, over a wide temperature range, below and above room temperature.

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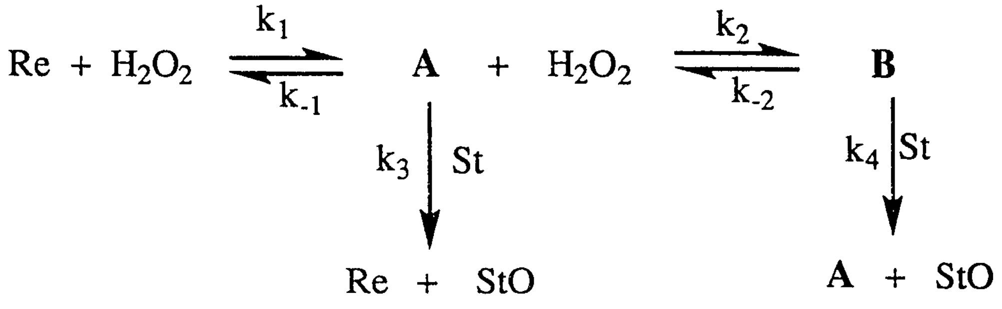
APPENDIX: DERIVATION OF THE RATE LAW FOR REACTIONS OF A STYRENE WITH **A** AND **B**



$$\text{rate} = -\,d[\text{St}]/\,dt = \{k_3[\mathbf{A}] + k_4[\mathbf{B}]\}\,[\text{St}]$$

- Steady state approximation on **B** and **A** :-

$$\frac{d[B]}{dt} = k_2[H_2O_2][A] - k_{-2}[B] - k_4[B][St] = 0 \qquad (1)$$

$$[B] = \frac{k_2[H_2O_2][A]}{k_{-2} + k_4[St]} \qquad (2)$$

$$\frac{d[A]}{dt} = k_1[H_2O_2][Re] + k_{-2}[B] + k_4[B][St] - k_{-1}[A] - k_2[H_2O_2][A] - k_3[A][St] = 0 \qquad (3)$$

- Add eq 1 to eq 3 :-

$$\frac{d[A]}{dt} - \frac{d[B]}{dt} = k_1[H_2O_2][Re] \; - k_{-1}[A] \; - k_3[A][St] = 0 \qquad (4)$$

- The mass balance of the catalyst :-

$[Re] = [Re]_T - [A] - [B]$

- Substitute [B] from eq 2 into eq 5 :-

$$[\mathrm{Re}] = [\mathrm{Re}]_T - [A] - \frac{k_2[H_2O_2][A]}{k_{-2} + k_4[\mathrm{St}]} \tag{6}$$

- Replace the [Re] in eq 4 by eq 6 :-

$$k_1[H_2O_2][\mathrm{Re}]_T - k_1[H_2O_2][A] - \frac{k_1k_2[H_2O_2]^2[A]}{k_{-2} + k_4[\mathrm{St}]} - k_{-1}[A] - k_3[A][\mathrm{St}] = 0 \tag{7}$$

- $[A]_{ss}$ from eq 7 :-

$$[A] = \frac{k_1[H_2O_2][\mathrm{Re}]_T}{k_{-1} + k_3[\mathrm{St}] + k_1[H_2O_2] + \dfrac{k_1k_2[H_2O_2]^2}{k_{-2} + k_4[\mathrm{St}]}} \tag{8}$$

- and $[B]_{ss}$ from eq 2 andeq 8 :-

$$[B] = \frac{k_2[H_2O_2]}{k_{-2} + k_4[\mathrm{St}]}\left\{\frac{k_1[H_2O_2][\mathrm{Re}]_T}{k_{-1} + k_3[\mathrm{St}] + k_1[H_2O_2] + \dfrac{k_1k_2[H_2O_2]^2}{k_{-2} + k_4[\mathrm{St}]}}\right\} \tag{9}$$

- replace $[A]_{ss}$ and $[B]_{ss}$ (from eq 8 and 9) into the rate law gives :-

$$\mathrm{rate} = \frac{k_1[H_2O_2][\mathrm{Re}]_T[\mathrm{St}]\left\{k_3 + \dfrac{k_2k_4[H_2O_2]}{k_{-2} + k_4[\mathrm{St}]}\right\}}{k_{-1} + k_3[\mathrm{St}] + k_1[H_2O_2] + \dfrac{k_1k_2[H_2O_2]^2}{k_{-2} + k_4[\mathrm{St}]}} \tag{10}$$

CHAPTER II. KINETICS AND MECHANISM OF THE EPOXIDATION OF ALKENES BY H_2O_2, CATALYZED BY METHYLRHENIUM TRIOXIDE

A paper submitted to the *Journal of the American Chemical Society*

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ABSTRACT

Kinetic studies on the epoxidation of alkyl-substituted alkenes by H_2O_2 as catalyzed by methylrhenium trioxide, CH_3ReO_3 (MTO), were carried out in 1:1 CH_3CN/H_2O at pH 1 and in methanol. Reactions of alkenes with the bis-peroxide, $CH_3Re(O)(O_2)_2$, **B**, were studied by ^1H NMR (in methanol-d_4), thermometric and spectrophotometric (in CH_3CN/H_2O) techniques. The epoxidation reactions in CD_3OD (or CH_3OH) are about one order of magnitude slower than in CH_3CN/H_2O acidic solutions. The various trends in reactivity are medium-independent. The rate constants for reactions of **B** with the aliphatic alkenes correlate closely with the number of the alkyl groups on the olefinic carbons. The rate constants increase with the alkene nucleophilicity and slightly sensitive to steric hindrance. The rate constants for the catalytic epoxidation of olefins by **B** and those reported for the stoichiometric epoxidation by dimethyldioxirane show very similar trends in reactivity. These findings suggest a concerted mechanism that involves external attack of the olefin on the peroxy oxygen of **B**.

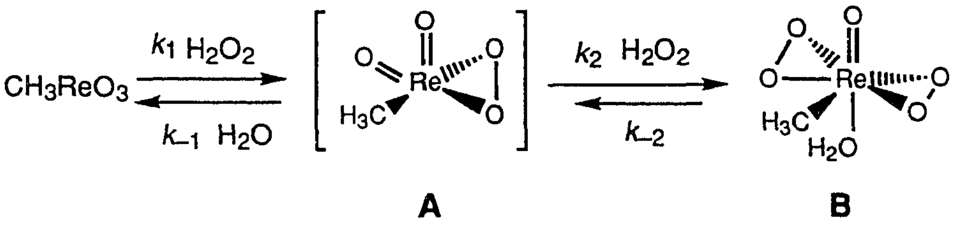
INTRODUCTION

Epoxides are useful intermediates for the preparation of a wide variety of products.[1] The epoxide ring is highly reactive and may be ring-opened with different nucleophilic and electrophilic reactants.[2] Glycols, the products from hydration of epoxides, find some important applications such as anti-freeze components, food additives or for the preparation of condensation polymers.[3] The reaction of epoxides with alcohols provides glycol ethers, used as polar solvents.[4]

Many oxidants, such as molecular oxygen, hydrogen peroxide and organic peroxides have been used to epoxidized olefins under catalytic and noncatalytic conditions. For many reasons hydrogen peroxide, "Mr. Clean", is potentially considered as an ideal oxygen transfer reagent.[2] Reactions of free hydrogen peroxide with olefins, however, are slow and nonselective. Owing to the amphoteric nature of hydrogen peroxide, it has been activated, heterolytically, by basic and acidic catalysts, such as low valent and high valent transition metals.[3] The electrophilic character of H_2O_2 increases upon coordination to high valent metals.

High valent metals of group IV-VI are excellent catalysts for epoxidation of olefins with organic peroxides. With H_2O_2 some of these species, such as Ti^{IV} and V^{V}, catalytically decompose H_2O_2.[3] Mo^{VI} and W^{VI} complexes have been reported as the best catalysts among these.[5] Heterolytic activation of H_2O_2 by early transition metal complexes to achieve high reactivity and selective oxygen transfer has posed a challenge.

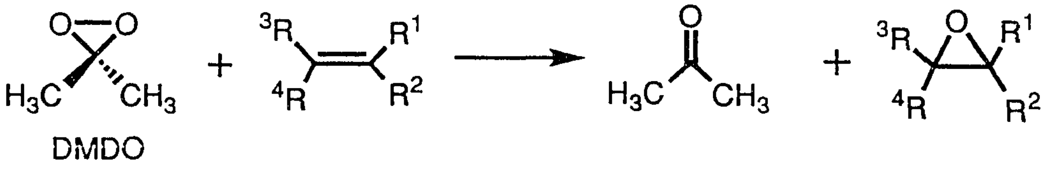
Methylrhenium trioxide, CH_3ReO_3 (MTO), activates H_2O_2 by formation of a mono-peroxide, **A**, and a bis-peroxide, **B**, species eq 1. MTO has efficiently catalyzed epoxidation of olefins by H_2O_2 in semi-aqueous and organic solvents, such as alcohols, at low and moderately high temperatures with very high activity and turnover.[6,7] Recent studies[7] on olefin epoxidation by H_2O_2/MTO catalytic system in tert-butanol have suggested that only the bis-peroxide, **B**, is active toward epoxidation of olefins.



(1)

Both peroxo species **A** and **B** are active toward oxygen transfer to other organic and inorganic substrates, such as anilines, PR_3, R_2S, Br^- and Cl^-.[8-12] Recently,[6] In Section I, I have shown that the active species for epoxidation of styrenes are both the mono-peroxide, **A**, and the bis-peroxide, **B**.[6] The epoxidation reactions are stereospecific. The rates increase with the styrene nucleophilicity and remain relatively insensitive to steric hindrance. The rate constants for reactions of **A** and **B** with styrenes increase with the solvent polarity and the concentration of water. External nucleophilic attack of the styrene on the peroxy oxygen of **A** (or **B**) has been proposed.[6]

Kinetic studies on the stoichiometric epoxidation of styrenes and alkenes by dimethyldioxirane in acetone, eq 2, have shown that reactions of styrenes with dimethyldioxirane, DMDO, are insensitive to steric hindrance.[13,14]



(2)

Reactions of substituted alkenes, however, are unusually sensitive to steric factors. Phenyl substituted olefins are more reactive than alkyl analogous. Furthermore, the rates of epoxidation of styrenes and alkenes are enhanced with the concentration of water. In the case of styrenes the rates are more sensitive to water concentration.[13]

In this work the kinetics of epoxidation of a series of alkyl-substituted olefins (alkenes) were investigated in organic and semi-aqueous solutions. Reactions of substituted (including open, cyclic and bicyclic) alkenes were studied to explore the electronic and steric effects on the alkene reactivity toward **B**. The reactions were studied by three different techniques: *NMR* (in methanol-d_4), *thermometric* and *spectrophotometric* (in 1:1 CH_3CN-H_2O at pH 1). In the thermometric method the temperature increases accompanying the exothermic reactions were used to obtain kinetic data. The kinetic results obtained in this study have been compared with these obtained for the catalytic epoxidation of styrenes by **A** (and **B**) and for the stoichiometric epoxidation of olefins by dimethyldioxirane. Some similarities in the kinetics and mechanistic behavior of **B** (or **A**) and dimethyldioxirane have been noted.

EXPERIMENTAL

Materials

Water was purified by a Millipore-Q water purification system. HPLC grade acetonitrile (Fisher) was used. Acetonitrile-d_3 and methanol-d_4 (Cambridge Isotope Laboratories) were used without further purifications. In semi-aqueous solutions the pH was maintained by $HClO_4$ stock solutions prepared by diluting 70% $HClO_4$ (Fisher).

Methylrhenium trioxide, MTO, was prepared by a recently published method.[15] It was purified first by sublimation then by recrystallization from CH_2Cl_2/ hexane and finally by a second sublimation. Solutions of MTO (0.01-0.20 M) were prepared in CD_3OD (NMR method) or in CH_3CN (thermometric and spectrophotometric methods) , stored at 5 °C, and used within one or two weeks. The concentration was determined spectrophotometrically by diluting in 0.1 M $HClO_4$: 239 nm (ε 1900 L mol^{-1} cm^{-1}) 270 nm (ε 1300 L mol^{-1} cm^{-1}).[16]

Alkenes were purchased commercially from Aldrich. *Trans*-4-octene, 1-octene and 1-hexene were purified by distillation. Other alkenes were used without further purification. Stock solutions of hydrogen peroxide 30% (in water) (Fisher) were used and standardized weekly by iodometric titration.

Kinetics

NMR method. ^1H NMR spectra were obtained with a VXR 300 MHz spectrometer referenced to $(CH_3)_4Si$. The kinetic reactions were carried out in methanol-d_4 (total volume = 0.6 mL) at 25 °C with the last reagent added being the alkene. All the experiments were done in the presence of $[H_2O_2]$ =0.5 M. The alkene (0.05-0.1 M) and the catalyst (1-50 mM) were of lower concentrations. The ^1H NMR spectrum was recorded at 2-10 min increaments over the 2-5 hr reaction time. The changes in intensity of the alkene signal(s) with time followed first-order kinetics. The pseudo-first-order rate constants were evaluated by non-linear fitting of the relative intensity-time data to a single-exponential decay equation, eq 3.

$$Y_t = Y_\infty + (Y_0 - Y_\infty) \exp(-k_\psi t) \tag{3}$$

where Y = *relative intensity* (NMR method) or *absorbance* (spectrophotometric method).

Thermometric method. The thermometric measurements were recorded by a Parr 1455 calorimeter, equipped with a thermistor in a platinum resistance probe. The kinetic data were collected at temperatures very close to 25 °C in CH_3CN/H_2O (1:1 v/v) solutions at pH 1. This technique required a solution with total volume between 60-100 mL. Two solutions, one contains H_2O_2 and the catalyst, MTO, (50-80 mL) and another contains the alkene (10-20 mL) were prepared in 0.1 M $HClO_4$-CH_3CN/H_2O and put in a glass deware and a glass sample cell, respectively. Both solutions were thermally equilibrated before mixing for 20-30 min inside the calorimeter. The two solutions were then mixed and stirred for 1-2 min. The stirrer was then stopped and the temperature was recorded at a preset time intervals (5 or 10 seconds) by a computer with Lotus 1-2-3 software.

The expression for the temperature at a given time (T_t) is:

$$T_t = T_o + \Delta T_r + \Delta T_T \tag{4}$$

where T_o is the temperature at time = 0, ΔT_r is the temperature changes due to the reaction and ΔT_T is the temperature changes due to a thermal leakage. The total temperature changes was within the range 0.2-0.8 °C. With this small temperature changes the nonideal effects due to the thermal leakage is first-order (Newton's law of cooling).[17] Under the above conditions, the changes in temperature due to the reaction, ΔT_r, is also first-order kinetics. So the pseudo-first-order rate constants, k_ψ, were evaluated by non-linear fitting of the temperature-time curves to a biexponential equation, eq 5, where C_T and k_T are constants related to the temperature factor and the first-order rate constant, respectively, of the temperature change due to the thermal leakage.

$$T_t = T_\infty + (T_0 - T_\infty \pm C_T)\, e^{-k_\psi t} \pm C_T\, e^{-k_T t} \qquad (5)$$

Spectrophotometric method. The kinetic studies were carried out in 1:1 CH_3CN/H_2O solutions at pH 1 and 25 °C. The acid concentration and the ionic strength were maintained at 0.1 M unless specified otherwise. The temperature was maintained by immersing the cell in a thermostated water-filled holder throughout the experiment. Air was not excluded from the reactions. The kinetic data were obtained by following the loss of alkenes absorption in the region 200-225 nm using a UV-visible Shimadzu spectrometer. Spectrophotometric cells (quartz cuvettes) with different optical path length (0.01-0.2 cm) were used. Reaction mixtures were prepared in a spectrophotometric cell with the last reagent added being the alkene. All the experiments were done in the presence of large excess $[H_2O_2]$ ($\geq$ 0.3 M) over the alkene and the catalyst. Under these conditions the bis-peroxide, **B**, is only involved with constant concentration throughout the reaction time. The reactions followed first-order kinetics. The pseudo-first-order rate constants were evaluated by non-linear fitting of the absorbance-time curves to a single-exponential decay equation, eq 3.

RESULTS

The uncatalyzed reactions

It was found that reaction of H_2O_2 with β-pinene in methanol and 1:1 CH_3CN/H_2O solutions at pH 1 in the absence of the catalyst, MTO, were relatively very slow ($k_{cat} > 10^5\ k_{uncat}$), Figure II-1. It was not necessary to correct for the uncatalyzed reactions.

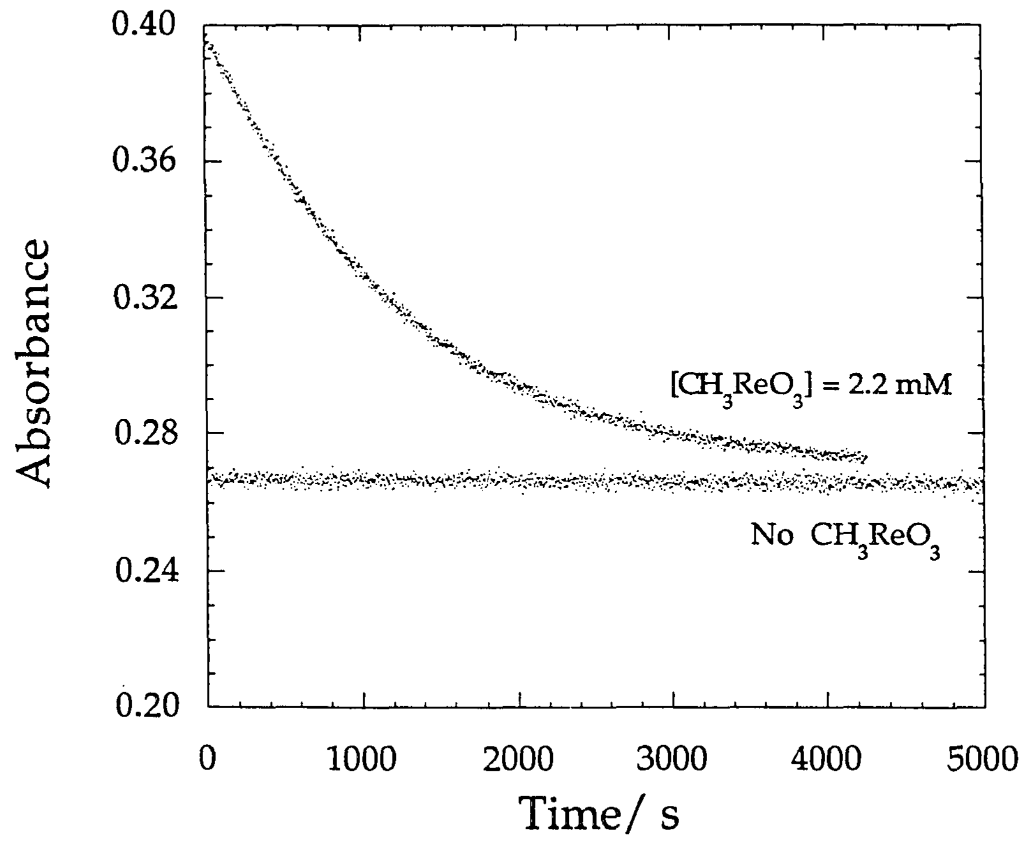
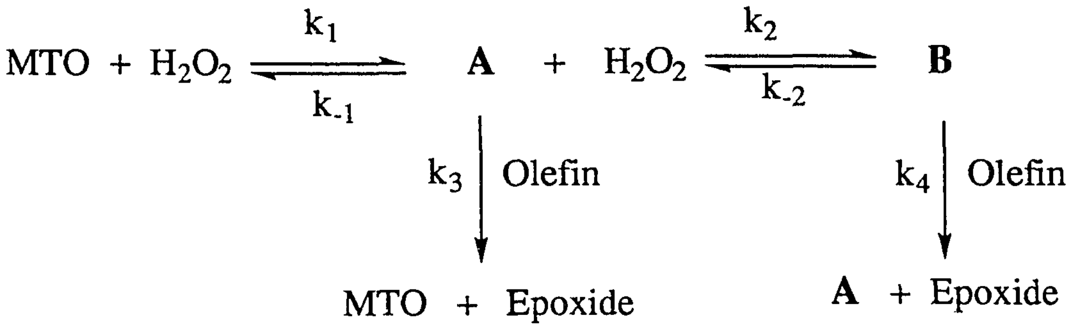


Figure II-1. Absorbance-time curves, at λ = 215 nm, for the reaction of H_2O_2 (0.4 M) with β-pinene (10 mM) in the presence and in the absence of the catalyst, CH_3ReO_3, in methanol at 25 °C.

Scheme II-1. Formation of the monoperoxorhenium(VII) complex, **A**, and the bisperoxorhenium(VII) complex, **B**, and thier reactions with an olefin.



Determination of the rate constants for the epoxidation reactions

According to scheme II-1 the rate of the reaction can be written as:

$$v = \frac{d[\text{epoxide}]}{dt} = \left(k_3[\mathbf{A}] + k_4[\mathbf{B}]\right)[\text{olefin}] \qquad (6)$$

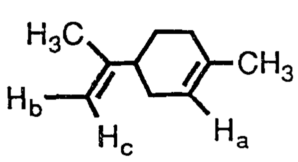
The total catalyst concentration, $[\text{Re}]_T$, is defined by $[\text{Re}]_T = [\text{MTO}] + [\mathbf{A}] + [\mathbf{B}]$. At high $[H_2O_2]$ the equilibrium is shifted to the formation of the bis-peroxide species, **B**. Considering the equilibrium rate constants ($K_1 = 13$ and $K_2 = 136\ M^{-1}$ in 0.1 M $HClO_4$-CH_3CN/H_2O (1:1 v/v),[9] and $K_1 = 261$ and $K_2 = 814\ M^{-1}$ in CH_3OH)[8] in which $[H_2O_2 \geq 0.3$ M, $([\text{MTO}] + [\mathbf{A}]) < 3\%$ of $[\mathbf{B}]$ (i.e. $[\mathbf{B}] \sim [\text{Re}]_T$). To insure that $[\mathbf{B}]$ remain essentially constant during the reaction $[H_2O_2]$ were at least five times more than the alkene concentration ($[\text{alkene}] \leq 0.1$ M). Furthermore H_2O_2 and the catalyst were added first and allowed to equilibrate with **B** before the alkene was added.

With essentially only **B** present and remain constant, the rate low in eq 6 simplifies to:

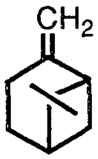
$$v = k_4[\mathbf{B}][\text{alkene}] = k_4[\text{Re}]_T[\text{alkene}] = k_\psi[\text{alkene}] \qquad (7)$$

NMR method. Since the rate of epoxidation of an olefin in organic solvents is sensitive to the amount of water present in the solution,[6] in all experiments [H_2O_2] was fixed at 0.5 M and so the amount of water introduced with H_2O_2 (30% stock) was the same ([H_2O]~ 1.5 M, i.e. 2.7%). Each experiment was also done with constant [alkene] = 0.05-0.10 M and constant $[\text{Re}]_T \sim [\mathbf{B}]$ = 1 - 50 mM. The changes of the relative intensities of ^{1}H NMR alkene signal(s) with time showed first-order kinetics, Figure II-2. The pseudo-first-order rate constants, k_ψ, were obtained from fitting the relative intensity-time data to eq 3. The values of k_4, Table II-1, were calculated from k_ψ and $[\text{Re}]_T$, $k_4 = k_\psi/[\text{Re}]_T$, eq 7.

The rate constants, k_4, for the epoxidation of the enternal and external olefinic groups of R-(+)-limonene, **1**, by **B** were determined separately by following the relative intensities of the ^{1}H NMR peaks at 5.4 ppm (H_a) or at 4.6-4.8 ppm (H_b and H_c), respectively, with time.



1



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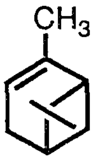

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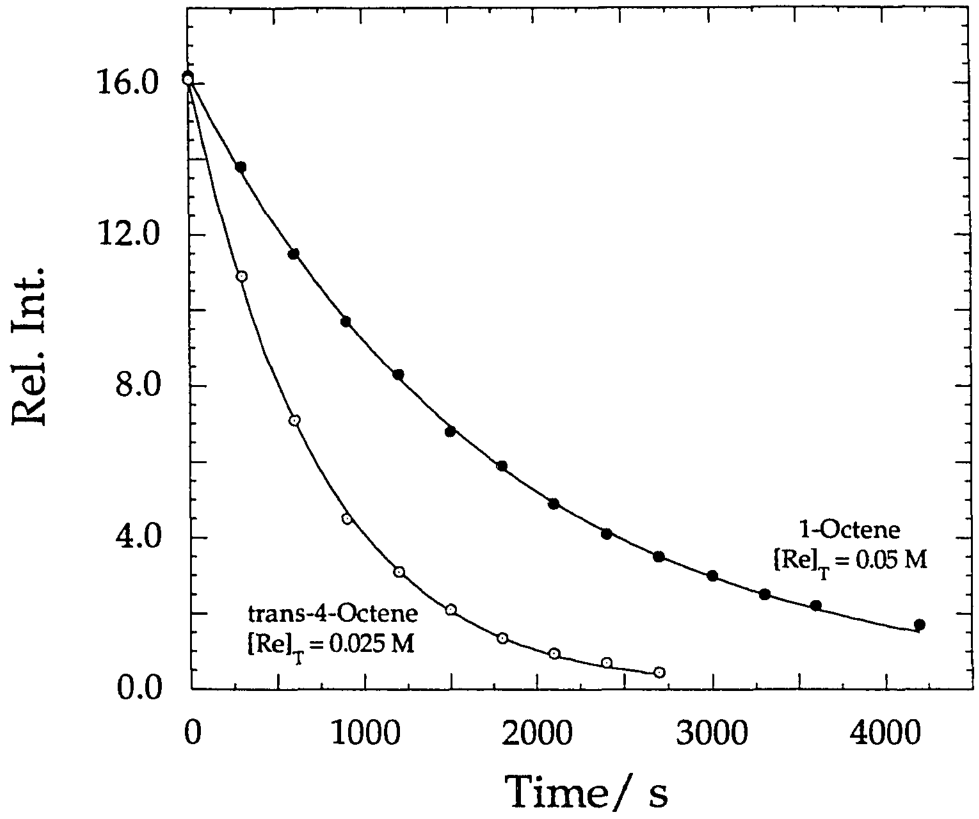
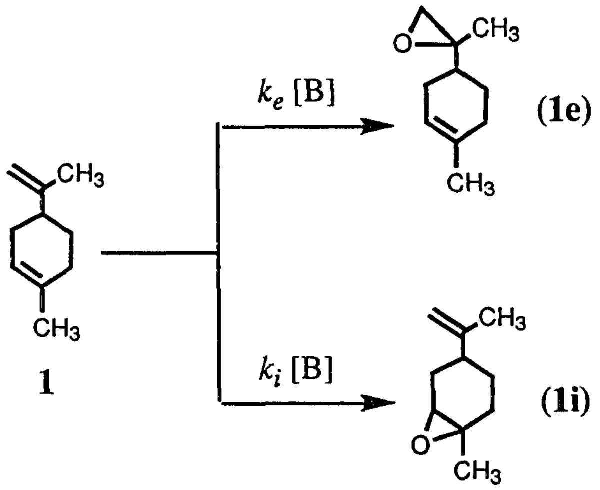


Figure II-2. Kinetic traces showing the epoxidation of 1-octene (0.1 M) and *trans*-4-octene (0.1 M) by **B** (~ $[Re]_T$) with $[H_2O_2]$ = 0.5 M in CD_3OD at 25 ^{o}C. The ^{1}H NMR signal intensities were recorded for an olefinic proton of 1-octene at δ = 5.6 ppm and *trans*-4-octene at δ = 5.4 ppm .

The value of k_ψ gave k_4 = 0.235 L mol^{-1} s^{-1}; the mathematics of this stituation is just like that for parallel reactions, eq 8, in that the rate constant is the sum of those for the separate pathways, *i.e.* $k_4 = k_\psi/[Re]_T = k_i + k_e$.. The ratio of the products [**1i**] /[**1e**] = 1.9 is equal to the ratio of k_i/k_e,. This measurment was carried out when only ca.

34% of the starting material had reacted, to minimize the influence of formation of the double-epoxide and the diols derived from all three epoxides. With this ratio, and the total rate constant, k_4, the values of k_i and k_e are 0.15 and 0.09 L mol^{-1} s^{-1}, respectively.



(8)

Thermometric method. For each alkene, a series of experiments was done with $[\mathrm{Re}]_T$ (~ [**B**]) varied from 0.2-5.0 mM, and with constant $[H_2O_2]$ = 1.0 M and [alkene] = 10-50 mM. Under these conditions [**B**] remain essentially constant throughout the reaction and so the reaction follows first-order kinetics.

The system is affected by a weak thermal leakage, especially in the later stages of the reaction. The chemical effect was, however, more rapid and showed more temperature changes. The temperature-time curves followed first-order biexponential kinetics (*rise & fall* or *rise & rise*), Figure II-3. The nonideal effects in the calorimeter are measured (by a biexponential fitting, eq 5) and separated from the process under study.

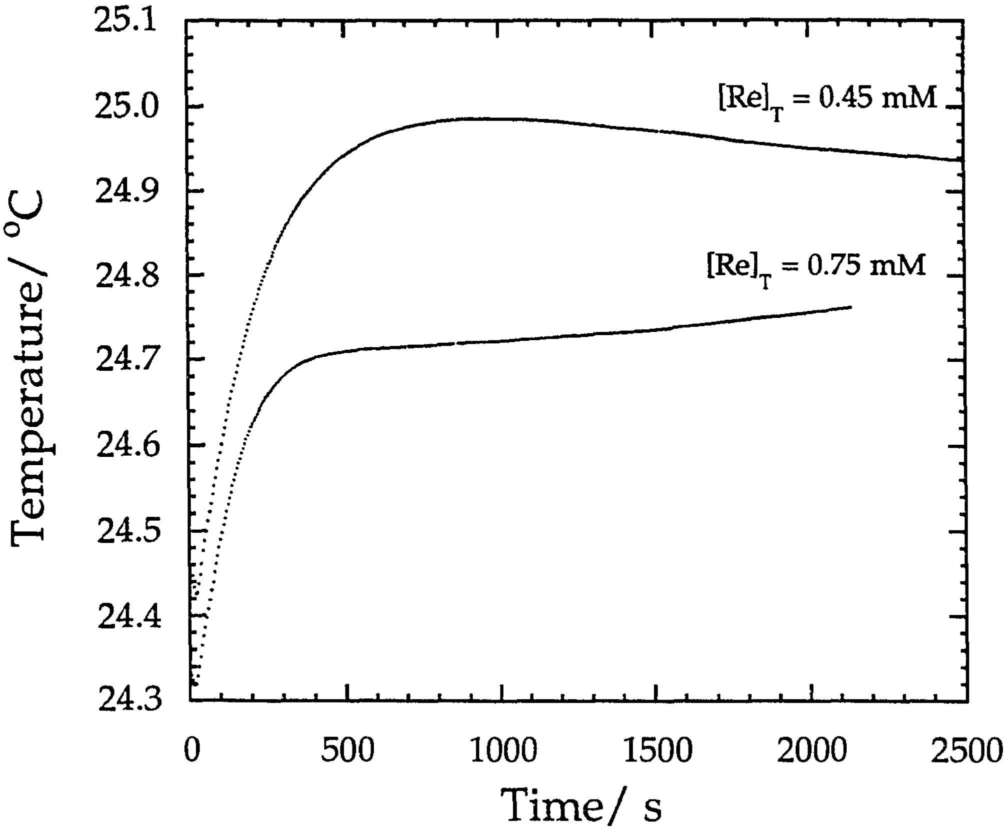


Figure II-3. Typical temperature-time curves for reaction of 2,3-dimethyl-2-butene (0.05 M) with **B**, in 0.1 M $HClO_4$, CH_3CN/H_2O (1:1 v/v) with $[H_2O_2]$ = 1 M and $[Re]_T$ = 0.45 and 0.75 mM.

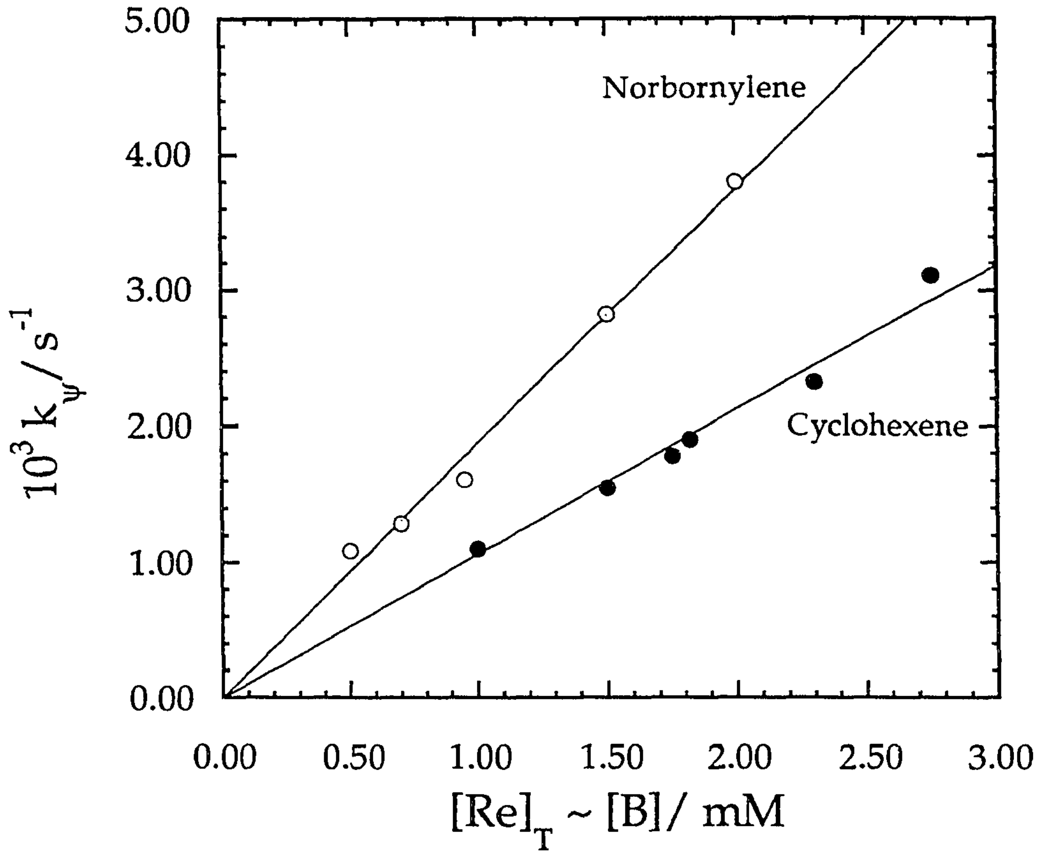


Figure II-4. Variation of the pseudo-first-order rate constants, k_ψ, for the reaction of cyclohexene (solid circle) and norbornylene (open circle) with [B] ~ $[Re]_T$ in 0.1 M $HClO_4$, CH_3CN/H_2O (1:1 v/v). The slopes of the lines are k_4, eq 7.

The pseudo-first-order rate constants, k_ψ, varied linearly with $[Re]_T$ (~ [B]), Figure II-4. The values of k_4 is given by the slope of the lines, Table II-1.

Spectrophotometric method. Most nonconjugated alkenes have maximum absorption at wavelengths ≤ 200 nm. Some alkenes, such as R-(+)-limonene, **1**, β-pinene, **2**, and α-pinene, **3**, absorb light (with relatively high extinction coefficient) in the range 200-225 nm. Reactions of **B** with several alkenes were studied spectrophotometrically by following the absorbance changes with time at wavelengths between 200-225 nm. Since the absorption background is large due to absorption of light in this range by the Re species, H_2O_2 and the alkene, short path length cells (0.01- 0.2 cm) were used. The reactions were performed under conditions involved only **B**. A series of experiments with constant $[H_2O_2] \geq 0.3$ M and [alkene] = 5-20 mM with $[Re]_T$ (~ [**B**]) varied between 0.2-5 mM were carried out in acidic CH_3CN/H_2O solutions. The solutions of H_2O_2 and CH_3ReO_3 were allowed to equilibrate with **A** and **B** (scheme II-1) for about 5-10 min. before adding the alkene. The pseudo-first-order rate constants obtained by non-linear fitting of the absorbance-time curves to a single-exponential decay equation, eq 3, were varied linearly with $[Re]_T$, Figure II-5. The values of the second-order rate constant, k_4, for reactions of **B** with alkenes are the slopes of the lines, Table II-1.

The reactions of styrene and β-pinene with **B** were carried out in CD_3OD (NMR method) and in CH_3OH (spectrophotometric method) at 25 °C. The rate constants were :

	k_4/ L mol^{-1} s^{-1} in CH_3OH	k_4/ L mol^{-1} s^{-1} in CD_3OD
Styrene	0.021 ± 0.001	0.019 ± 0.002
β-Pinene	0.38 ± 0.02	0.35 ± 0.01

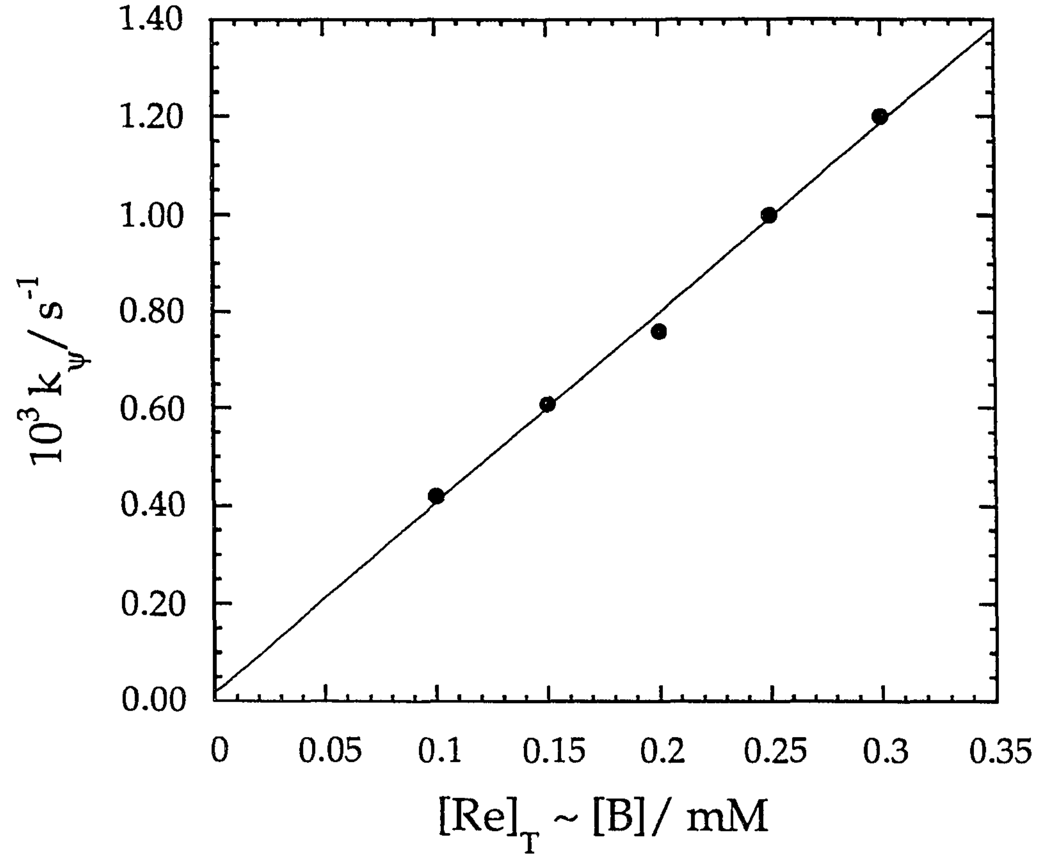
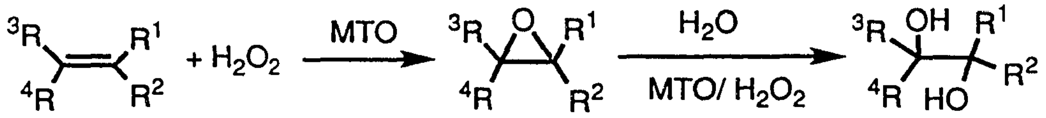


Figure II-5. Variation of the pseudo-first-order rate constants, k_ψ, with [B] (~ $[Re]_T$) for the reaction of β-pinene (5 mM) with H_2O_2 (0.4 M) in 1:1 CH_3CN/H_2O at pH 1 and 25 °C. The data are fitted to $k_\psi = k_4[B]$, eq 7.

Epoxide ring-opening and products

In methanol-d$_4$. In organic solvents, such as acetonitrile and methanol, ^1H NMR experiments have shown that reactions of alkenes with **B** give epoxides which then react with water introduced with H_2O_2 (30% stock) or produced during the reaction to yield 1,2-diols, eq 9.



(9)

In CD_3OD, under the kinetic conditions, formation of the epoxide was faster than its hydrolysis to 1,2-diol. Since $[H_2O]$ (~ 1.5 M) is much higher than [epoxide] in the solution, the epoxide-ring opening followed first-order kinetics. For *trans*-4-octene, when $[Re]_T = 0.025$ M and $[H_2O_2] = 0.5$ M, the pseudo-first-order rate constant of the epoxidation step was 1.34×10^{-3} s^{-1}. Under the same conditions the pseudo-first-order rate constant of the epoxide-ring opening of *trans*-4-octene oxide was 1.70×10^{-4} s^{-1}. It has been observed that MTO (the catalyst) catalyzes epoxide ring-opening.[6, 7] This step is largely enhanced in the presence of H_2O_2 and the catalyst.[7b]

In semi-aqueous. In 1:1 CH_3CN/H_2O at pH 1, the epoxide ring-opening is catalyzed by the acid and so this step becomes rapid and faster than the epoxidation reaction. The final products, 1,2-diols, were only observed under these conditions.[6]

Table 1. Second-order rate constants, k_4, for the reactions of olefins with $CH_3Re(O)(O_2)_2$, **B**, at 25 °C by various methods in two solvents.

Olefin	k_4/ L $mol^{-1}s^{-1}$ (method)[a]	k_4/ L $mol^{-1}s^{-1}$ (method)[b]
Styrene	0.019 ± 0.001(N) 0.021 ± 0.002(S)	0.11 ± 0.01(S)
4-Methoxystyrene		0.62 ± 0.05(T) 0.57 ± 0.04(S)
1-Methylcyclohexene	0.32 ± 0.01(N)	4.20 ± 0.16(T)
β-Pinene	0.35 ± 0.01(N) 0.34 ± 0.01(S)	3.63 ± 0.10(T) 3.88 ± 0.20(S)
α-Pinene		2.21 ± 0.15(S)
R-(+)-Limonene	0.15 ± 0.013(N)[c] 0.09 ± 0.006(N)[d]	2.79 ± 0.13(S)
Norbornylene	0.250 ± 0.001(N)	1.88 ± 0.04(T)
Cyclohexene	0.108 ± 0.003(N)	1.06 ± 0.02(T)
Methylenecyclohexane	0.096 ± 0.001(N)	0.97 ± 0.06(T)
2,3-Dimethyl-2-butene	1.33 ± 0.03(N)	8.93 ± 0.55(T)
2-Methyl-2-pentene	0.260 ± 0.007(N)	3.92 ± 0.04(T)

Table 1. continued

Olefin	k_4/ L mol^{-1}s^{-1} (method)^a	k_4/ L mol^{-1}s^{-1} (method)^b
2-Methyl-1-pentene	0.061 ± 0.001(N)	0.55 ± 0.06(T)
Cis-3-Hexen-1-ol	0.106 ±0.008(N)	
Trans-3-Hexen-1ol	0.039 ± 0.001(N)	
Trans-4-Octene	0.048 ± 0.003(N)	0.253 ± 0.003(T) 0.289 ± 0.005(S)
1-Octene	0.0126 ± 0.001(N)	0.098 ± 0.021(T)
1-Hexene	0.0124 ± 0.0002(N)	
3,3-Dimethyl-1-Butene	0.0087 ± 0.0003(N)	
5-Hexen-2-one		0.066 ± 0.003(S)
4-Hexen-3-one		0.0038 ± 0.0003(S)
Allyl alcohol	0.0033 ± 0.0002(N)	
Allyl phenyl ether	0.0052 ± 0.0001(N)	
2-Buten-1,2-diol		0.0326 ± 0.0004(S)
Cis-1-Bromopropene		0.012 ± 0.001(S)
Trans-1-Bromopropene		0.0051 ± 0.0003(S)

Table 1. continued

Olefin	k_4/ L mol^{-1}s^{-1} (method)[a]	k_4/ L mol^{-1}s^{-1} (method)[b]
1-Chloro-2-methyl-propene	0.0160± 0.0005(N)	
1-Bromo-2-methyl-propene	0.0098 ± 0.0003(N)	
Methyl acrylate		< 0.001(S)
1,4-Dicyano-2-butene		< 0.001(S)
Acrylnitrile		< 0.001(S)

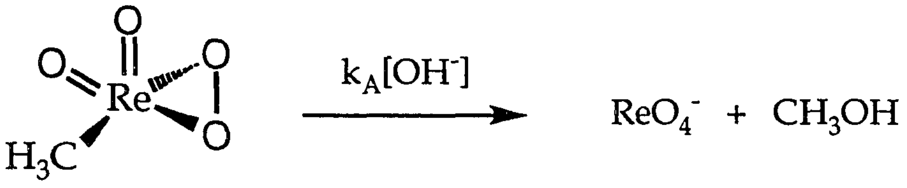
[a] In CD_3OD at 25 °C, by NMR method (N) (or spectrophotometric method (S)); [b] In CH_3CN/H_2O (1:1 v/v), 0.1 M $HClO_4$ at ~ 25 °C, by spectrophotometric (S) or thermometric (T) method; [c] For the epoxidation of the internal olefinic group; [d] For the epoxidation of the external olefinic group(see text).

DISCUSSION

The activities of A and B toward oxygen transfer

In the earlier kinetic studies on CH_3ReO_3 (MTO) catalyzes oxygen transfer from H_2O_2 to inorganic and organic substrates, such as PR_3, R_2S, Br^- and Cl^- [9-12], (including epoxidation of styrenes)[6] much effort was devoted to difining separately the reactivity of **A** (the monoperoxorhenium(VII) complex) as compared to **B**, the bisperoxo complex. In nearly every case the differences in reactivity between **A** and **B** were not remarkable (see Section I). The present study is simplified by limiting the effort to **B** only. The kinetic data were collected under conditions involve only **B**, i.e. $[H_2O_2]$ was in large excess relative to [alkene] and $[Re]_T$.

The advantages of using large excess $[H_2O_2]$ are :- **a)** the reaction follows first-order kinetics, **b)** the conditions are easily applied and give accurate results (the assumptions that only **B** is involved and constant are valid throughout the reaction) and **c)** the catalytic system, CH_3ReO_3/H_2O_2, is very stable in the presence of high $[H_2O_2]$.[18] The mono-peroxide, **A**, which present in significant amount at low $[H_2O_2]$ (< 0.1 M), decomposes irreversibly to CH_3OH and ReO_4^-, eq. 10.



A

(10)

In the presence of high $[H_2O_2]$, **A** reacts rapidly with H_2O_2 to give **B** and does not live long in the solution. Since the decomposition path, as shown in eq 10, increases with $[OH^-]$,[18] the reaction were carried out in 0.1 M $HClO_4$ semi-aqueous solutions or in organic solvents, such as methanol.

The Kinetic methods

The rate constants for most alkenes used in this study were determined by more than one method. In the NMR method the reactions were carried out in CD_3OD. The rate constant for epoxidation of an olefin by **B** in CD_3OD or in CH_3OH

were essentially the same. The thermometric and the spectrophotometric methods were performed in 0.1 M $HClO_4$ - CH_3CN/H_2O (1:1 v/v) solutions at temperatures between 24-26 °C and 25 °C, respectively. The changes in the temperature during a thermometric experiment were ≤ 0.6 °C. Under these adipatic-nonisothermal conditions, the rate constants increase with temperature. One may take as a guide to the effect of this variation in the rate constant for 4-methoxystyrene. For the epoxidation of 4-methoxystyrene by **B** in CH_3CN/H_2O at pH 1, the enthalpy of activation was determined: $\Delta H^{\ddagger} = 42.8$ kJ mol^{-1}.[6] With that, a 0.6 °C increase will cause k_4 to increase by 4.8%, and even less for smaller temperature changes. This shows that this effect is not significant within the experimental error, and have not allowed for it.

The thermometric method requires allowance for the thermal leakage of the calorimeter which depends on the room temperature from day to day. The values of the rate constants for reactions of **B** with several alkenes were confirmed by the spectrophotometric method under the same conditions. The rate constants obtained by both methods were in excellent agreements, Table II-1.

Alkenes reactivities and trends

Solvent effects. In general, the rate of the reaction of an alkene with **B** increases with the alkene nucleophilicity. Similar reactivity trends of alkenes have been observed in different solvents. The absolute reactivity of an alkene towards **B**, however, is medium dependent. The rate of epoxidation of an alkene by **B** in CD_3OD (or CH_3OH) is 5-12 times slower than in 0.1 M $HClO_4$ - CH_3CN/H_2O (1:1

v/v). This agrees with the earlier finding that the rate of the reaction of the styrene with **B** increases with the solvent polarity and the concentration of water.[6]

Electronic and steric effects. Correlation of the rate constants, k_4, with the number of the alkyl substituents on the olefinic carbons, Figure II-6, shows that the electronic factors are the most important in determining the olefin reactivity. The tetra-substituted alkenes, 2,3-dimethyl-2-butene, was 2-5 times more reactive than the trisubstituted alkene, 2-methyl-2-pentene, up to 20 times more reactive than disubstituted alkenes and about two order of magnitude more reactive than monosubstituted alkenes, Table II-1. 1,1-Disubstituted alkenes showed very similar reactivity to 1,2-disubstituted alkenes. Allyl alcohols and phenyl allyl ether were 2-3 times less reactive than mono-alkyl substituted olefins, such as 1-octene or 1-hexene. The presence of more electronegative group, CH_2OH or CH_2OPh, (relative to CH_2R) reduces the olefin nucleophilicity. Conjugated alkenes are much less reactive than non-conjugated ones. Epoxidation of 4-hexen-3-one by **B** was about 20-fold slower than epoxidation of 5-hexen-2-one, Table II-1. The rate of epoxidation of olefins with strong electron withdrawing group(s), such as acrylanitrile, 1,4-dicyano-2-pentene and methyl acrylate, was very slow ($k_4 < 10^{-3}$ L mol^{-1} s^{-1}).

Steric factors have slight effects on the epoxidation rates. A monosubstituted alkene, 3,3-dimethyl-1-butene, with tert-butyl group (bulky) was only ~1.5 times less reactive than 1-octene and 1-hexene, Table II-1. An olefin with substituted chloride was slightly more reactive than the corresponding substituted bromide and *cis*-1-bromopropene is approximately 2-fold more reactive than the *trans* isomer, Table II-1.

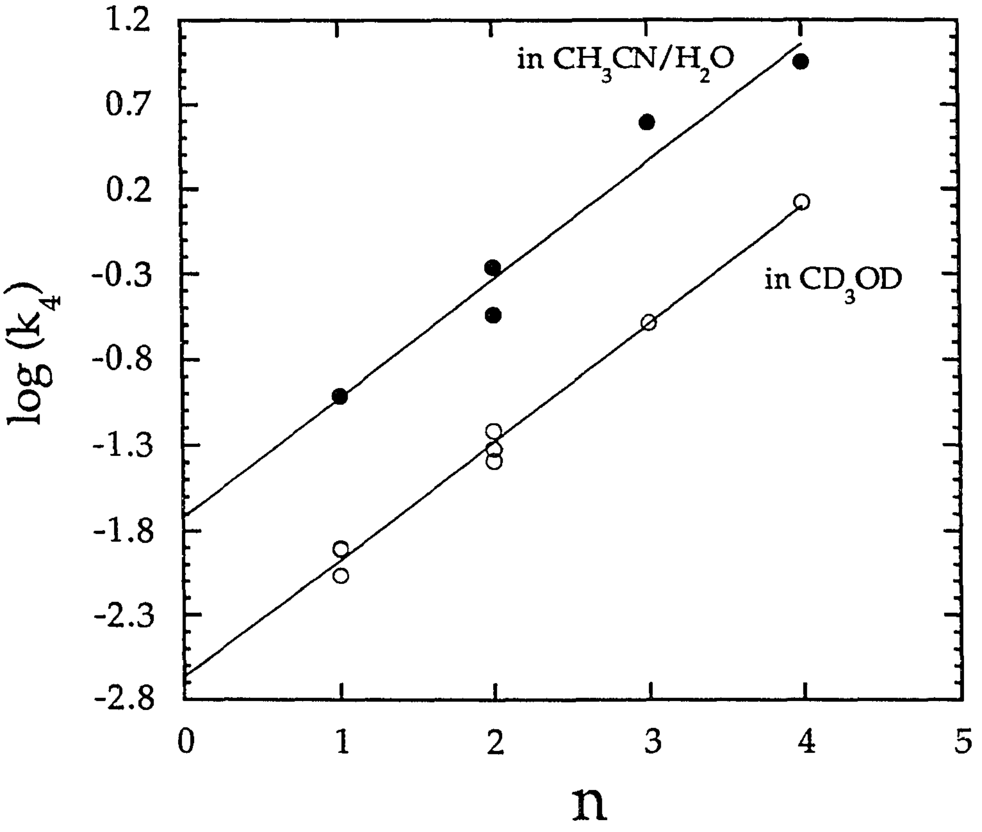
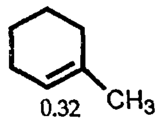


Figure II-6. Correlation of the rate constants, k_4, for the reactions between aliphatic alkenes and **B** with the number of alkyl substituents, **n**, on the olefinic carbons.

Epoxidation of cyclic alkenes. Although both alkenes are 1,1-disubstituted, reaction of β-Pinene with **B** was about four-fold faster than reaction of methylenecyclohexane with **B**. β-pinene has a much higher angle strain because it is a bicyclic system. This factor may account for the rate enhancement, since upon epoxidation, in the transition state, the hybridization of the olefinic carbons change from sp^2 to sp^3. This change reduces the angle strain and gives relatively low energy transition state. Similar comparisons could be made between norbornylene and cyclohexene with relative rates of 2.4 and 1.8 in CD_3OD and CH_3CN/H_2O, respectively, Table II-1, and between norbornylene and *trans*-4-octene, with relative rates of 7.4.

Based on the electronic effects only, α-pinene should be more reactive than β-pinene. It was found that the ratio of the rate constants for epoxidation of β-pinene to that of α-pinene by **B** is ~1.4. This may be due to steric factors. In the case of α-pinene, the attack of the olefinic group on the peroxy oxygen is satirically hindered by the two methyl groups. R-(+)-limonene, **1**, has two different olefinic groups, trisubstituted-internal and disubstituted-external groups. The internal olefinic group



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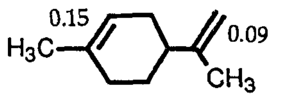

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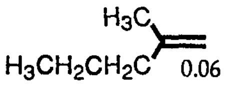
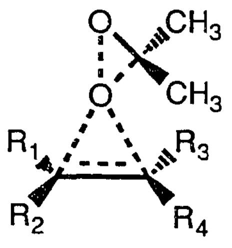


5

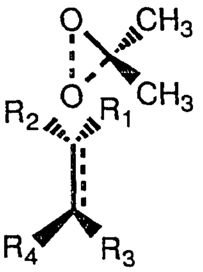
is about two times less reactive than trisubtituted alkene, such as 1-methylcyclohexene, **4**. The external group, on the other hand, is 1.5 times more reactive than similar 1,1-disubstituted alkenes, such as 2-methy-l-pentene, **5**, This may suggest that there is some interactions between these two olefinic groups in limonene through single bonds.

B (and A) versus dimethyldioxirane

An interesting analogy might be drawn between two cyclic peroxides, **B** and dimethyldioxirane, DMDO. The kinetics of epoxidations of aromatic and aliphatic olefins by DMDO have been reported, eq 2.[13,14] The similarities between **B** and DMDO are striking. In both cases the epoxidation reactions are stereospecific. They proceed at rates that increase with the olefin nucleophilicity, and are slightly sensitive to steric hindrance (in styrenes epoxidation). In both cases *cis*- and *trans*-β-methylstyrene have very similar reactivities. The ratios of the rate constants of epoxidation of *cis* and *trans* aliphatic alkenes, such as 3-hexene for dimethyldioxirane and 3-hexen-1-ol for **B**, however, are different. The rate of epoxidation of *cis*-3-hexene by dimethydioxirane is about 8 times larger than that of the *trans* isomer.[14] Epoxidation of *cis*-3-hexen-1-ol by **B** was only about 2.5 times faster than epoxidation of the *trans* isomer. The rate of the epoxidation reactions are enhanced with the solvent polarity and $[H_2O]$ in the solution. The rate constants for epoxidation of para and meta substituted styrenes by **B** [6] and dimethyldioxirane[13] were correlated with σ^+ and gave $\rho = -0.92$ and -0.90, respectively. Similar kinetic factors run throughout the entire series. Figure II-8 displays a plot of log k_4 (B) versus log k (DMDO). This figure records an excellent correlation for several alkenes and styrenes. The respective slopes are 0.84 and 1.18, with correlation coefficients of 0.99 and 0.98. The strong correlation allows certain comparisons to be drawn between the structures of the transition states in both cases. For epoxidation of olefins by dimethyldioxirane, a concerted mechanism with a cyclic *planar* or *spiro* transition state has been proposed.[13]



planar



spiro

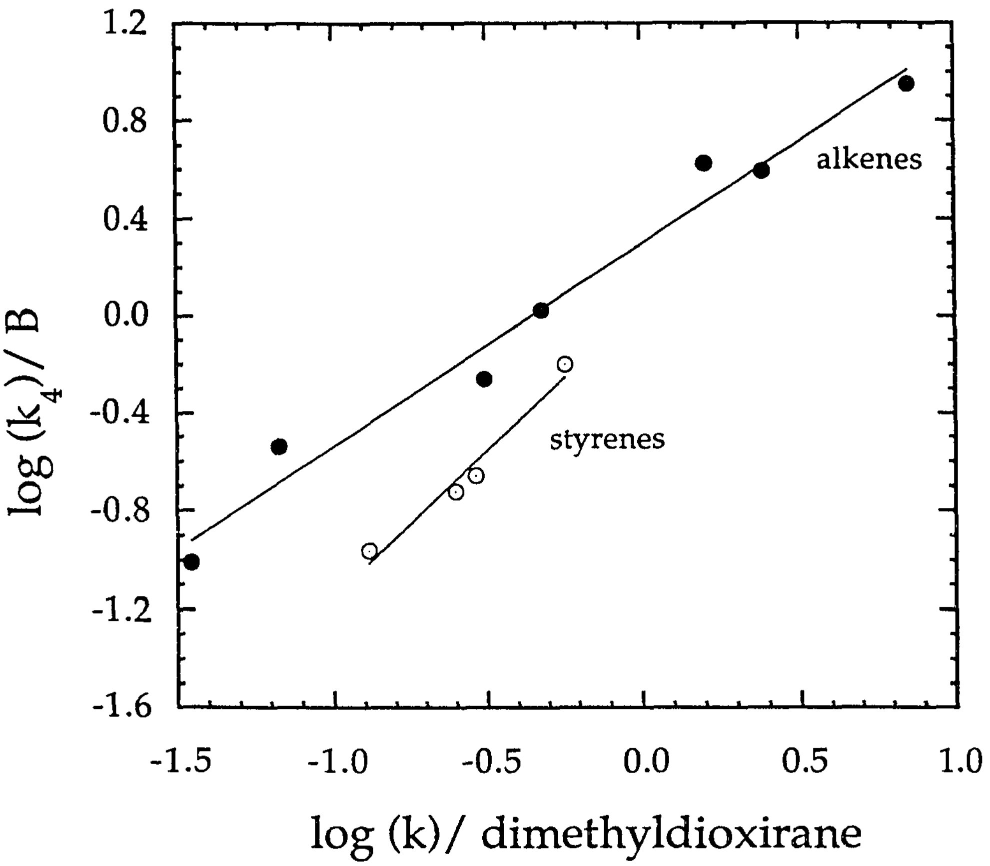
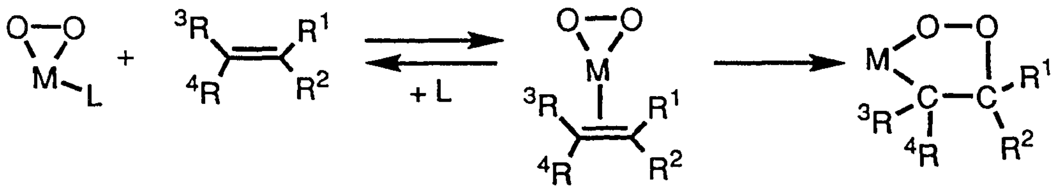


Figure II-7. Correlation of the rate constants for the epoxidation of several olefins by **B**, in 1:1 CH_3CN/H_2O at pH 1, with those for dimethyldioxirane in acetone.

Mechanistic considerations

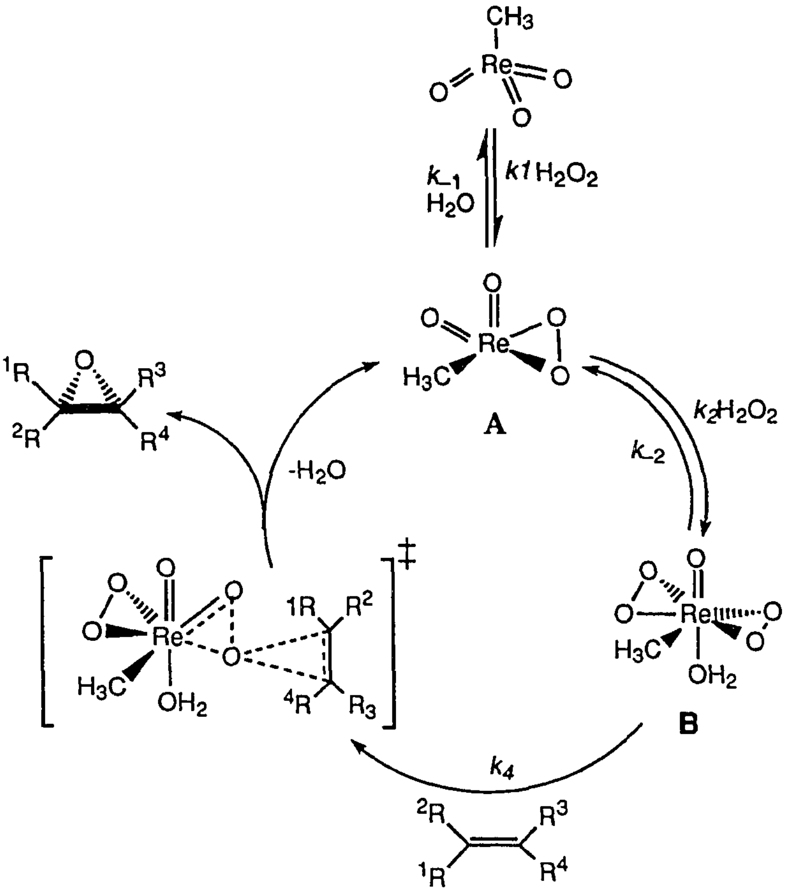
In the case of $CH_3Re(O)(O_2)_2$, **B**, two major modes of attack are possible:- a) external nucleophilic attack of the olefin on a peroxy oxygen[19] and b) binding of the olefin to the metal, first, followed by insertion into the M-OO bond to form a five membered peroxometallacycle intermediate in a rate determining step, eq 11. Then this intermediate rapidly yields the epoxide.[20]



(11)

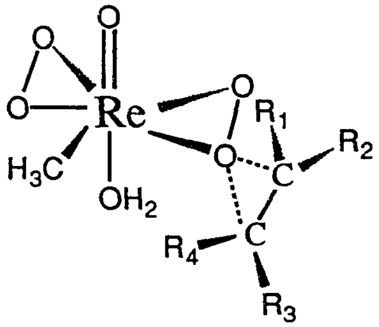
The later mechanism has been proposed for epoxidation of olefins by some early and late transition metal peroxo complexes. It is, however, more favorable for late transition metals.[21] An electron rich metal stabilizes binding of an olefin by a back bonding. Also the five-membered peroxometallacycle, eq 11, was only isolated from reaction of Pt and Rh peroxo complexes with tetracyanoethene.[22] In the case of high valent early transition metal peroxo complexes, group IV-VI, such intermediates have never been isolated.[23] One piece of evidence for prior binding of the olefin to a metal peroxide is that the reaction is inhibited by the presence of basic ligands and solvents.[24] Here the reactions are enhanced by the solvent polarity and the concentration of water. Furthermore allyl alcohols are epoxidized more readily by d^0 early transition metals peroxo complexes than normal olefins. An allyl alcohol binds the metal through its OH group prior to oxygen transfer.[25] Our results on epoxidation of olefins by **B** in CH_3CN/H_2O and CD_3OD show that allyl alcohols and allyl ethers are less reactive than the corresponding olefins. These may indicate that the oxygen transfer occurs without binding the olefin to Re.

Scheme II-2. The catalytic cycle for the epoxidation of an olefin by **B**.



Mechanism for epoxidation of olefins by B (or A)

The similarities between B (or A) and dimethyldioxirane[13,14] toward oxygen transfer to olefins, the results on the epoxidation of allyl alcohols and the slight effect of steric hindrance suggest external nucleophilic attack, scheme II-2. This mechanism has been proposed for epoxidation of styrenes by B (or A).[6] It has been supported by the kinetic and the mechanistic results obtained on reactions of aliphatic olefins by B. The olefin can approach the peroxy oxygens by different modes of attack leading to different transition states. The findings that *cis*- and *trans*-β-methylstyrene have very similar reactivities and cis-3-hexen-1-ol is ~ 2.5 times more reactive than the trans isomer may suggest the following geometrical configuration that might be present in the transition state:



In this transition state the olefinic carbons are in a plane parallel to the plane that has the peroxy oxygens and Re. For *cis*- (R_2 = Ph, R_3 = CH_3) and *trans*-β-methylstyrene , R_1 =Ph, R_3 = CH_3, (k_{cis} / k_{trans} ~ 1.3) the Ph ring and the olefinic carbons are in the same plane and the rotation around the Ph-C bond is rigid due to π-interaction. There should not be a significant difference in the steric hindrance between the *cis* and the *trans* isomers. In the case of *cis*- and *trans*-3-hexen-1-ol, R_1 or R_2 = CH_2CH_2OH, R_3 = CH_2CH_3, (k_{cis} / k_{trans} ~ 2.5) there is a free rotation around the C=C—CH_2R single bond and also alkyl groups, such as CH_2CH_3 and CH_2CH_2OH, are more bulky than Ph. The attack should be more hindered when R_1 = alkyl (trans) than when R_1 = H (cis). Epoxidation by dimethyldioxirane is more sensitive to steric hindrance (k_{cis}/k_{trans} ~ 8)[18] probably because the two methyl groups on the dioxirane carbon are closer to the peroxy oxygen. In the case of **B** (or **A**) the peroxy group(s) are relatively far from the other ligands on the Re due to longer Re-Ligand bonds compare with C-CH_3 bond. This geometry also agrees with the finding that 1,1-disubstituted olefins (R_1 = R_2 = alkyl) and 1,2-disubstituted (R_1 or R_3 = alkyl) have similar reactivities. The substituents R_2 and R_3 (H or alkyl) do not affect the olefin attack.

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CHAPTER III. HYDRIDE ABSTRACTION FROM 1,2-DIOLS BY THE PENTAAQUA(OXO)CHROMIUM(IV) ION

A paper published in *Inorganic Chemistry*[1]

Ahmad M. Al-Ajlouni, Andreja Bakac and James H. Espenson

ABSTRACT

Kinetic studies of the oxidation of 1,2-diols by pentaaqua(oxo)-chromium(IV) ion, $(H_2O)_5Cr^{IV}{=}O^{2+}$, were carried out in dilute aqueous solutions of perchloric acid. These reactions yield the superoxochromium(III), $CrOO^{2+}$, providing evidence that the two-electron reduction of $Cr^{IV}O^{2+}$ to Cr^{2+} occurred in a single step. The rate constants for the primary and secondary diols are comparable to each other, and approximately ten times larger than that for pinacol ($k = 3.7$ L mol^{-1} s^{-1}). The kinetic isotope effect of the O-H hydrogens is negligible, $k_H/k_D = 0.95$-1.3, whereas that for the C-H hydrogens is substantial, $k_H/k_D = 3.7$-4.8. A two-equivalent mechanism is proposed, in which CrO^{2+} abstracts a hydride ion from an α-position in the primary and secondary diols and from a β-position in pinacol.

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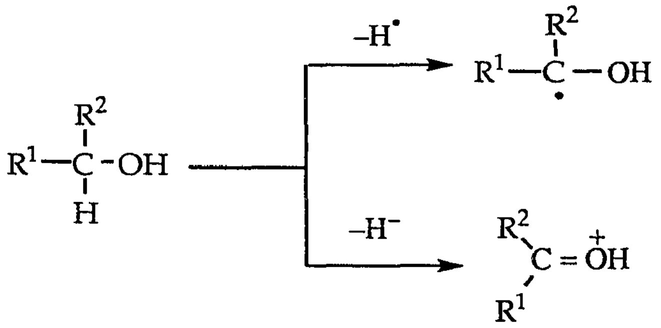
[1] Al-Ajlouni, A.M.; Bakac, A.; Espenson, J. H.; *Inorg. Chem.*, **1994**, 33, 1011.

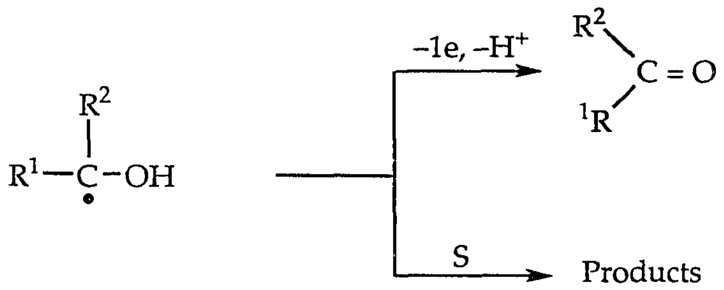
INTRODUCTION

The oxidations of alcohols by high-valent chromium, O_2, or peroxides, as activated by low-valent chromium, might take place by either a one-electron (H atom) or a two-electron transfer (H^- ion) as shown in eq 1.[1-5]



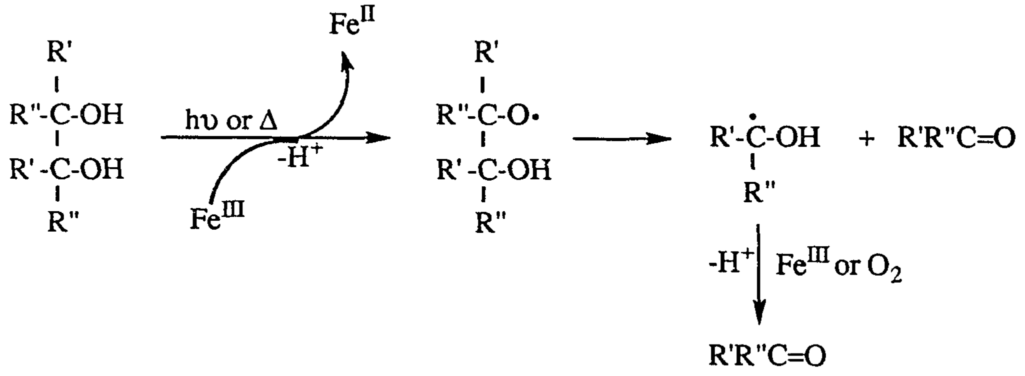
(1)

The radical formed by the H–atom pathway in eq 1 would then react further with the oxidant or other substrates (S) present in solution (eq 2).[6]



(2)

The limited data on the oxidation of diols[7-10] include the observation of oxidative cleavage of the C–C bond by Ce^{IV} and Pb^{IV}. The formation of a bidentate intermediate was reported with lead but not with cerium.[7] It has recently been shown that photochemical oxidation of tertiary diols by an Fe(III) porphyrin yields the corresponding alkoxyl radicals, which then decompose to alkyl radicals and ketones. The alkyl radicals are then further oxidized by Fe(III) or O_2 to the corresponding ketone (eq 3).[11]



(3)

The pentaaqua(oxo)chromium(IV) ion, $(H_2O)_5CrO^{2+}$ (hereafter CrO^{2+}), is a powerful and reactive oxidant. [5] It is sufficiently long-lived ($t_{1/2}$ = 30 s in 1.0 M $HClO_4$ at 25 °C) to be used as a reagent in mechanistic studies. A 2-equivalent (hydride transfer) mechanism has been identified for the oxidation of primary and secondary alcohols,[5] and for the reaction of H_2O_2[12a], by CrO^{2+}. The oxidation of phenols, however, involves a one-electron path, which leads to the formation of the corresponding phenoxyl radical in the rate determining step.[12b] As such, the phenols are distinct from all the others.

In this section results from the study of the oxidation of diols by CrO^{2+} in aqueous acidic solution are reported. The reaction involves cleavage of the C–C bond and yields the corresponding ketones or aldehydes.

EXPERIMENTAL SECTION

Reagents

Water was purified by passing the laboratory distilled-and-deionized water through a Millipore water system. Ethylene glycol, *cis-* and *trans*-1,2-cyclohexanediol (Aldrich), deuterium oxide (99.9 atom % D) and ethylene glycol-d_4 were used without purification. Pinacol was purified by sublimation under vacuum. The kinetic isotope effect (*kie*) of the O–H bond was determined by conducting experiments in D_2O and H_2O. Deuterated pinacol (pinacol-d_{12}) was prepared from acetone-d_6 by a modification of a literature method.[13] The temperature was controlled in all the kinetic experiments by means of a thermostated cell holder connected to a circulating water bath set at the desired temperature.

The UV-visible absorption spectra and kinetic measurements were recorded with a Shimadzu UV-3101PC scanning spectrophotometer. The organic products were identified by using a Hewlett-Packard Model 5790 gas chromatograph and a 3390A integrator. The products were chromatographed on an OV-101 column at 30 °C by injection of liquid-phase samples. The concentration of acetone was determined from the GC peak areas by using an external standard. Formaldehyde was determined by chromotropic acid analysis.[14]

Reactions

All the reactions were carried out in O_2-saturated solutions. The perchloric acid concentration and the ionic strength ($HClO_4$ + $LiClO_4$) were both 0.10 M except in experiments designed to study the effects of these variables. Solutions of Cr^{2+} (0.01 M) in dilute perchloric acid were prepared by the anaerobic reduction of Cr^{3+} with Zn/Hg. Injection of Cr^{2+} into an acidic aqueous solution saturated with O_2 gives rise to CrO^{2+}. Some $CrOO^{2+}$ was also formed, eq 4-5,[15] but it did not interfere. The saturated solutions of O_2 were prepared by bubbling O_2 through the solution for about 10 minutes. In a typical kinetic experiment CrO^{2+} was formed *in situ* by injecting 100 µL of 0.01 M Cr^{2+} ($[Cr^{2+}]_{final}$ = 0.2 mM) into a 2-cm spectrophotometric cell filled with 5.0 mL of an O_2–saturated solution (1.26 mM at 25 °C) of 1.0-3.0 mM diol (excess). Under these conditions the reaction between Cr^{2+} and O_2 rapidly produced ~0.04 mM CrO^{2+} (~20% based on total Cr^{2+}), which then reacted with the diol.

$$Cr(H_2O)_6^{2+} + O_2 \xrightarrow{\sim 10^8\ L\ mol^{-1}\ s^{-1}} (H_2O)_5CrOO^{2+} \tag{4}$$

$$Cr(H_2O)_6^{2+} + (H_2O)_5CrO_2^{2+} \xrightarrow{rapid} (H_2O)_5Cr^{IV}{=}O^{2+} \tag{5}$$

Kinetic Measurements

The kinetic data for the oxidation of diols by CrO^{2+} were collected by following the formation of the product, $CrOO^{2+}$, at 290 nm (ε=3100 L mol^{-1} cm^{-1}), Figure III-1.[16] The rate constant k_ψ of eq 6 was obtained by fitting the absorbance-time data to the first-order kinetic expression $Abs_t = Abs_\infty + (Abs_0 - Abs_\infty)\exp(-k_\psi t)$, where Abs = absorbance.

$$\frac{d[CrO_2^{2+}]}{dt} = k_\psi[CrO^{2+}] \tag{6}$$

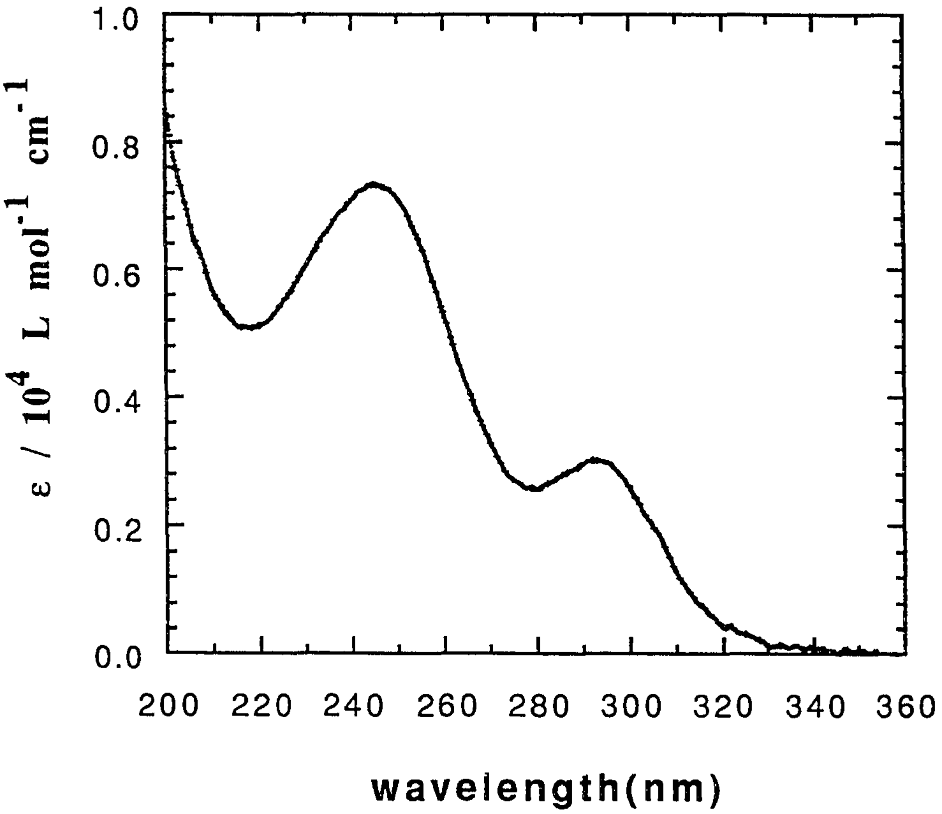


Figure III-1. The UV-vis spectrum of the superoxochromium(III), $CrOO^{2+}$, in 0.1 M $HClO_4$ aqueous solution.

RESULTS

Reaction of 1,2-diols with CrO^{2+}

The diols studied were ethylene glycol, *cis*- and *trans*-1,2-cyclohexanediol and pinacol. All the reactions were carried out in O_2-saturated solutions. Under these conditions Cr^{2+} reacts rapidly with O_2 to yield $CrOO^{2+}$ and CrO^{2+} (eq 4-5).

The superoxochromium(III) ion does not react with diols under these conditions. The oxochromium(IV) ion, a strong oxidant,[12a] reacts with the diols in the presence of O_2 to yield aldehydes and/or ketones, (eq 7).

$$(H_2O)_5Cr^{IV}{=}O^{2+} + \text{diol} \xrightarrow{O_2} (H_2O)_5CrOO^{2+} + \text{aldehydes/ ketones} \quad (7)$$

Formation of $CrOO^{2+}$ (eq 7) which was detected by its absorption bands at 290 nm (ε = 3100 L mol^{-1} cm^{-1}) and 245 nm (ε = 7000 L mol^{-1} cm^{-1}),[16] Figure I-1, is an evidence for two electron reduction of CrO^{2+} to Cr^{2+}. The reduction product, Cr^{2+}, reacts rapidly with O_2 to yield $CrOO^{2+}$, eq 4.

As shown in Figure III-2, the pseudo-first-order rate constants k_ψ (eq 8) varied linearly with the diol concentration at constant ionic strength and acidity, yielding the second-order rate constants (k_{diol}). The values of the rate constants (k_{diol}) are summarized in Table III-1.

$$k_\psi = k_{dec} + k_{diol}[\text{diol}] \quad (8)$$

The kinetic isotope effect (*kie*) on the O-H groups were negligible, Table III-1. The oxidation of ethylene glycol-d^4, however, showed a significant *kie*, $k_H/k_D = 3.7$.

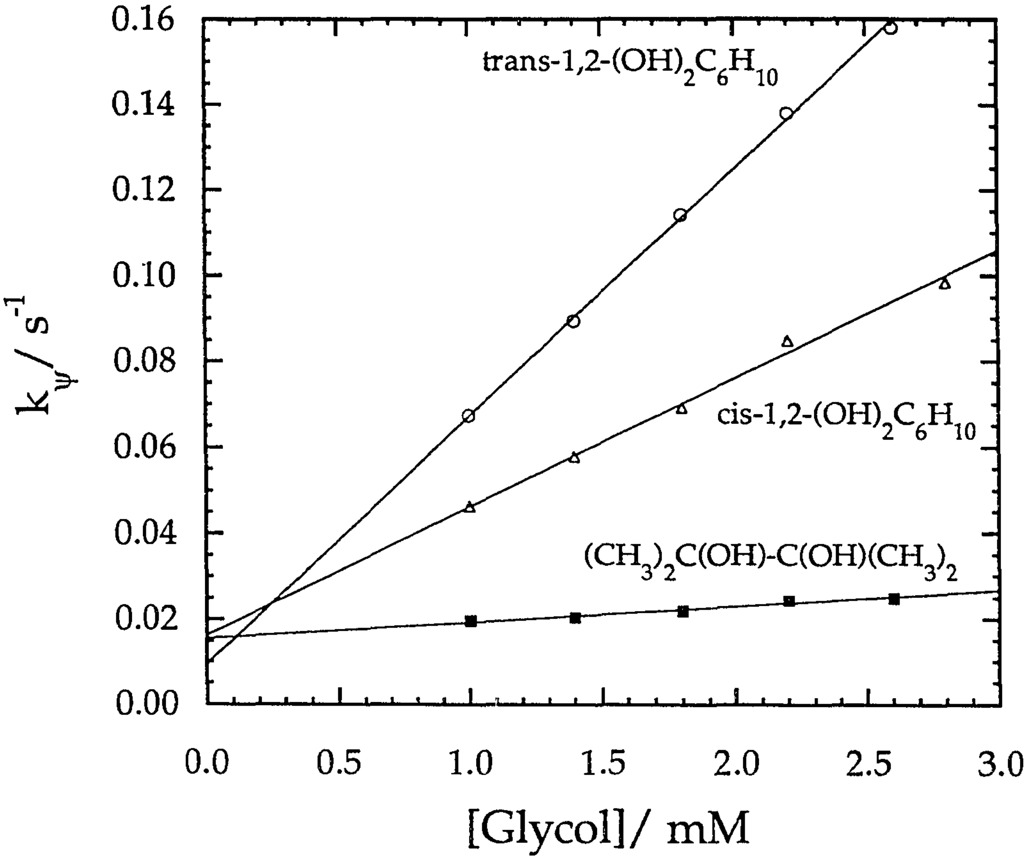


Figure III-2. Dependence of the pseudo-first-order rate constants (k_ψ) for the oxidation of 1,2-diols by CrO^{2+} on the concentration of diols in 0.1 M perchloric acid at 25 °C.

Table III-1. The second-order rate constants and the kinetic isotope effects for the oxidation of 1,2-diols by CrO^{2+} in 0.1 M perchloric acid at 25 °C.

diol/ alcohol	k($L\ mol^{-1}\ s^{-1}$)	k_H/k_D	ref
$CH_2(OH)CH_2(OH)$	33 ±2		this work
$CH_2(OD)CH_2(OD)$	28 ±3[a]	1.2	this work
$CD_2(OH)CD_2(OH)$	8.9 ±0.5[c]	3.7	this work
cis-1,2-$(OH)_2C_6H_{10}$	30 ±1		this work
cis-1,2-$(OD)_2C_6H_{10}$	26 ±3[b]	1.2	this work
trans-1,2-$(OH)_2C_6H_{10}$	57 ±1		this work
$[(CH_3)_2C(OH)]_2$	3.7 ±0.2		this work
$[(CH_3)_2C(OD)]_2$	3.9 ±0.7[b]	0.95	this work
$[(CD_3)_2C(OH)]_2$	0.77 ±0.10[c]	4.8	this work
CH_3OH	52.2 ±1.4		5
CD_3OH	15.1 ±1.7[c]	3.5	5
CH_3CH_2OH	88.4 ±4.4		5
$C_6H_5CH_2OH$	56.0 ±3.5		5
$(CH_3)_2CHOH$	12.0 ±0.4		5

[a] The rate contants were not corrected for the further oxidation of the product, HCHO (eq 9). [b] in D_2O. [c] in H_2O.

Decomposition of CrO^{2+}

The small intercepts in Figure III-2 represent the rate constant for the decomposition of CrO^{2+} in the absence of the diol. The range of values is k_{dec} = 0.01-0.02 s^{-1} at 25 °C in 0.1 M $HClO_4$. At this point the decomposition of CrO^{2+} is not completely understood, but there is some indication that the order of the self-decomposition reaction with respect to [CrO^{2+}] is higher than unity.[12] This unspecified kinetic order may be one reason that k_{dec} shows some scatter; others are the fact that in most situations decomposition is a very small part of the observed process and that secondary reactions (such as those to be described shortly, in which a product undergoes further reaction) cause a rate enhancement that is taken up in the intercept, since that part is independent of [diol].

Ionic strength and acidity effects

It was observed that the pseudo-first-order rate constant increased with an increase in the ionic strength of the solution. This was shown to be caused by the enhancement of k_{dec} (representing the rate of decomposition of CrO^{2+}, but not necessarily the correct reaction order) with ionic strength, and not to a variation of k_{diol}.[12a,c] The pseudo-first-order rate constant, however, was independent of the solution acidity in the range 0.1-1.0 M $HClO_4$.

Activation parameters

The activation parameters for the reactions of 1,2-cyclohexanediols with CrO^{2+} were obtained from the variation of the rate constants with temperature, Table III-2. The isokinetic relationship plot, Figure III-3, shows that $\Delta H^{\ddagger}$ is a linear function of $\Delta S^{\ddagger}$ for the reactions of primary and secondary alcohols and 1,2-cyclohexanediols with CrO^{2+}. The slope, the *isokinetic temperature*, is 264 ± 37 K.

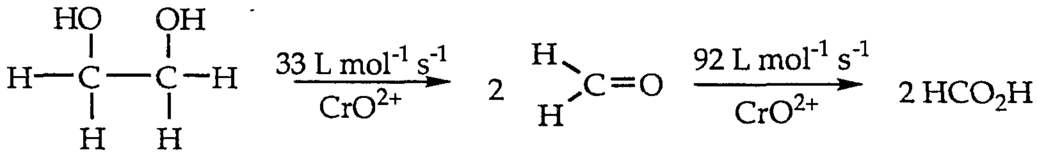
Table III-2. Activation Parameters for the Oxidation of Diols, Methanol and 2-Propanol by CrO^{2+} in 0.1 M $HClO_4$ Solutions.

Substrate	Activation parameters	
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
cis-1,2-$(OH)_2C_6H_{10}$	43 ±3	-73 ±5
trans-1,2-$(OH)_2C_6H_{10}$	51 ±5	-39 ±4
$(CH_3)_2CHOH$	33 ±3[a]	-112 ±14[a]
$[(CH_3)_2C(OH)]_2$	57 ±5	-39 ±4

[a] Reference 5.

Reaction stoichiometry

According to the expected stoichiometry, $[HCHO]_\infty/[CrO^{2+}]_0$ = 2:1, eq 9. The reaction of 40 μM CrO^{2+} with 1 mM ethylene glycol yielded 66 μM formaldehyde. This actually represents a 94% yield, since the calculation must also take into account the losses of HCHO and CrO^{2+} in the secondary reaction as shown in eq 9.[5] A theoretical yield of 70 μM HCHO was calculated for this experiment by use of the program KINSIM.[17]



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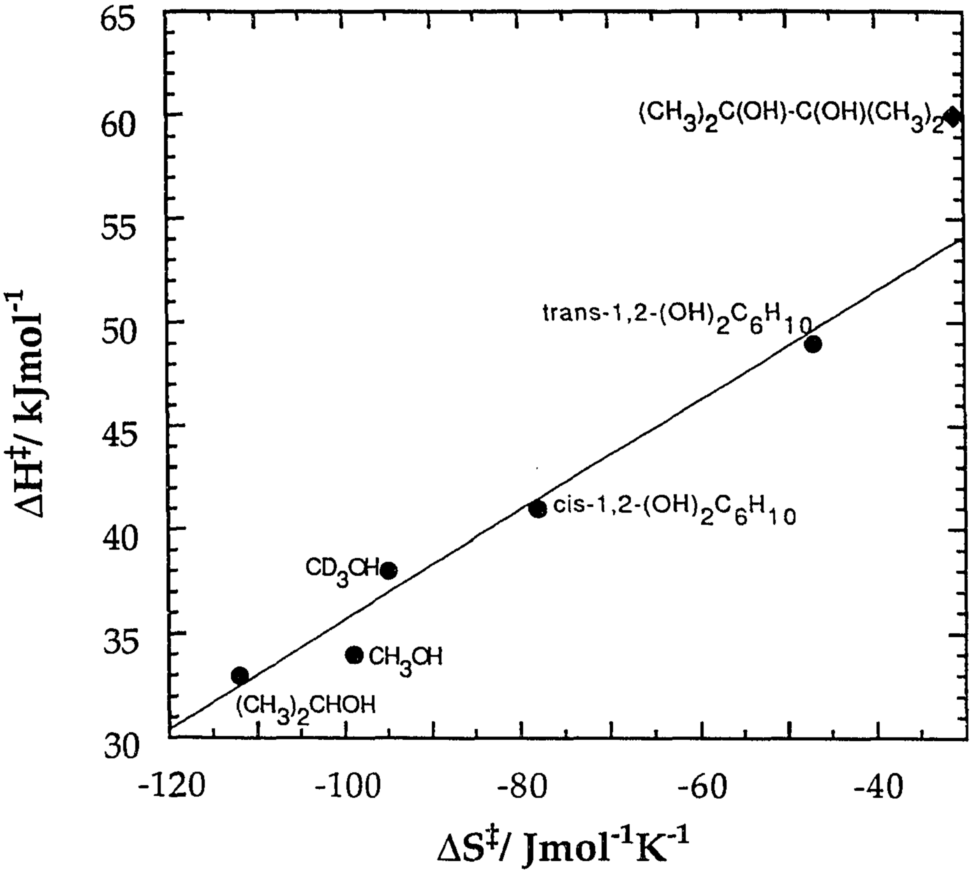
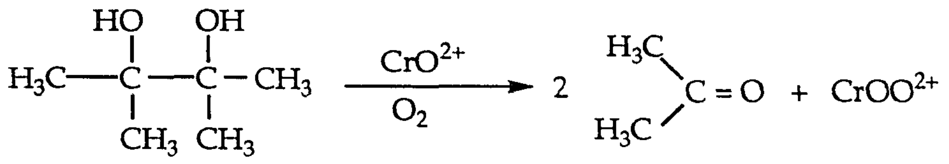


Figure III-3. The plot of $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$ for the reactions of alcohols and 1,2-diols with CrO^{2+} in 0.1 M $HClO_4$.

Reaction of pinacol with CrO^{2+}

The oxidation of pinacol by CrO^{2+} in 0.1 M $HClO_4$ in the presence of O_2 yielded $CrOO^{2+}$. Acetone was also formed in almost quantitative yield, eq 10. The pseudo-first-order rate constants are linearly dependent on the concentration of pinacol, with an intercept of 0.016 s^{-1} and a slope of 3.7 ± 0.2 L mol^{-1} s^{-1} at 25 °C, Figure III-4.



$$(CH_3)_2C(OH){-}C(OH)(CH_3)_2 \xrightarrow[O_2]{CrO^{2+}} 2\ (H_3C)_2C{=}O + CrOO^{2+} \qquad (10)$$

The second-order rate constant is acid-independent in the range 0.1-1.0 M H^+. The *kie* on deuteration of OH groups of pinacol (experiments in D_2O) was again negligible $k_H/k_D = 0.95$. On the other hand the *kie* of the C-H (β) hydrogens, when pinacol-d_{12} was oxidized, is significant, $k_H/k_D = 4.8$, as given in Table III-1 and Figure III-4.

DISCUSSION

One- vs two-equivalent reduction of CrO^{2+}

The one-equivalent reduction of CrO^{2+} yields Cr(III), which does not undergo any further oxidation-reduction reactions under the experimental conditions. A two-equivalent reduction, on the other hand, produces Cr^{2+} as a reactive intermediate, eq 11.

$$(H_2O)_5Cr^{IV}{=}O^{2+} + SH_2 \xrightarrow{k_S} Cr(H_2O)_6^{2+} + S \qquad (11)$$

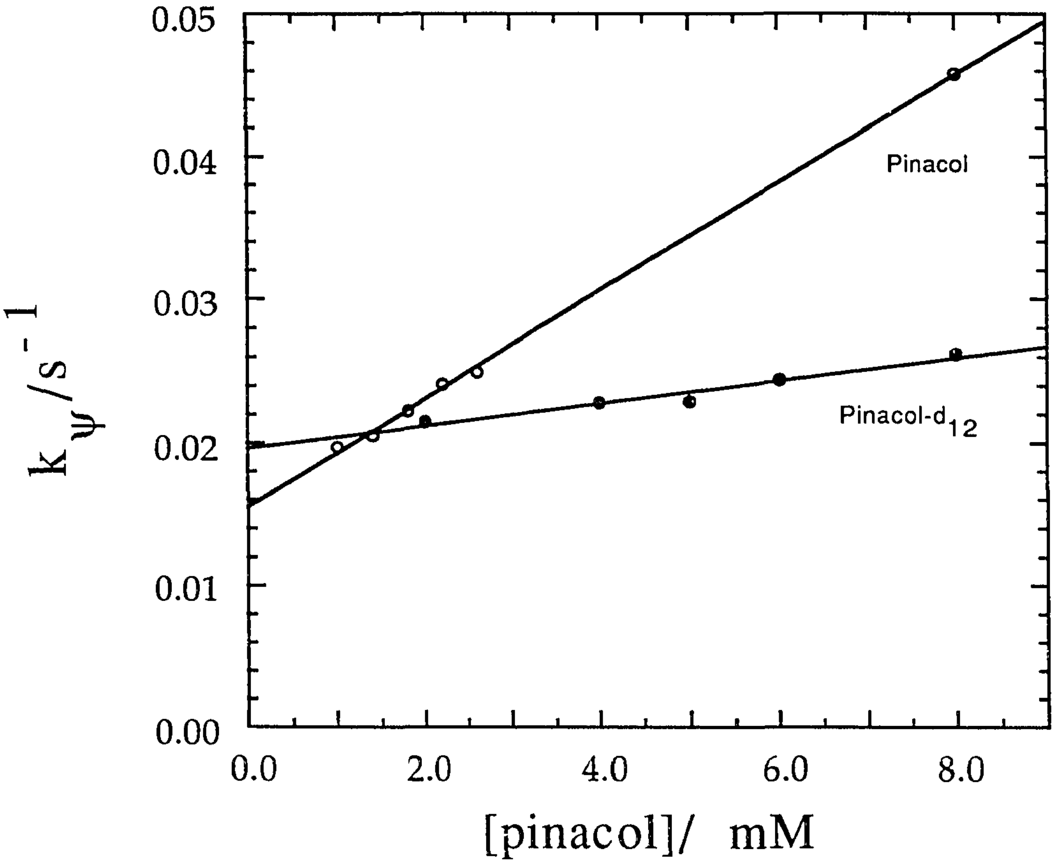


Figure III-4. Dependence of k_ψ on the concentration of pinacol and pinacol-d_{12} for the oxidation of pinacol with CrO^{2+} in 0.1 M perchloric acid at 25 °C.

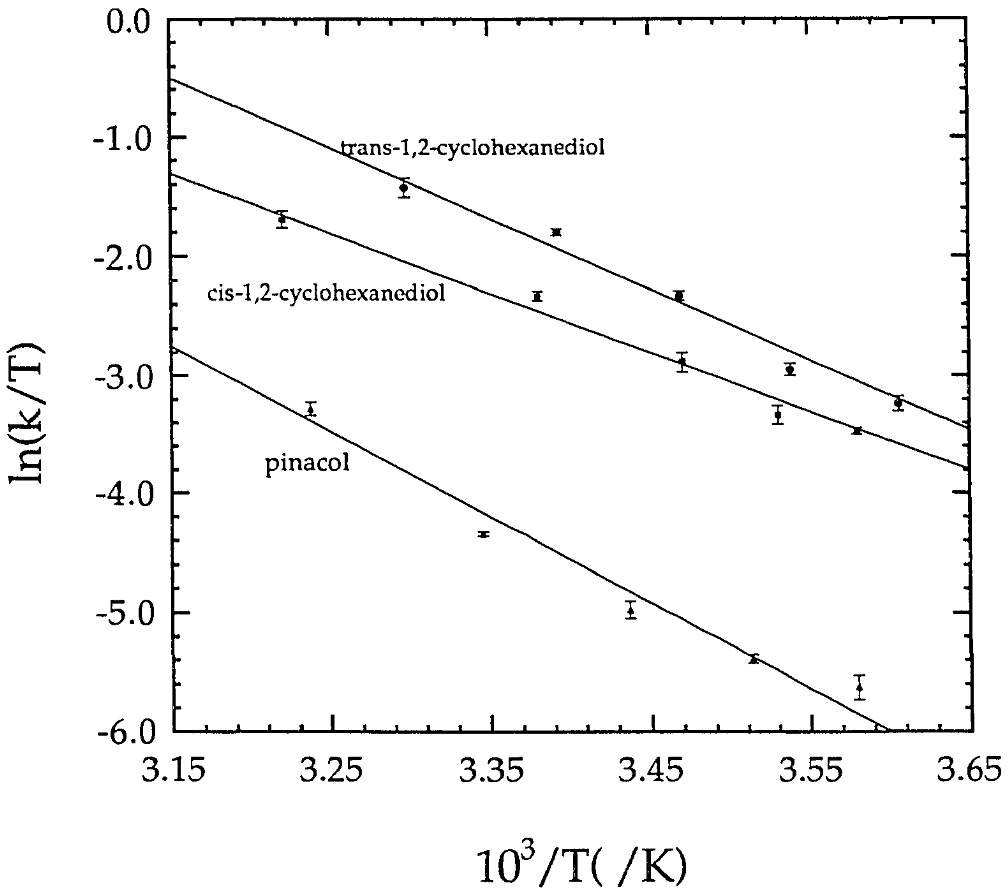


Figure III-5. Plot of ln(*k*/T) against $1/T$ for the reaction of various diols with CrO^{2+} in 0.1 M $HClO_4$.

In this work the intermediate Cr^{2+} was trapped by O_2 to yield $CrOO^{2+}$ (eq 4). Therefore the formation of $CrOO^{2+}$ from reduction of CrO^{2+} in the presence of O_2 can be taken as sound evidence for a two-electron mechanism.

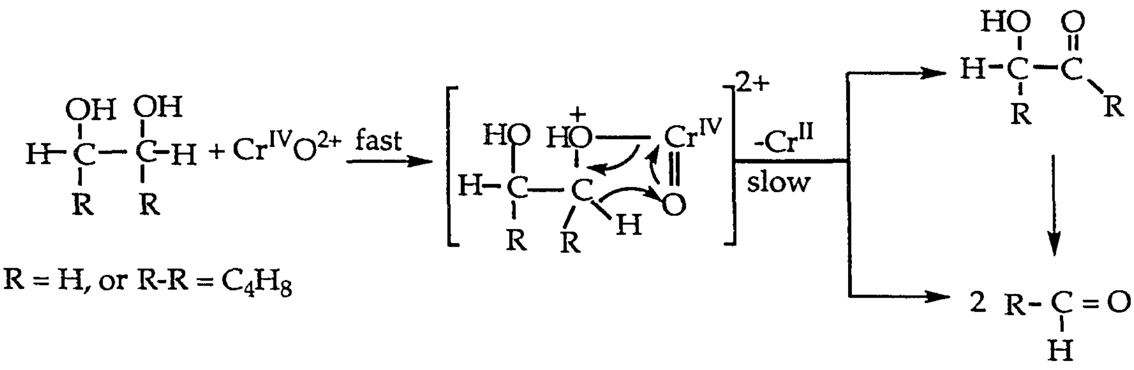
α-Hydride abstraction from ethylene glycol and 1,2-cyclohexanediols with CrO^{2+}

In our previous study[5] of the oxidation of numerous alcohols by chromyl ion, CrO^{2+}, a two-equivalent mechanism was identified. It was proposed that CrO^{2+} abstracts a hydride ion from the α-C of the alcohol. The Cr^{2+} produced in the reaction reacts rapidly with O_2, yielding $CrOO^{2+}$. The reactions of 1,2-diols with CrO^{2+} also yield the superoxochromium(III) ion, indicating that Cr^{2+} was again produced in a single-step, two-equivalent process.[15] This result and the significant primary *kie* found for the C-H bond of the glycol, together with the absence of a *kie* upon deuteration of the O-H bond, suggest a hydride abstraction mechanism for the oxidation of primary and secondary diols by CrO^{2+}.

The mechanism

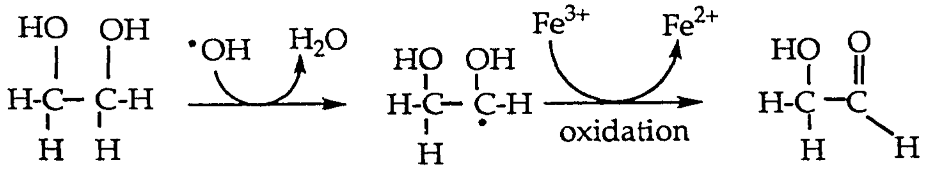
It should be noted that this is exactly opposite to the findings for phenols, where there is no *kie* for C–H bonds, but a marked *kie* for O–H bonds. From this and other evidence, we inferred that phenols react by a one-equivalent mechanism.[12b] Thus we propose for the diols a mechanism that is similar to the hydride abstractions from primary and secondary alcohols.[5] This is shown for ethylene glycol and 1,2-cyclohexanediols in Scheme III-1.

Scheme III-1. Mechanism of oxidation of primary and secondary1,2-diols by CrO^{2+}.



The hydride abstraction and the C–C bond cleavage in the oxidation of ethylene glycol may take place concertedly. On the other hand, it is possible that the reaction yields hydroxyacetaldehyde, Scheme III-1, which then rearranges to formaldehyde in an acid-catalyzed process prior to or during the analysis of formaldehyde by the chromotropic acid method.[14] The intermiediacy of hydroxyacetaldehyde would seem plausible, given that the reaction of ethylene glycol with goethite, α-FeOOH, yields both formaldehyde and hydroxyacetaldehyde in the relative yields that depend on the solution acidity.[11a] Also, in the oxidation of ethylene glycol to formaldehyde and formic acid at a platinum electrode in aqueous medium, hydroxyacetaldehyde has been reported as an intermediate.[18]

The oxidation of ethylene glycol by Fenton's reagent involves hydrogen atom abstraction by HO• to yield a carbon-centered radical.[19] This is then followed by the oxidation of the radical to hydroxyacetaldehyde or by rearrangement and reduction to acetaldehyde, eq 12.



(12)

In the present work the one-electron process can be clearly ruled out on the basis of the nature of the chromium product, $CrOO^{2+}$, which can result only from a two-equivalent process.

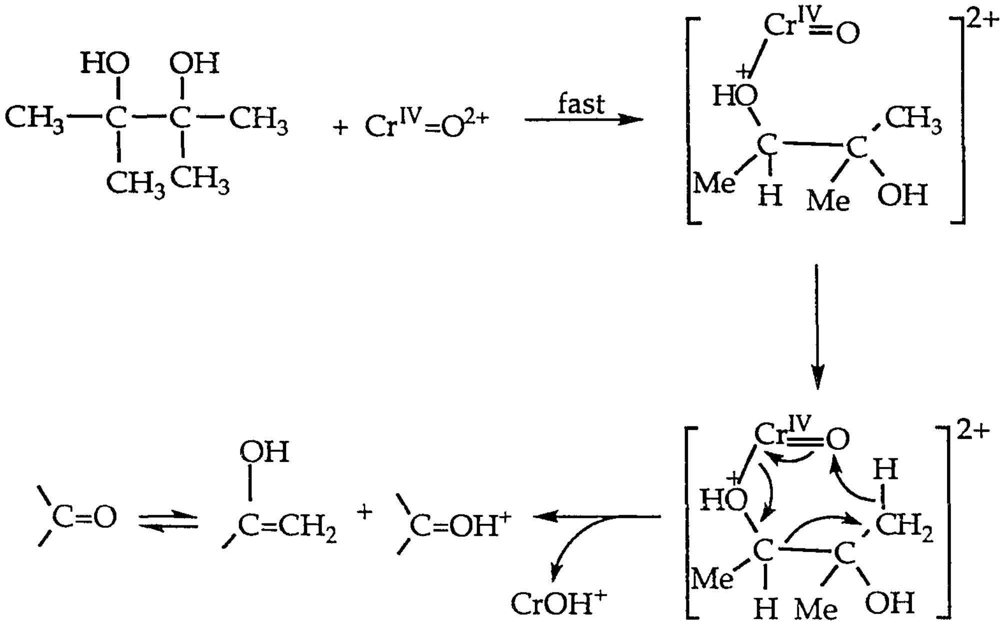
The enthalpy of activation, $\Delta H^{\ddagger}$, for the oxidation of 1,2-cyclohexandiols is somewhat higher than that obtained for secondary alcohols. This difference may be attributed to the increased steric demands of the cyclohexane ring, relative to the acyclic alcohols, in the transition state for hydride abstraction. Furthermore, the intramolecular H-bonding in 1,2-diols may reduce the efficiency of the binding of the diol to Cr(IV), leading to a higher energy transition state.

The rate constant for the oxidation of *trans*-1,2-cyclohexanediol is about twice as large as that for the cis isomer. The similarity in the rate constants between cyclopentanol (30.6 L mol^{-1} s^{-1})[5] and the two 1,2-cyclohexanediols strongly argues against the chelation in the reaction of the diols. This is different from the oxidation of diols by Pb(IV),[7] where a chelated intermediate has been proposed.

Reaction of Pinacol with CrO^{2+}

The quantitative formation of acetone and $CrOO^{2+}$ from the oxidative cleavage of pinacol by CrO^{2+} , eq 10, and the failure of all attempts to trap alkyl radicals using acrylonitrile or Ni(III), provide clear evidence for the two-equivalent oxidation path. Furthermore the *kie* on β-CH ($k_H/k_D = 4.8$) was significant. All these data are consistent with the mechanism shown in Scheme III-2. The rate-controlling step is the abstraction of a hydride ion from the β-position of pinacol. This is followed by the cleavage of the C-C bond and the formation of acetone and an enol, which tautomerizes to the more stable acetone.

Scheme III-2. Mechanism of oxidation of pinacol by CrO^{2+}.



Pinacol versus primary and secondary 1,2-diols

The slower reaction of pinacol, compared to other diols in this work, is probably a result of several factors. As shown in Scheme III-2, the reaction with pinacol proceeds through a six-membered cyclic transition state. In case of primary and secondary diols, the reactions involve the more favorable five-membered cyclic transition states, Scheme III-1. The steric effect of the methyl groups may contribute to a slower reaction. Also, the heterolytic bond strength of the C-H bond may be greater in the case of pinacol, where a methyl group is involved. This effect may be minor, however, since it has been shown that alcohols with very different homolytic C-H bond strengths have similar rate constants for the reactions with CrO^{2+}.[5]

The activation parameters (Table III-2) were calculated from the plot of log(*k*/*T*) vs. 1/*T*, Figure III-5. The enthalpy of activation of pinacol is higher than those for *cis*-1,2-cyclohexanediol and 2-propanol (Table III-2), and is in part responsible for the rate constant of pinacol being small relative to those of the 1,2-cyclohexanediols and 2-propanol. The enthalpy of activation, $\Delta H^{\ddagger} = 60 \pm 6$ kJ mol^{-1}, lies between the values for the oxidation of pinacol by Cr(VI), $\Delta H^{\ddagger} = 40.5$ kJ mol^{-1},[8] and Os(VIII), $\Delta H^{\ddagger} = 78$ kJ mol^{-1}.[10] Oxidative cleavage of pinacol has been proposed as the rate-controlling step for both oxidants, although the nature of the proposed intermediate is different. In the case of Cr(VI) a chromate ester is believed to be involved, whereas Os(VIII)-glycol complexes have been invoked in the case of OsO_4.

α- versus β-hydride abstraction

There is a possibility of β-hydride abstraction from primary and secondary diols (or alcohols) by CrO^{2+} in these reactions. However, many alcohols, such as CH_3OH and $C_6H_5CH_2OH$, as shown in Table III-1, have no β-hydrogen and the rates of the hydride abstraction from these alcohols by CrO^{2+} are all comparable, and at least ten times greater than for pinacol. The rate constants for oxidation of these alcohols by CrO^{2+} are also close to the rate constants for other alcohols, such as CH_3CH_2OH and 1,2-diols which have both α- and β-hydrogens, Table III-1. Finally the isokinetic plot of the activation parameters, ($\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$) Figure III-2, suggests similar mechanisms for oxidations of primary and secondary alcohols and 1,2-diols.

The point for pinacol lies away from the line; it evidently adopts a different mechanism, as put forth in Scheme III-2.

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CHAPTER IV. KINETICS AND MECHANISM OF THE OXIDATION OF PHENOLS BY THE OXOCHROMIUM(IV) ION

A paper published in *Inorganic Chemistry*[1]

Ahmad M. Al-Ajlouni, Andreja Bakac and James H. Espenson

ABSTRACT

The oxidation of phenols by the (pentaaqua)oxochromium(IV) ion, $(H_2O)_5CrO^{2+}$, in acidic aqueous solutions yields *p*-benzoquinone as a major product. Small amounts of the unstable 4,4'-biphenoquinone were also produced, as evidenced by an increase (fast stage) and then a decrease (slow stage) in absorbance at 400 nm where there is an intense absorption band. The fast stage is first-order in CrO^{2+} and first order in phenol. The slow stage follows a first-order exponential decay. There is a large kinetic isotope effect for the first stage, k_H/k_D = 14.7, on deuteration of the hydroxylic hydrogen. There is, however, no kinetic isotope effect of deuteration of the C-H hydrogen, k_H/k_D = 1.0. The rate constants of different meta-substituted phenols follow the Hammett relationship with $\rho = -1.7$. The activation parameters are $\Delta H^‡ = 15.2 \pm 1.5$ kJ mol^{-1} and $\Delta S^‡ = -144 \pm 15$ J mol^{-1} K^{-1}. We propose a mechanism according to which the phenols are first oxidized by one electron to the corresponding phenoxyl radicals; this occurs by hydrogen atom abstraction. The superoxochromium(III), $(H_2O)_5CrO_2^{2+}$, which is also present in

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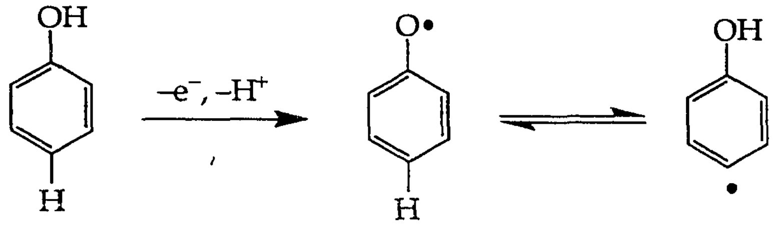
[1] Al-Ajlouni, A. M.; Bakac, A; Espenson, J. H. *Inorg. Chem.*, **1993**, 32, 5792.

solution, then oxidizes the phenoxyl radical to benzoquinone. The rate constants for both stages increase with increasing ionic strength of the medium. The solution acidity was found to decrease the rate of the first stage and enhance the rate of the second, but both effects are relatively small. The activation parameters for the second stage are $\Delta H^{\ddagger} = 46 \pm 4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -129 \pm 11$ J mol^{-1} K^{-1}.

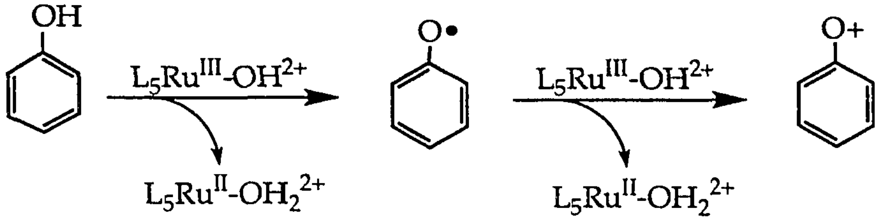
INTRODUCTION

Phenols are used as inhibitors of free radical autoxidations because of their facile reaction with alkylperoxyl radicals.[1] The catalytic and noncatalytic activation of O_2 towards phenols by transition metals has therefore been studied extensively.[2,3] These reactions often take place by a radical mechanism wherein a hydrogen atom is transferred from phenol to an oxidant to yield a phenoxyl radical or its carbon-centered isomer.[4-6]



(1)

The oxidation of phenols by transition metal oxidants can take place by either inner-sphere or outer-sphere mechanisms. Inner-sphere reactions are prevalent for the substitutionally labile oxidants, whereas the inert ones, such as Mn(acac)$_3$ and Co(acac)$_3$, react by an outer-sphere mechanism.[7] The oxidation of phenols by chromium(VI) in aqueous perchloric acid takes place by a hydride-transfer leading to the formation of an intermediate phenonium cation.[8] The hydroxoruthenium(III) complex, $(bpy)_2(py)Ru\text{-}OH^{2+}$, on the other hand, has been found to oxidize phenol in one path by an inner-sphere mechanism and in another by an outer-sphere mechanism, eq 2.[9] The outer-spher path leads to the formation of a phenonium cation which then reacts with water to produce hydroquinone .



(2)

A mechanism that involves electrophilic attack on the aromatic ring has been proposed for the oxidation of phenol to benzoquinone by the ruthenium(IV) reagent $(bpy)_2(py)Ru^{IV}{=}O^{2+}$.

The oxidation of phenols produces primarily the corresponding benzoquinone; however, other products, such as biphenoquinone, biphenol, and dicarboxylic acids, may also be formed as intermediates or products.[5,6] The selectivity to a particular product depends upon the oxidant, the solvent and the substituent(s) on the phenol.[5]

The chromyl or (pentaaqua)oxochromium(IV) ion, $(H_2O)_5CrO^{2+}$, is a strong oxidizing agent.[10] It can function as either a one-electron or a two-electron oxidant, and it has been shown to adopt different mechanisms in its reactions with organic materials: hydride abstraction from alcohols and hydrogen peroxide, hydrogen atom abstraction from cyclobutanol, and O-atom transfer to PPh_3.[10,11]

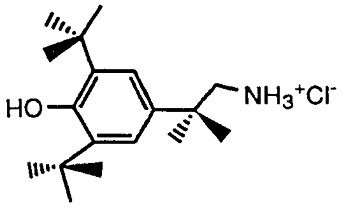
The chromyl, CrO^{2+}, is a flexible oxidant. It presents variety of mechanistic possibilities. It may function as an active species in catalytic reactions involving chromium and O_2.[10] From the point of view of the mechanistic chemist CrO^{2+} has an additional advantage over some other oxidants in that the presence or absence of the easily identifiable CrO_2^{2+} as a reaction product under aerobic conditions unequivocally shows that the reaction takes place in two- or one-electron steps, respectively.[10]

In this work results of the kinetic and mechanistic study of the oxidation of several phenols by CrO^{2+} are presented. The effects of the acidity, ionic strength and isotopic substitution on the kinetics and products were examined. The rate constants for the meta-substituted phenols were correlated by the Hammett equation. The organic products were found to be mainly *p*-benzoquinones. In addition, the reaction yielded some 4,4'-biphenoquinone, which subsequently decomposed in aqueous acidic solution.

EXPERIMENTAL SECTION

Reagents

Water was purified by passing the laboratory distilled and deionized water through a Millipore water system. Phenol, *o*-cresol, 3-nitrophenol, 3-hydroxybenzoic acid, 3-aminophenol, 3-methoxyphenol, 3-(α,α,α-trifluoromethyl)cresol and $Tl_2(SO_4)_3$ were used without further purification. *m*–Cresol was purified by distillation. Deuterium oxide and 98 atom % phenol-d_6 were used as received. 2-Methyl-2-(4-hydroxyl-3,5-ditert-butylphenyl)propyl ammonium chloride, **ArOH**, was synthesized by a published method.[12]



ArOH

The kinetic isotope effect k_{PhOH}/k_{PhOD} was determined by conducting experiments in H_2O and D_2O. The temperature was controlled by means of a thermostated cell holder connected to a circulating water bath set at the desired temperature. The quartz cuvette in which the reaction was conducted was immersed in the water-filled holder throughout the experiment to ensure precise temperature control. The holder has quartz windows that allow the analyzing light of the spectrophotometer to pass through. The water bath creates a small but constant absorbance background.

Reactions

Solutions of Cr^{2+} (0.01 M) in dilute perchloric acid were prepared by the anaerobic reduction of Cr^{3+} with Zn/Hg. In a typical kinetic experiment CrO^{2+} was formed *in situ* by injecting 100 µL of 0.01 M Cr^{2+} into a spectrophotometric cell containing 5.0 mL of an O_2–saturated solution of the phenol. Under these conditions Cr^{2+} and O_2 react rapidly to produce 0.04 mM CrO^{2+} (~20% based on total Cr^{2+}), which then reacts with the phenol already present in solution. For anaerobic experiments the CrO^{2+} was prepared by injecting Cr^{2+} into a spectrophotometric cell that contained a 2-3 fold excess of air-free Tl^{3+} and the phenol (0.2-0.6 mM).

The acid concentration and the ionic strength were both kept at 0.10 M except in experiments designed to study the effects of these variables. The pH was maintained by perchloric acid and the ionic strength by lithium perchlorate. Solutions of CrO_2^{2+} were prepared by mixing Cr^{2+} and excess O_2 as previously described.[10]

Products identifications

Chromium(II), 0.5 mL of 0.01 M, was injected into 10 mL of O_2-saturated 0.1 M $HClO_4$ that contained 0.2 mM CrO_2^{2+} and 0.2 mM phenol. The procedure was repeated ten times and all the solutions combined in a separatory funnel.[13] The organic product(s) were extracted by CH_2Cl_2 (2 × 10 mL) and dried over $MgSO_4$. Finally, the CH_2Cl_2 was evaporated at room temperature. The yield of benzoquinone was determined by a spectrophotometric titration with a standard solution of Cr^{2+}. The reaction occurs with a 2:1 stoichiometry and yields a binuclear chromium(III) quinone complex that can be easily identified and quantified by its UV-visible spectrum, λ_{max} 292 nm (ε 6.5×10^3 L mol^{-1} cm^{-1}) and 590 nm (ε 2.4×10^2 L mol^{-1} cm^{-1}).[14]

The UV-visible spectra were recorded with a Shimadzu spectrometer. The FT-IR spectra were obtained in chloroform solution using NaCl plates. The ^{1}H-NMR spectra were recorded with $CDCl_3$ as solvent and referenced to tetramethylsilane.

Kinetic measurements

The kinetic data for the oxidation of phenols by CrO^{2+} were collected by following the absorbance changes at about 400 nm. The reactions were carried out with a large excess of phenol over CrO^{2+}. The sequential first-order rate constants were calculated by fitting the kinetic trace to a biexponential function (eq 3).[15]

$$Abs_t - Abs_\infty = \alpha \exp(-k_f t) + \beta \exp(-k_s t) \tag{3}$$

where

$$\alpha = \frac{(\varepsilon_I - \varepsilon_A)k_f - (\varepsilon_A - \varepsilon_P)k_s}{k_s - k_f}[\mathrm{CrO}^{2+}]_0 \text{ and } \beta = \frac{(\varepsilon_P - \varepsilon_I)k_f}{k_s - k_f}[\mathrm{CrO}^{2+}]_0$$

In these expressions ε_A, ε_I and ε_P are the molar absorptivities of the reactant, the intermediate and the product, and k_f and k_s the rate constants for the fast and slow stages. Since the reactants and products have no significant absorption at 400 nm, *i.e.* $\varepsilon_A \sim \varepsilon_P \sim 0$, the expression simplifies to :

$$\alpha = -\beta = \frac{\varepsilon_I k_f}{k_s - k_f}[\mathrm{CrO}^{2+}]_0$$

RESULTS

Reaction of 2-Methyl-2-(4-hydroxyl-3,5-ditert-butylphenyl)propyl ammonium chloride, ArOH, with CrO^{2+}

The oxidation of ArOH leads to the formation of a stable, green-colored phenoxyl radical (eq 4), which was identified by its characteristic UV-visible spectrum (Figure IV-1).[16,12] This was taken as an indication that the other phenols, which do not give such an easily-recognized product, may react analogously. This is strongly supported by the observed kinetic isotope effects, and by the correlation of the kinetic data to the Hammet equation (see later), and by the failure to observe the formation of CrO_2^{2+} in the presence of O_2, the product of a possible two-electron reaction [10]

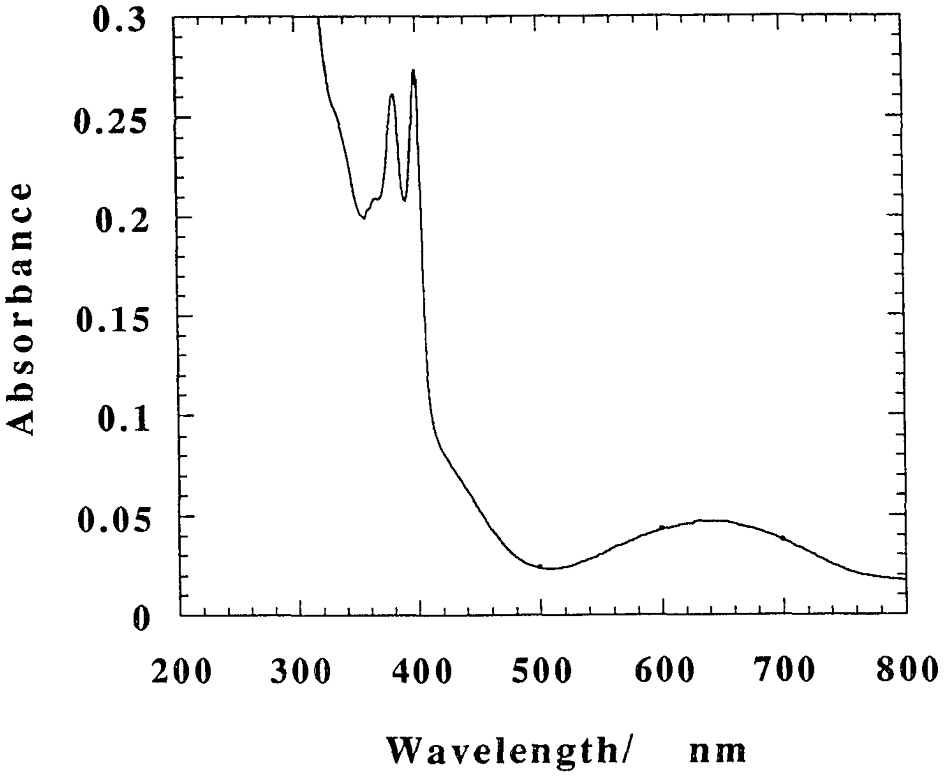
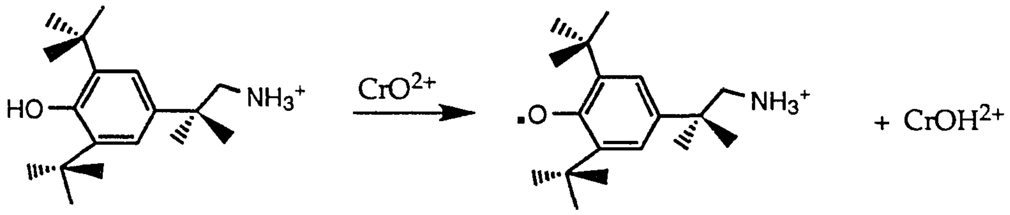


Figure IV-1. UV-vis spectrum of the phenoxyl radical (λ_{max} 381, 399 nm and 620 nm) from reaction of 2-methyl-2-(4-hydroxyl-3,5-di-*tert*-butylphenyl)-propyl ammonium chloride, ArOH, (0.3 mM) with CrO^{2+} (~0.04 mM) in 0.1 M $HClO_4$ at 25 °C.

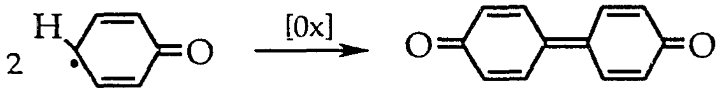


ArOH ArO•

(4)

Reaction of other phenols with CrO^{2+}

The intermediates. In the oxidations of other phenols by CrO^{2+}, the addition of Cr^{2+} causes the colorless solutions of phenol and oxygen to turn yellow rapidly and then to fade slowly, Figure IV-2. The yellow intermediate has a maximum absorption close to 400 nm (the exact value depends on the identity of the phenol), characterized by a high molar absorptivity.[17] This absorption band is typical for 4,4'-biphenoquinone, which is formed by the coupling of phenoxyl radicals followed by oxidation (eq 5).[18] In aqueous solutions this species hydrolyses to other organic products. It also reacts with phenol to produce biphenol.[19]



4,4'-biphenoquinone

(5)

The final products. The UV-visible spectrum of the reaction mixture at the end of the reaction showed a strong absorption at 245 nm characteristic of *p*-benzoquinone ($\varepsilon_{245} \sim 2 \times 10^4$ L mol^{-1} cm^{-1}). The product was also characterized by UV-vis, ^{1}H NMR and FT-IR spectra (Figure IV-3 and Figure IV-4). Reaction of p-cresol with CrO^{2+} yielded the corresponding o-quinone (λmax ~ 390 nm). The second-o rder rate constant was about 900 $M^{-1}s^{-1}$.

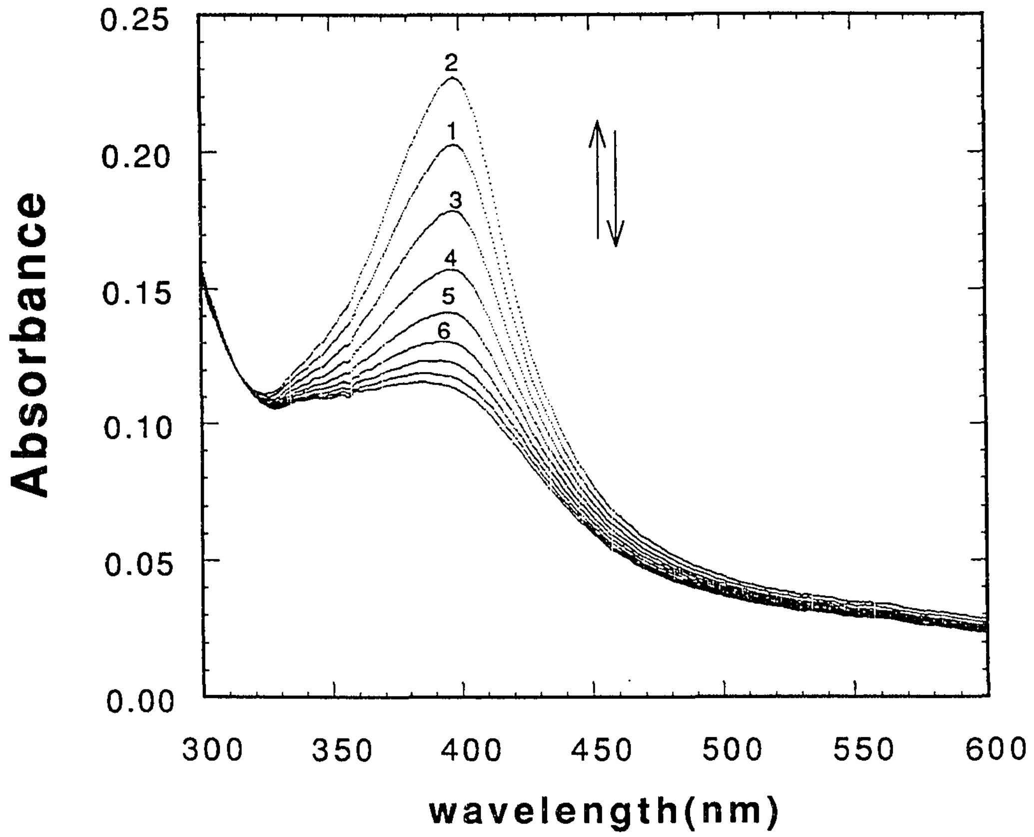


Figure IV-2. Successive spectral changes at 30 s intervals during the oxidation of phenol (0.3 mM) by CrO^{2+} (~0.04 mM) in 0.1 M $HClO_4$ at 25 °C.

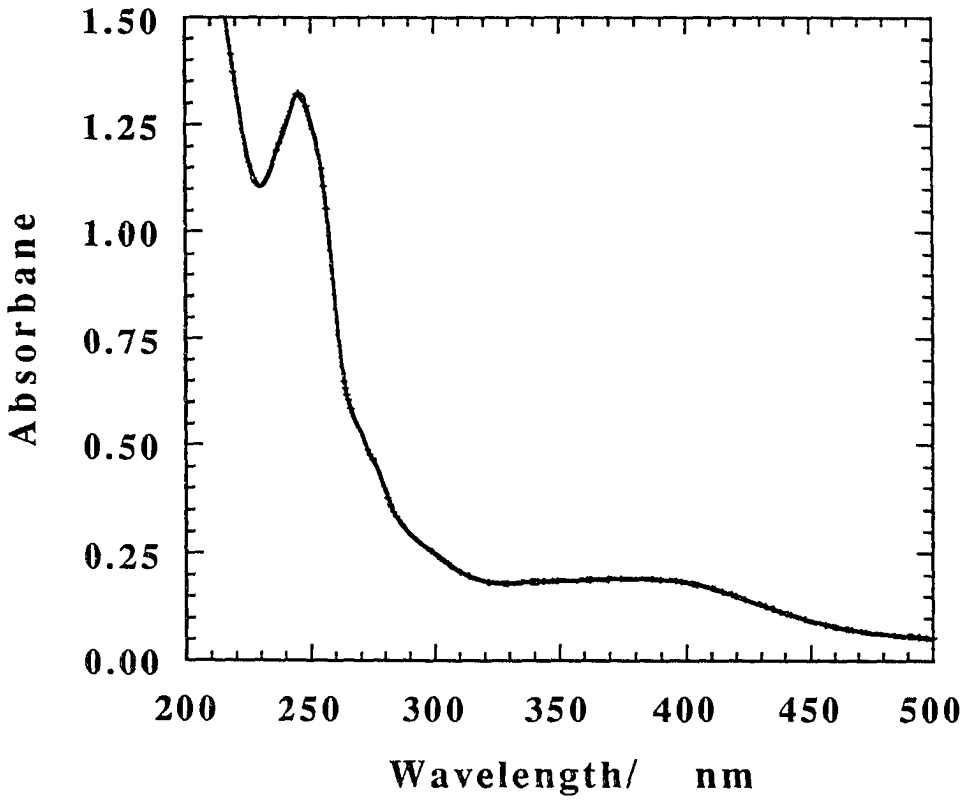


Figure IV-3. The UV-vis spectrum in H_2O/ 0.1M $HClO_4$ solution of the organic products (benzooquinones) of the oxidation of phenol by CrO^{2+} in the presence of O_2.

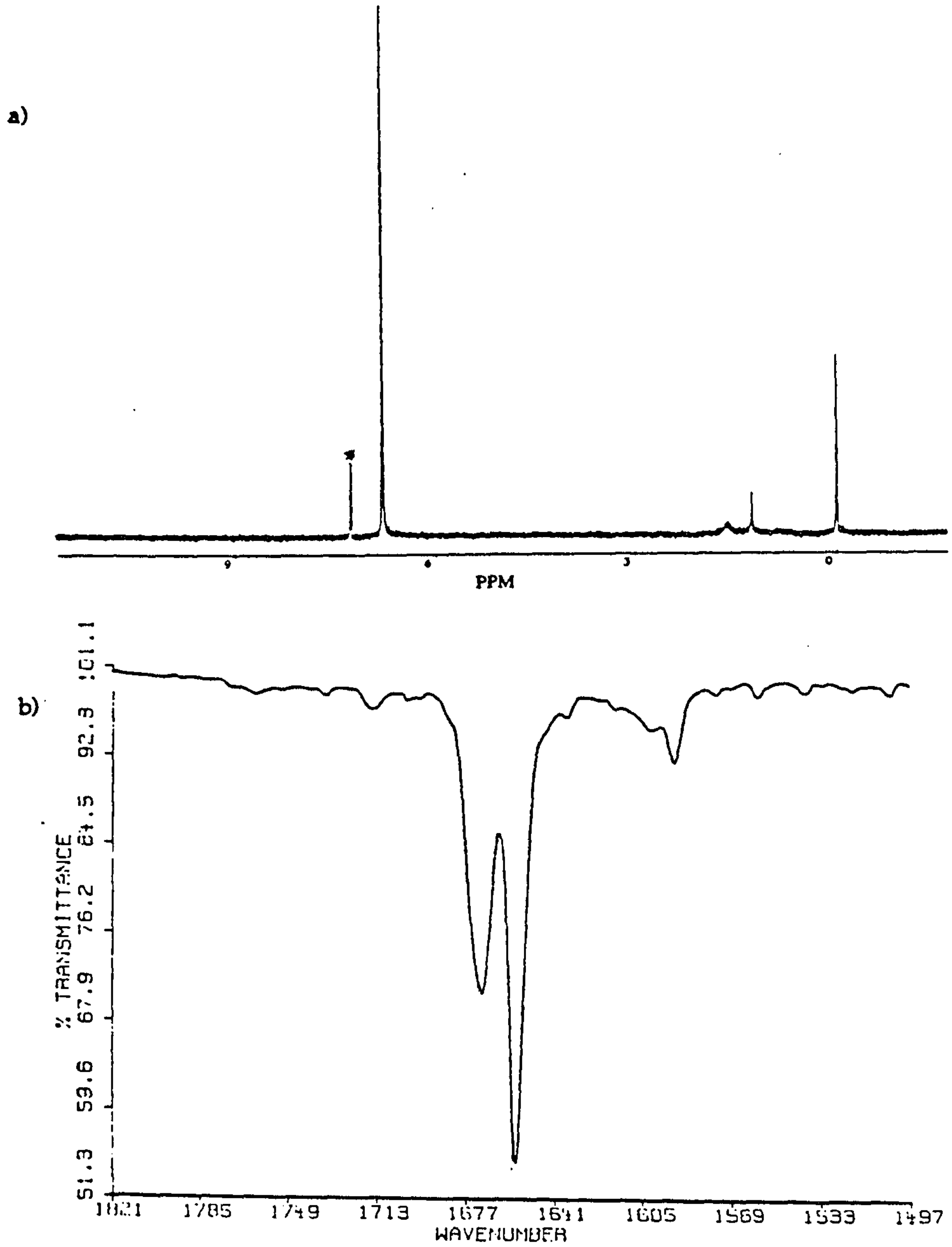


Figure IV-4. a) The ^{1}H NMR spectrum in $CDCl_3$ of the organic products of the oxidation of phenol by CrO^{2+} in the presence of O_2 after extraction with CH_2Cl_2, * $CDCl_3$ peak. b) The FT-IR spectrum of the same sample.

The effect of the superoxochromium(III), $CrOO^{2+}$

The relative yields of the products obtained by the oxidation of phenol by CrO^{2+} were affected by added CrO_2^{2+}. The absorbance at 245 nm increased, and that at 400 nm decreased, with increasing concentrations of CrO_2^{2+}. In the presence of 0.2 mM CrO_2^{2+} the yield of *p*-benzoquinone was 83%, and in the absence of added CrO_2^{2+} (see the Experimental section) the yield was 27%. The reaction rate, however, remained independent of both $[CrO_2^{2+}]$ and $[O_2]$. In each experiment both *p*-benzoquinone and biphenoquinone were formed.

Kinetics

Bulid-up and disappearance of biphenoquinone intermediates. The reaction products, *p*-benzoquinone and 4,4'-biphenoquinone, are formed in rapid post-rate-controlling steps, see later. The rate constant for the disappearance of the reactants can thus be obtained by monitoring the build-up of either of the products. The kinetic data were collected at the maximum absorption of 4,4'-biphenoquinone, a relatively minor product that absorbs strongly at ~400 nm, Figure IV-5.

Figure IV-5 shows the spectral changes that occurred with time in a solution that initially contained 0.3 mM phenol and 0.04 mM CrO^{2+}. Similar absorption changes were observed for the other phenols used in this study. With the phenol in a large excess over CrO^{2+}, the rate of the formation (fast stage) of 4,4'-biphenoquinone followed first-order kinetics. The subsequent absorbance decrease (slow stage) was found to depend on the concentration of the phenol RC_6H_4OH for R = H, but not for R = alkyl.

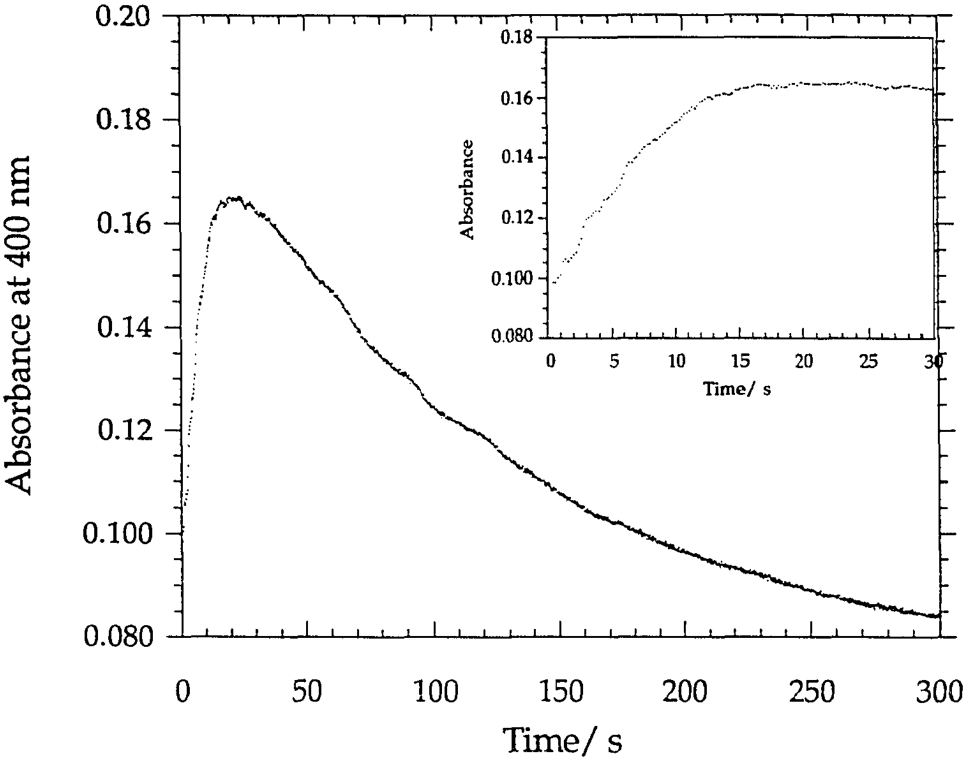


Figure IV-5. The absorbance change versus time at 400 nm from reaction of phenol (0.5 mM) with CrO^{2+} (~ 0.04 mM) in 0.1 M $HClO_4$ at 25 °C. The inset shows the build up of the intermediate in the first 30 s.

Table IV-1. Rate Constants[a] for the Oxidation of Phenols by CrO^{2+} (k_f) and for the Decomposition of 4,4'-Biphenoquinone Intermediates (k_s).

Phenol	k_f/L mol^{-1}s^{-1}	k_s/10^{-3} s^{-1}	k_f^H/k_f^D	k_s^H/k_s^D
C_6H_5OH	471[a]	6.2[a]		
C_6H_5OD	32[b]	5.6[b]	14.7	1.1
C_6D_5OH	465[c]	4.6[c]	1.0	1.3
3-CH_3-C_6H_4OH	645[a]	11[a]		
2-CH_3-C_6H_4OH	1064[a]	5.5[a]		
2-CH_3-C_6H_4OD	63[b]	3.5[b]	16.9	1.8
ArOH[d]	240[a]	5.0[a]		

[a] Oxidation of the phenol in H_2O (0.1 M $HClO_4$) at 25 °C in the presence of O_2 ($[CrO_2^{2+}]\sim0.1$ mM). The standard deviation of the rate constants was estimated as ≤ 5%. [b] Oxidation of RC_6H_4OD in D_2O. [c] Oxidation of C_6D_5OH in H_2O. [d] 2-Methyl-2-(4-hydroxyl-3,5-di-*tert*-butylphenyl)propyl ammonium chloride.

The pseudo-first-order rate constants for the two steps were obtained by fitting the data to a biexponential equation (eq 3). The rate constants obtained for the fast stage at constant ionic strength and acidity varied linearly with the phenol concentration. The values of the second-order rate constants obtained from the slopes are shown in Table IV-1. The intercepts of these plots, 0.00–0.04 s^{-1}, correspond to the decomposition of CrO^{2+}. The rate constant cannot be determined very accurately, however, since it is such a small component of the reaction. Further comments on the decomposition of chromyl ion have been given before.[11]

Kinetic isotope effects. Large kinetic isotope effects (k_H/k_D = 14.7 for C_6H_5OH) were observed upon changing the solvent from H_2O to D_2O. They relate the rate constants for the reactions of C_6H_5OH with $(H_2O)_5CrO^{2+}$in H_2O to those for the reactions of C_6H_5OD with $(D_2O)_5CrO^{2+}$ in D_2O. The oxidation of C_6D_5OH and C_6H_5OH by $(H_2O)_5CrO^{2+}$ in H_2O showed no kinetic isotope effect, $k_H/k_D \sim 1.0$, Table IV-1.

Acidity and ionic strength effects. At constant ionic strength (0.1 M) the rate of the fast step decreased with increasing acidity of the solution. The rate of the slow stage, however, increased with acidity. Both of these effects are relatively small, however, as can be seen from the data in Table IV-2. An increase in the ionic strength was found to enhance the rates of both stages of the reactions (Table IV-2).

Table IV-2. The Acidity and Ionic Strength Dependence of k_f and k_s at 25 °C.

$[HClO_4]$/M	k_f/L mol^{-1} s^{-1}	k_s/10^{-3} s^{-1}
0.03	514[a]	4.1[a]
0.06	504[a]	5.0[a]
0.10	471[a] 635[b]	6.2[a] 11.5[b]

[a] μ = 0.10 M. [b] μ = 1.0 M.

The effect of a substituent on the phenol reactivity. The electronic effect of one substituent in the meta position of the phenol on the rate constants have been correlated by the Hammett equation, log $(k_X/k_H) = \rho\sigma$.[20] The plot of $\log(k_X/k_H)$ against σ is linear (Figure IV-6), with a slope $\rho = -1.7 \pm 0.2$.

Table IV-3. Relative Rate Constants for Meta-Substituted Phenols.

X	k_X/k_H	σ^a
H	1.0	0.0
CH_3	1.37	-0.06
OCH_3	0.760	0.10
CO_2H	0.244	0.35
CF_3	0.145	0.46
NO_2	0.060	0.71

[a] Hammett substituent constants for X.

Temperature dependence studies. The effect of temperature in the range 4.5 - 32.2 °C on k_f and k_s for the oxidation of C_6H_5OH by CrO^{2+} yielded the activation parameters for the two stages. The values for the fast stage are $\Delta H^\ddagger = 15.2 \pm 1.5$ kJ mol^{-1} and $\Delta S^\ddagger = -144 \pm 15$ J mol^{-1} K^{-1} and for the slow stage $\Delta H^\ddagger = 46 \pm 4$ kJ mol^{-1} and $\Delta S^\ddagger = -129 \pm 11$ J mol^{-1} K^{-1}.

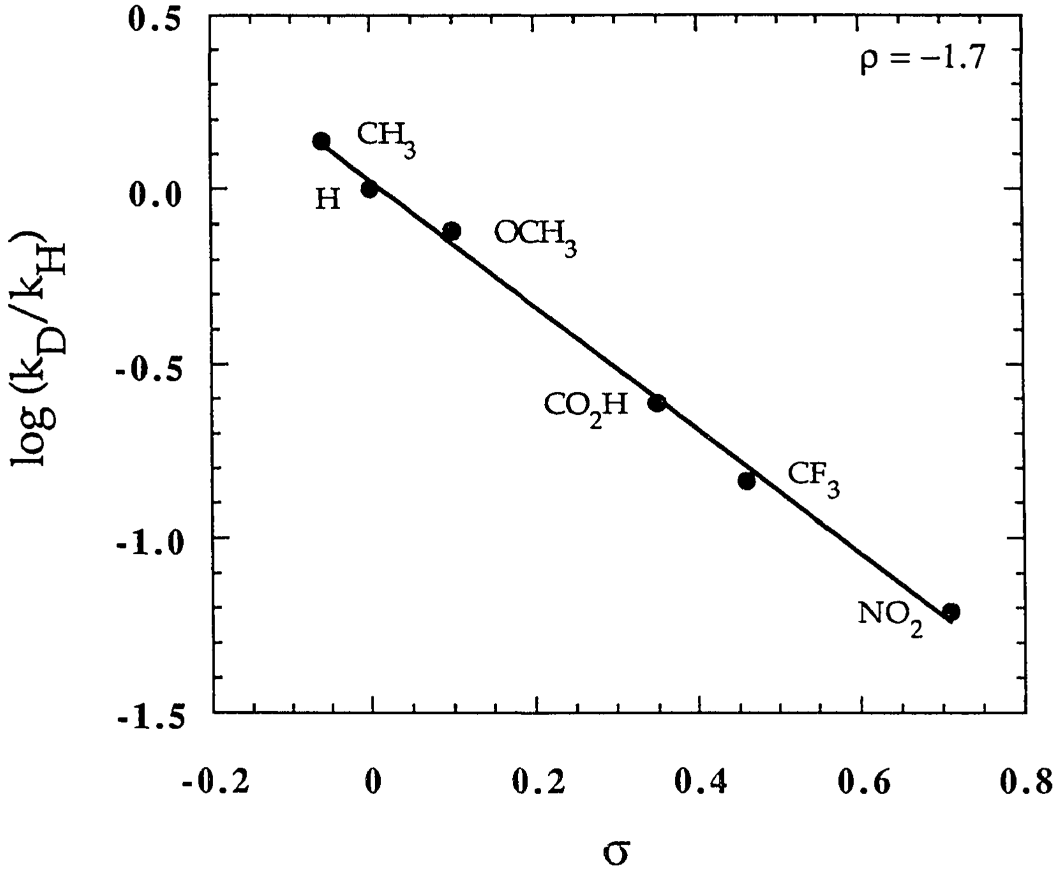
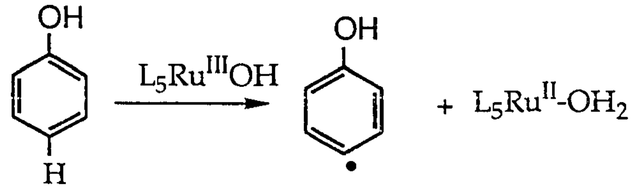


Figure IV-6. A plot of log(k_X/k_H) against σ for the reaction of meta substituted phenols with CrO^{2+} in 0.1 M $HClO_4$ at 25 °C. The slope ρ is −1.7 ± 0.2.

DISCUSSION

Phenoxyl radicals formation

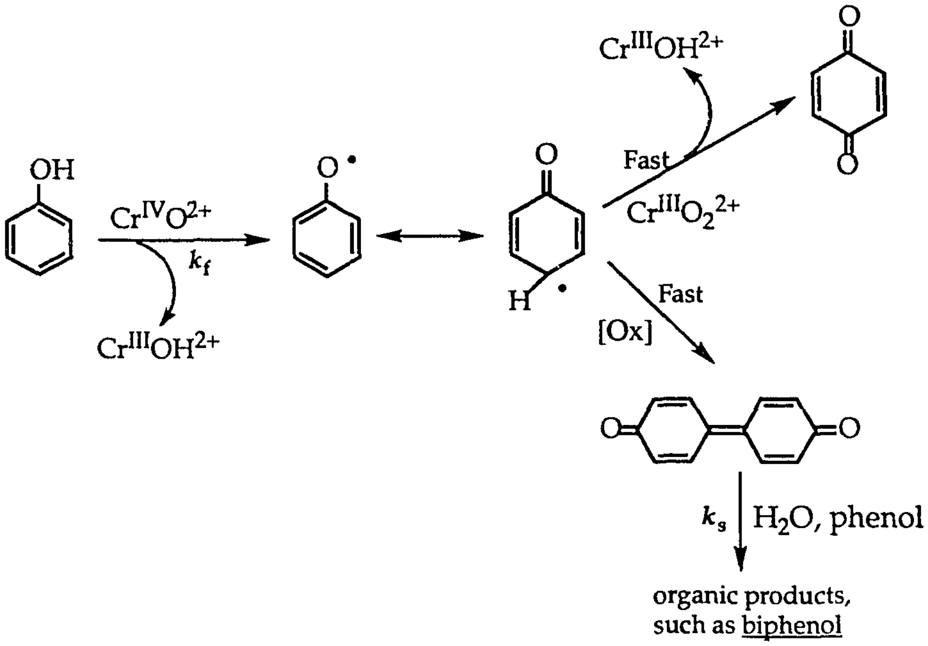
The results obtained in this study show that the oxidation of phenols by CrO^{2+} begins with the formation of the phenoxyl radical, Scheme IV-1. Clear evidence for such one-electron process is provided by the direct observation of the stable phenoxyl radical in the reaction of CrO^{2+} with ArOH. The large kinetic isotope effects in the reaction between CrO^{2+} and C_6H_5OH in H_2O versus C_6H_5OD in D_2O, (k_H/k_D = 14.7), and the absence of a kinetic isotope effect for C_6H_5OH in H_2O versus C_6D_5OH in H_2O, provide convincing evidence that O-H but not C-H bond breaking is involved in the rate-controlling step. Hydrogen atom abstraction from O-H has also been observed in the oxidation of phenols by (salen)$Co^{III}O_2$[5] and of hydroquinone by $[(py)(bpy)_2Ru^{IV}{=}O]^{2+}$.[23] On the other hand, oxidations of phenols by $[(py)(bpy)_2Ru^{III}\text{-}OH]^{2+}$ showed primary isotope effects of C-H but not O-H hydrogens, indicating hydrogen atom abstraction from C-H in the rate controlling step, eq 7.[9]



(7)

The phenoxyl radicals undergo two rapid competitive reactions: oxidation to benzoquinone, and coupling followed by oxidation to biphenols or biphenoquinones, Scheme IV-1.

Scheme IV-1. Mechanism of Oxidation of phenols by CrO^{2+} in the presence.

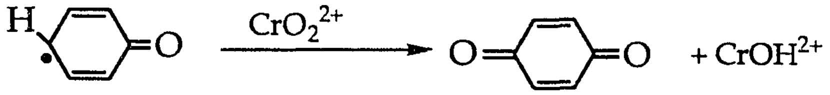


Biphenoquinones

The biphenoquinones, we believe, are the observed yellow intermediates absorbing at 400 nm.[17] The biphenoquinone formed here is mostly the more stable isomer 4,4'-biphenoquinone. Formation of other isomers, such as 2,2'-biphenoquinone, is possible, the UV-visible spectra, however, did not show any other absorption bands close to 400 nm. Perhaps the broad band absorption at 400 nm may include small absorption of other isomers. We did not find UV-visible spectra for any of these possible isomers in the literature to compare it with that obtained for 4,4'-biphenoquinone. Consistent with this assignment is an increase in the decay rate of the 400 nm absorbance with increasing acid and phenol concentrations.[21] The reaction with phenol produces biphenol.[21]

The role of $CrOO^{2+}$

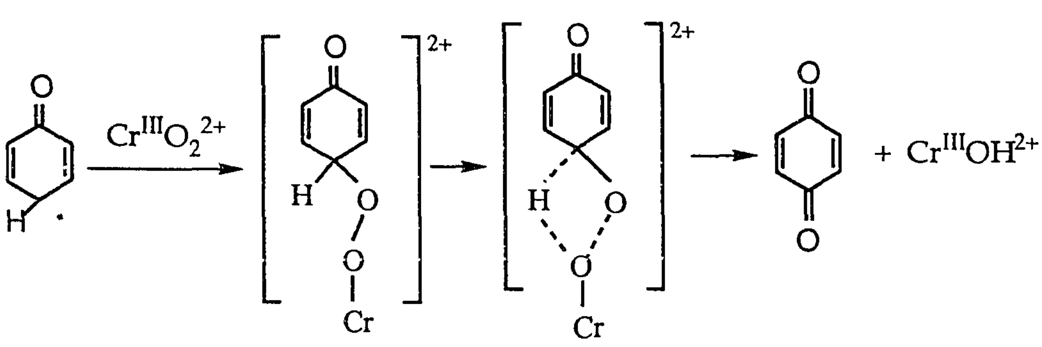
Most of the three-electron oxidation of phenoxyl radicals to the major product, benzoquinone, seems to be carried out by CrO_2^{2+}, a natural impurity in solutions of CrO^{2+} prepared from Cr^{2+} and O_2. The role of CrO_2^{2+} in the product-forming step(s) of eq 6 is demonstrated clearly by the decrease in the yield of benzoquinone with a decrease in $[CrO_2^{2+}]$. We infer that the oxidation of the phenoxyl radical by CrO_2^{2+} is rapid, since the observed rate constants showed no dependence on the CrO_2^{2+} concentration. In the absence of CrO_2^{2+} the oxidation of the radical was presumably carried out by CrO^{2+} itself, and in air-free experiments also by the Tl^{3+} left over from the CrO^{2+} preparation step.



(6)

The oxidation of the phenoxyl radicals by CrO_2^{2+} probably occurs by the coupling of phenoxyl radicals with CrO_2^{2+} resulting in the one-electron reduction of the coordinated superoxide to peroxide, Scheme IV-2.

Scheme IV-2. Proposed formation of quinones from the reaction of a phenoxy radical with $CrOO^{2+}$.



The reaction is then completed by oxygen transfer from the new peroxo ligand to the ring. A similar mechanism has been proposed for the oxidation of phenols by $L_5Co^{III}O_2$, (L_5 = bis(3-(salicylideneamino)-propyl)methylamine).[22]

The major products

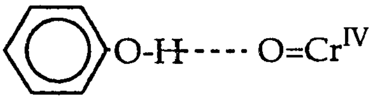
The oxidation of phenols that are not substituted in the ortho position might be expected to yield some 2,2'-biphenoquinone and *o*-benzoquinone in addition to the thermodynamically more stable 4,4'-biphenoquinone and *p*-benzoquinone. The UV-visible spectra showed that CrO^{2+} yields only the second pair of products. Also, the ^1H NMR spectrum of the products showed only one singlet, as expected for *p*-benzoquinone. No signal corresponding to *o*-benzoquinone was observed. The IR absorptions at 1671 and 1657 cm^{-1} ($\upsilon_{C=O}$) of the same sample are also characteristic of *p*-benzoquinone (Figure IV-3). This selectivity of CrO_2^{2+} for the para position of the phenoxyl radical may be caused by the unfavorable steric effects of the C=O π-system in the ortho position.

Hammett correlation

The rate of the reaction is enhanced by the electron donating power of the group in the meta position of the phenol, as shown in Table IV-3. The linear correlation between the rate constants and the Hammett substituent constant σ_m (Figure IV-6) indicates that all the phenols react with CrO^{2+} by the same mechanism. The negative value of the reaction constant ($\rho = -1.7 \pm 0.2$) calculated from the slope in Figure IV-6 is further evidence for the formation of the electron-deficient phenoxyl radical intermediate. The ρ value obtained from this work is consistent with values were obtained from oxidation of phenols by one electron in the rate determining step(RDS) yielding phenoxyl radical intermediate for example, $Fe(bpy)_3^{3+}$ has $\rho = -1.4$. [24a] Reactions involve two-elecreon transfer RDS were found, however, to have much higher structure constant values ($\rho > 4$).[24b]

Activation parameters

The enthalpy of activation for the first stage is low (15.2 ± 1.5 kJ mol^{-1}) suggesting the formation of the hydrogen bond between the oxo ligand of CrO^{2+} and the acidic hydrogen of phenol prior to the proton-coupled electron transfer step as shown below.



The idea of hydrogen bond formation is supported by the large kinetic isotope effect on the O-H bond, since the isotopic change here is expected to affect the acidity, the hydrogen bond strength and the O-H bond strength. Also, the slight decrease in the rate constant k_f with increasing acidity supports this suggestion. The relatively large negative entropy of activation ($\Delta S^{\ddagger} = -144 \pm 15$ J mol^{-1} K^{-1}) agrees with the entropies of activation determined for the oxidation of hydroquinone by other oxidants.[23] This is typical of a bimolecular reaction in the rate-controlling step. The decomposition of 4,4'-biphenoquinone has an enthalpy of activation of $\Delta H^{\ddagger} = 46$ ± 4 kJ mol^{-1}. Bond breaking, most probably of the C=C bond between the two rings, may be involved in this stage.

The substituent effect on the stability of 4,4'-biphenoquinones

The decomposition of 4,4'-biphenoquinone under these conditions arises from its self-decomposition (acid-catalyzed) and from a reaction with phenols.[21] Biphenoquinones with electron-donating groups, such as CH_3 or $C(CH_3)_3$, are expected to be less stable than unsubstituted biphenoquinones owing to steric and electronic factors. Also, substituted phenols are less likely to react with substituted biphenoquinones on steric grounds. Thus the presence of a substituent may enhance the self-decomposition of biphenoquinones and reduce the rate of the reaction with phenol. Consistent with this, we find that the disappearance of the substituted biphenoquinones does not depend on the concentration of the phenol.

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13. This procedure, utilizing the combination of several small preparations, resulted in better yields of products than an experiment based on a single preparation on a larger scale. The reason for this is the extreme sensitivity of the yields of CrO^{2+} on the reaction conditions, such as the local concentrations, mixing and volumes of the reagents used.

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CHAPTER V. REACTION OF HYDROGEN PEROXIDE WITH THE OXOCHROMIUM(IV) ION BY HYDIDE TRANSFER

A paper published in *Inorganic Chemistry*[1]

Ahmad M. Al-Ajlouni, Andreja Bakac and James H. Espenson

ABSTRACT

Oxidation of hydrogen peroxide by (pentaaqua)oxochromium(IV), $(H_2O)_5CrO^{2+}$, in aqueous acidic solutions (0.10-1.0 M $HClO_4$) yields the superoxochromium(III) ion, $(H_2O)_5CrOO^{2+}$. The same product is obtained in both the presence and absence of oxygen. In 0.10 M $HClO_4$ the second-order rate constant at 25 °C is 190 ± 10 L mol^{-1} s^{-1} in O_2-saturated solutions, and 172 ± 8 L mol^{-1} s^{-1} in Ar-saturated solutions, independent of acidity and ionic strength in the range 0.10-1.0 M ($HClO_4$/$LiClO_4$). In D_2O as solvent the rate constant is $k_D = 53 \pm 3$ L mol^{-1} s^{-1} resulting in the kinetic isotope effect $k_H/k_D = 3.6$. Experiments in the temperature range 6.8-38.4 °C yielded $\Delta H^‡ = 25 \pm 3$ kJ mol^{-1} and $\Delta S^‡ = -116 \pm 8$ J mol^{-1} K^{-1}. A hydride transfer mechanism is suggested for the oxidation of H_2O_2 by CrO^{2+}. It involves the coordination of H_2O_2 to Cr(IV) prior to the hydride abstraction step. The reaction of $HCrO_4^-$ with H_2O_2 under the same conditions also yields $(H_2O)_5CrOO^{2+}$, which was identified by its characteristic UV spectrum. Possible mechanisms for these reactions are discussed.

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INTRODUCTION

Hydrogen peroxide usually oxidizes low valent metal complexes in one-electron steps. Most such reactions follow the Fenton mechanism, producing hydroxyl radicals as intermediates.[1-4] Indeed, any other mechanism, such as that adopted by the reaction between Cu_{aq}^+ and hydrogen peroxide,[5] is considered exceptional. In any case, an open coordination site for peroxide seems to be a prerequisite.

On the other hand, high valent metal complexes, such as Cr(VI), Fe(IV) and Cu(II), produce bound or free superoxide ions or molecular oxygen.[6-12] Peroxotitanium[13] and peroxovanadium[14] complexes are produced from hydrogen peroxide and oxotitanium(IV) and dioxovanadium(IV) ions.

$$VO_2^+ + H_2O_2 \rightarrow V(O)(O_2)^+ + H_2O \qquad (1)$$

$$V(O)(O_2)^+ + H_2O_2 \rightarrow V(O)(O_2)_2^- + 2H^+ \qquad (2)$$

Heating $V(O)(O_2)^+$ in dilute acid causes the peroxo group to disproportionate, yielding O_2 and vanadium(V), eq 3. In concentrated acid, or upon treatment with the strongly oxidizing hexaaquacobalt(III) ion, VO^{2+} and O_2 are formed, eq 4.[15] Decreasing the pH reduces the extent of peroxide coordination by virtue of pH equilibria, the coordinating forms being HO_2^- and O_2^{2-}.[6a]

$$2\,VO(O_2)^+ \rightarrow 2\,VO_2^+ + O_2 \qquad (3)$$

$$VO(O_2)^+ + Co(H_2O)_6^{3+} \rightarrow VO^{2+} + O_2 + Co(H_2O)_6^{2+} \qquad (4)$$

Oxidation-reduction pathways have been found for other high-valent metals including Fe, Co, Ni, Cu, and Ag.[16-20] With coordination sites available, electron transfer involves M-OOH^{n+} intermediates that rapidly yield O_2 or a superoxide adduct, eq 5 [18,19]. On the other hand, H_2O_2 is oxidized by (bpy)$_2$(py)-RuO^{2+}, which lacks a coordination site, by H-atom abstraction from non-coordinated H_2O_2, eq 6.[26]

$$M^{n+1} + HOO^- \rightarrow M\text{-}OOH^n \rightarrow M^{n-1} + O_2 + H^+ \qquad (5)$$

$$(bpy)_2(py)Ru{=}O^{2+} + H_2O_2 \longrightarrow (bpy)_2(py)RuOH_2^{2+} + O_2 \qquad (6)$$

The reaction of Cr(VI)[6a] with H_2O_2 first forms the oxodiperoxide CrO_5 (K_f ~2 × 10^8 at 25 °C),[11] eq 7. This is followed by the reduction of Cr(VI) by the peroxo group to yield Cr(III) and O_2 via a Cr(III)-peroxyl radical intermediate. [11,12] A relatively stable diperoxochromium(IV) species, prepared from ammonium dichromate and hydrogen peroxide in aqueous ammonia, decomposes in acidic solution to Cr(VI), Cr(III) and O_2.[6a]

$$HCrO_4^- + 2\,H_2O_2 + H^+ \overset{K_f}{\rightleftharpoons} CrO(O_2)_2 + 3\,H_2O \qquad (7)$$

Only one example of the reaction of H_2O_2 with Cr(IV) has been reported. The diperoxo Cr(IV) complex, $Cr(O_2)_2(en)H_2O$ reacts with H_2O_2 to produce the oxodiperoxo Cr(VI) species, $CrO(O_2)_2(en)$ (k= 48 L mol^{-1} s^{-1}).[6c] In this reaction H_2O_2. oxidizes Cr(IV). However, in a different environment the reduction potentials may be reversed and H_2O_2 may reduces Cr(IV) to Cr(III) or Cr(II) . An example of this type of chemistry was encountered in this work. We report the kinetics of oxidation of H_2O_2 by the hydrated oxochromium(IV) ion[22], $(H_2O)_5Cr{=}O^{2+}$. This reaction is particularly striking in that it forms $CrOO^{2+}$ in the presence *and absence* of O_2.

EXPERIMENTAL SECTION

Reaction of H_2O_2 with $(H_2O)_5CrO^{2+}$

Solutions of Cr^{2+} (0.01 M) in dilute perchloric acid were prepared by anaerobic reduction of Cr^{3+} with Zn/Hg. Injection of Cr^{2+} into an acidic aqueous solution saturated with O_2 gives rise to CrO^{2+},[23,24] as described in more detail later. A fresh solution of CrO^{2+} was prepared immediately prior to each experiment. The acid concentration and the ionic strength were both 0.10 M except in experiments designed to study the effects of these variables. The pH was maintained by perchloric acid and the ionic strength by lithium perchlorate. Commercial hydrogen peroxide (30%, Fisher) and $Tl_2(SO_4)_3$ were used without further purification. The kinetic isotope effect was determined by conducting experiments in D_2O and H_2O as solvents. The temperature was controlled in all the experiments by means of a thermostated cell holder connected to a circulating water bath set at the desired temperature.

In a typical kinetic experiment CrO^{2+} was formed *in situ* by injecting 100 μL of 0.01 M Cr^{2+} (final $[Cr^{2+}]$ = 0.2 mM) into a spectrophotometric cell filled with an O_2-saturated (1.26 mM at 25 °C) solution containing at least 0.5 mM H_2O_2. Under these conditions Cr^{2+} and O_2 react to produce ~ 0.04 mM CrO^{2+} (~20% based on total Cr^{2+}). This is then followed by the reaction of interest between H_2O_2 and CrO^{2+}. For anaerobic experiments CrO^{2+} was prepared by injecting Cr^{2+} into a spectrophotometric cell that contained a solution of 2-3 equivalents of air-free Tl^{3+}. Hydrogen peroxide (0.5-1.5 mM) was also present in the solution. In both of these procedures, the reaction with hydrogen peroxide was followed from the build-up of the product, $CrOO^{2+}$. This is the superoxochromium(III) ion,[22] well known from earlier work.[24] The formation of $CrOO^{2+}$ was monitored at 290 nm where its molar absorptivity is 3100 L mol^{-1} cm^{-1}.

The rate constant k_ψ of eq 8 was obtained by fitting the absorbance-time data to the first-order kinetic expression $Abs_t = Abs_\infty - (Abs_0 - Abs_\infty)\exp(-k_\psi t)$, where Abs = absorbance.

$$\frac{d[CrOO^{2+}]}{dt} = k_\psi[CrO^{2+}] \tag{8}$$

Reaction of H_2O_2 with $HCrO_4^-$

The oxidation of H_2O_2 by $HCrO_4^-$ was studied both in the presence and absence of O_2. In each experiment a solution containing 3×10^{-4} M $HCrO_4^-$ was allowed to react with 2.0 mM H_2O_2 in 0.1 M $HClO_4$. The absorption spectra of the products were recorded at 200-400 nm .

RESULTS

Reaction of H_2O_2 with CrO^{2+}

In the presence of O_2. In the presence of O_2 the oxidation of H_2O_2 by CrO^{2+} produces $CrOO^{2+}$ (eq 9) which was detected by its absorption bands at 290 nm (ε = 3100 L mol^{-1} cm^{-1}) and 245 nm (ε = 7000 L mol^{-1} cm^{-1}).[25] When H_2O_2 was in large excess over CrO^{2+}, the rate of formation of $CrOO^{2+}$ followed first-order kinetics, Figure V-1.

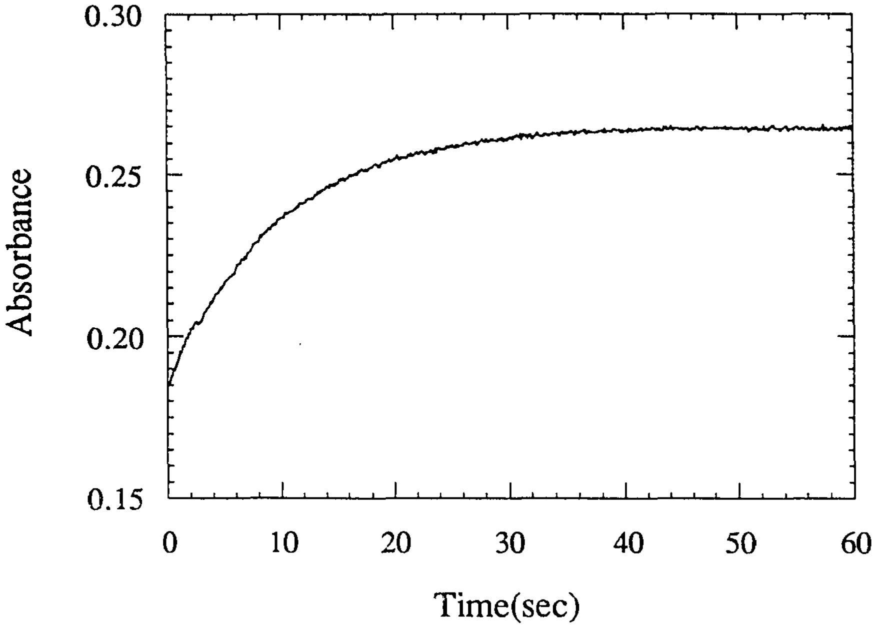


Figure V-1. Absorbance change versus time at 290 nm for formation of CrO_2^{2+} from reaction of H_2O_2 (M) with CrO^{2+} (~ 0.05 M) in 0.10 M perchloric acid at 25 °C.

The pseudo-first-order rate constants, Table V-1, varied linearly with H_2O_2 concentration at constant ionic strength, as expected from eq 9-10.

$$CrO^{2+} + H_2O_2 \xrightarrow{k_9} CrO_2{}^{2+} + H_2O \tag{9}$$

$$-\frac{d[CrO^{2+}]}{dt} = (k_{dec} + k_9[H_2O_2])[CrO^{2+}] \tag{10}$$

A plot of k_ψ vs. $[H_2O_2]$ at 25.0 °C and 0.1 M ionic strength has a slope of $k_9 = 191 \pm 10$ L mol^{-1} s^{-1} in H_2O and 53 ± 3 L mol^{-1} s^{-1} in D_2O, giving $k_H/k_D = 3.6$, as shown in Figure V-2.

Table V-1. The dependence on the peroxide concentration of the pseudo-first-order rate constants (k_ψ) for the oxidation of H_2O_2 and D_2O_2 by CrO^{2+} in 0.1 M $HClO_4$ at 25 °C.

$[H_2O_2]/10^{-4}M$	k_ψ/s^{-1}	$[D_2O_2]/10^{-4}M^{a,b}$	k_ψ/s^{-1}
3.0	0.054[b] (0.058)[c]	5.0	0.041
5.0	0.092[b] (0.098)[c]	8.0	0.051
8.0	0.162[b]	10	0.063
10.0	0.182[b] (0.180)[c]	13	0.083
12.0	0.228[b]		

[a] In D_2O. [b] In the presence of O_2. [c] In the absence of O_2.

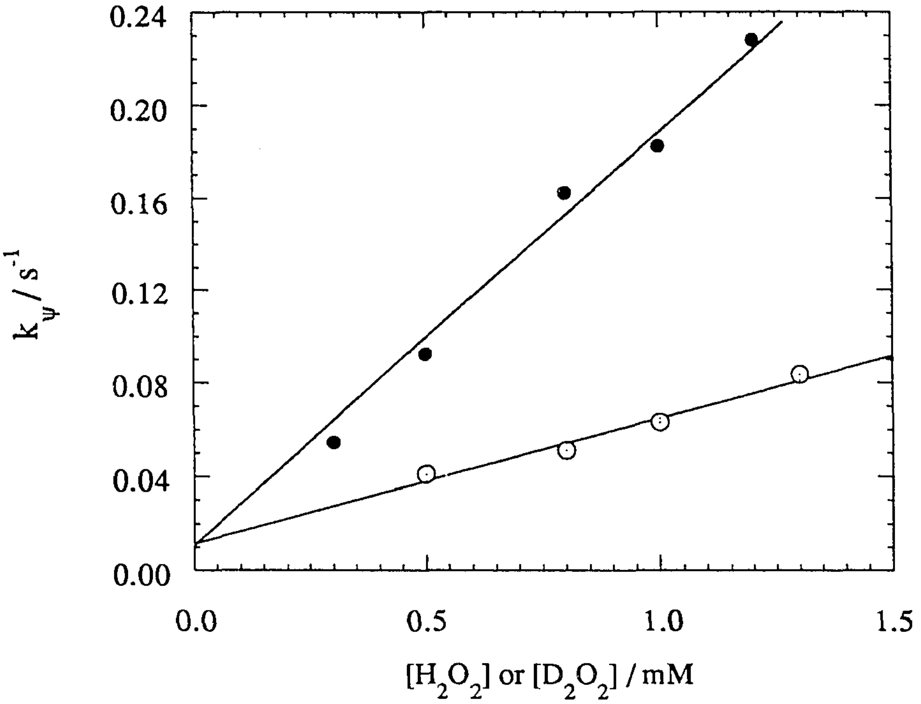


Figure V-2. The dependence of (k_ψ) on the concentration of H_2O_2 in H_2O (filled circles) and D_2O_2 in D_2O (open circles) for the reaction of hydrogen peroxide with CrO^{2+} in 0.10 M perchloric acid at 25 °C.

The ionic strength and acidity effects. The small intercept in these plots corresponds to the decomposition of CrO^{2+}. Analysis of the data on this basis yields k_{dec} = 0.01 - 0.03 s^{-1} at 25.0 °C.[26] The effects of the acidity and ionic strength on k_ψ were studied over the range 0.10 –1.0 M ($HClO_4/LiClO_4$) by changing one parameter at a time. The pseudo-first-order rate constant was found to be independent of $[H^+]$ and proportional to the ionic strength (Figure V-3). Further analysis showed that only k_{dec} increases with ionic strength and that the second-order rate constant k_9 is independent of ionic strength. This is as expected from the charge types involved.

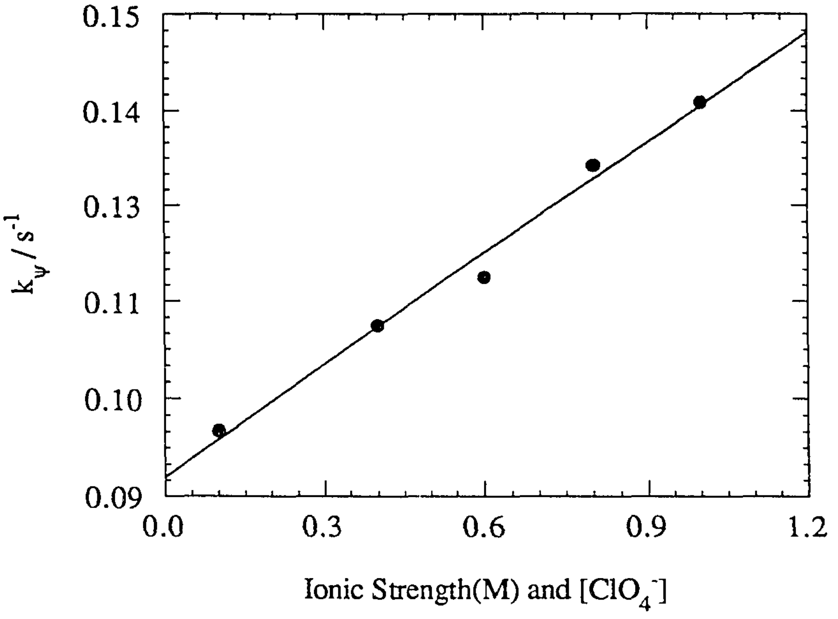


Figure V-3. The ionic strength dependence of the observed rate constants k_ψ for the reaction of H_2O_2 (0.50 mM) with CrO^{2+} in 0.10 M perchloric acid at 25 °C. The sole source of the dependence is k_{dec}, eq 10.

Table V-2. The ionic strength dependence of k_9 and k_{dec} in 0.1 M $HClO_4$ at 25 °C.[a]

Ionic strength/ M ($HClO_4/LiClO_4$)	k_{dec}/ s^{-1}	k_9/ L mol^{-1} s^{-1}
0.1	0.009 ±0.001	191 ±10
0.4	0.018 ±0.001	182 ±13
0.6	0.023 ±0.002	184 ±9
1.0	0.029 ±0.003	188 ±12

[a] The rate law is given by eq 10.

Temperature Dependence Studies. The variation of k_9 with temperature over the range 6.8–38.4 °C, Figure V-4, yielded the activation parameters $\Delta H^{\ddagger} = 25 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -116 \pm 8$ J mol^{-1} K^{-1}, Figure V-5.

In the absence of O_2. Even in the absence of O_2 the reaction of CrO^{2+} with H_2O_2 yielded $CrOO^{2+}$ as in reaction 9. Just as in the presence of O_2, formation of $CrOO^{2+}$ followed pseudo-first-order kinetics when peroxide was in excess. The second-order rate constant was determined to be $k_9 = 172 \pm 7$ L mol^{-1} s^{-1}.

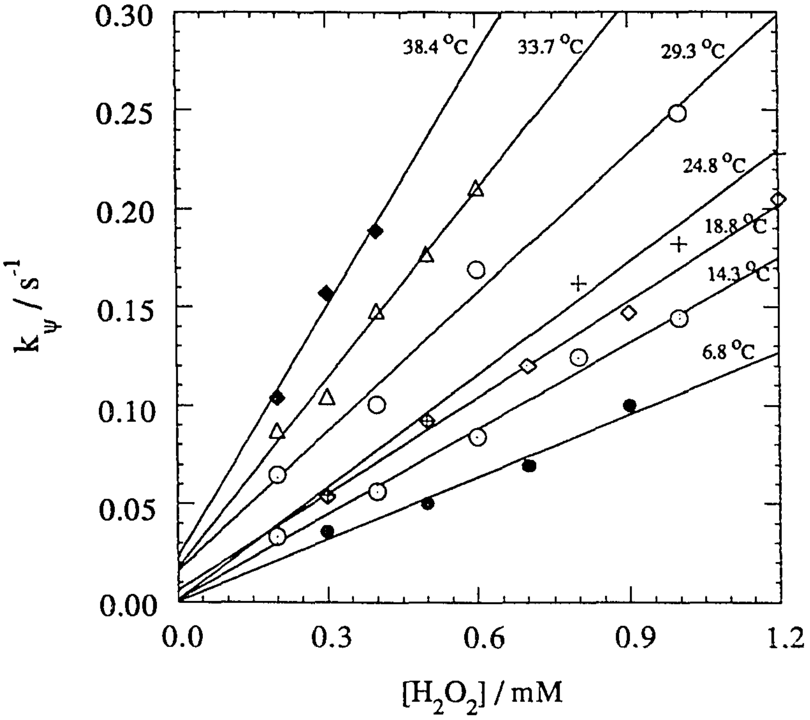


Figure V-4. The dependence of (k_ψ) on the concentration of H_2O_2 for the reaction of hydrogen peroxide with CrO^{2+} in 0.10 M perchloric acid at different tempretures.

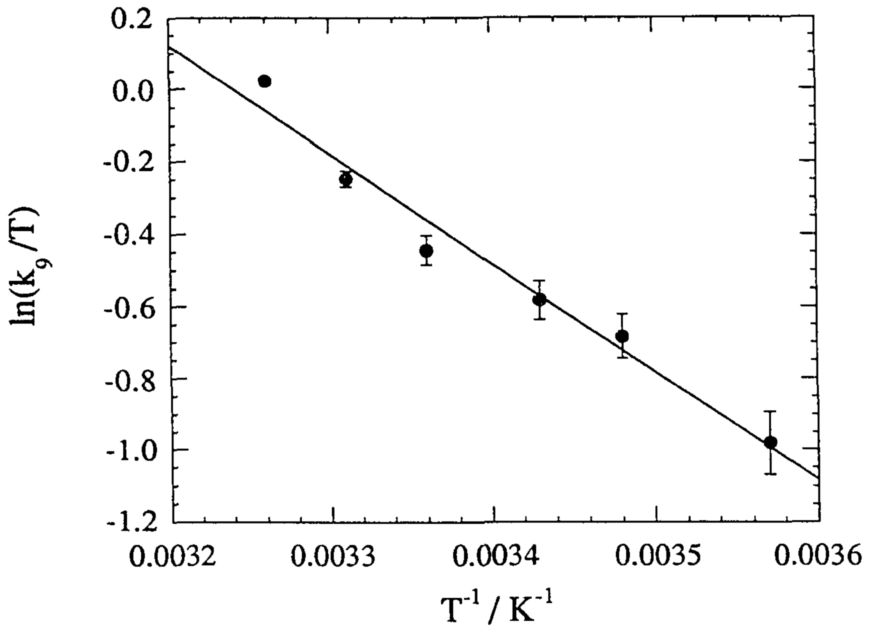


Figure V-5. A plot of $\ln k_9$ against 1/T at 0.1 M $HClO_4$ for the reaction of H_2O_2 with CrO^{2+}.

Reaction of $HCrO_4^-$ with H_2O_2

The oxidation of H_2O_2 by $HCrO_4^-$ in aqueous solution was also carried out in the presence and in the absence of O_2. In both experiments the colorless solution rapidly turned blue, and then faded relatively slowly, owing to the formation and decomposition of oxodiperoxochromium(VI), $OCr(O_2)_2$.[11] The UV spectra recorded during these experiments showed that $CrOO^{2+}$ was formed in both cases.

DISCUSSION

The relative reactivity of CrO^{2+} to $HCrO_4^-$

As an oxidant, CrO^{2+} is more reactive kinetically than $HCrO_4^-$. Whereas it takes several hours to reduce dilute solution of $HCrO_4^-$ by 2 mM methanol in 0.10 M $HClO_4$ at 25 °C, with CrO^{2+} the reaction is complete in 3 min.[23] This is not surprising, in that Cr(IV) is thermodynamically more oxidizing than Cr(VI). Some of the relevant reduction potentials are: Cr(VI)/Cr(V); 0.55 V,[27] Cr(VI)/Cr(III), 1.33 V; Cr(IV)/Cr(III), ca. 1.5-1.7 V. Some of the differences seen in these potentials reflect the major changes in coordination number and geometry that accompany some of the reduction steps but not others.[24]

Mechanistic considerations

The second-order rate constants. The values of the rate constant k_9 under O_2 (191 ± 10 L mol^{-1} s^{-1}) and Ar (172 ± 7 L mol^{-1} s^{-1}) are acceptably close to allow us to conclude that O_2 plays no role in the rate-controlling reaction. These values are the same within the experimental error. The rate constant obtained under argon has the greater systematic error from the substantial background absorbance of both Tl^{3+} and Tl^+, which are present only in the air-free experiments.

Activation parameters. The activation parameters were determined only in the presence of O_2. The large negative value of $\Delta S^‡$, −116 J mol^{-1} K^{-1}, suggests a bimolecular rate-controlling step. The low value of $\Delta H^‡$, 25 kJ mol^{-1}, indicates a mechanism featuring compensating bond breaking and bond making, as proposed below. As a guide to the mechanism of the hydrogen peroxide reaction, we turn to what was previously established for CrO^{2+}. The activation parameters obtained in this study are similar to those obtained in oxidation of alcohols by CrO^{2+} ($\Delta H^{\ddagger}$ = 33–38 kJ mol^{-1}, $-\Delta S^{\ddagger}$ = 95–112 J mol^{-1} K^{-1}). A hydride transfer mechanism was proposed for these reactions. The only exception is cyclobutanol ($\Delta H^{\ddagger}$ = 46 kJ mol^{-1}, $\Delta S^{\ddagger}$ = -61 J mol^{-1} K^{-1}) which reacts by hydrogen atom abstraction *via* a carbon-centered radical intermediate.[24]

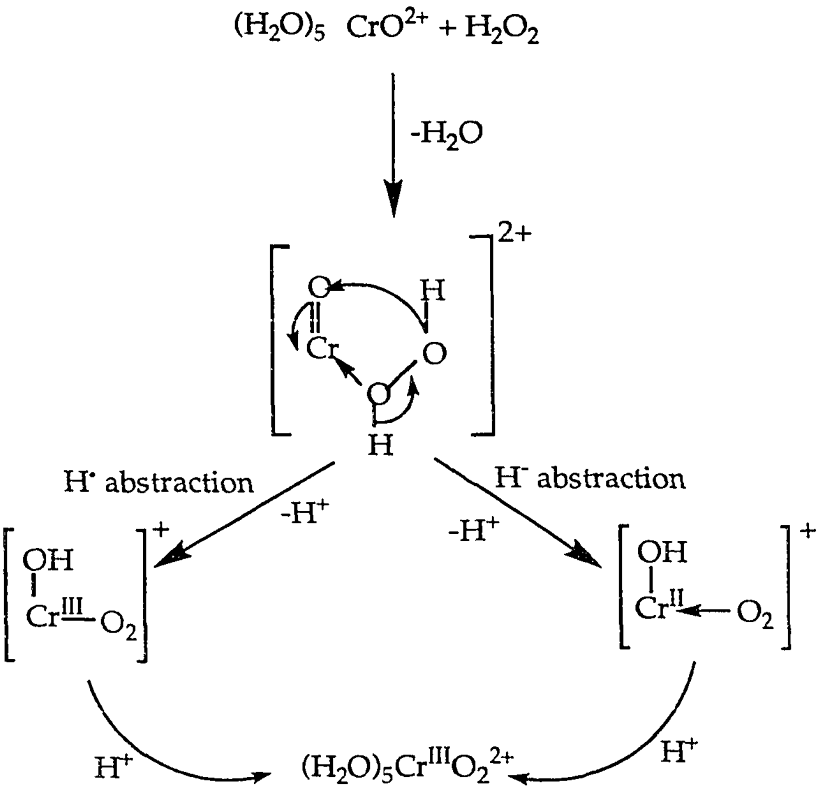
Reduction of CrO^{+2}. The one-electron reduction of CrO^{2+} produces Cr(III), which is inert toward further oxidation or reduction by other reagents present in the solution. On the other hand, the two-electron reduction of CrO^{2+} produces Cr^{2+} which binds O_2 rapidly ($k = 1.6 \times 10^8$ L mol^{-1} s^{-1}) and completely, forming $CrOO^{2+}$.[25] Formation of $CrOO^{2+}$ from Cr^{2+} normally occurs upon reaction with O_2. Our results show that $CrOO^{2+}$ is formed from CrO^{2+} and H_2O_2 both in the presence *and absence* of O_2. From these results we conclude that the source of oxygen in $CrOO^{2+}$ is H_2O_2 and not the free O_2 in solution. Therefore there is no evidence that Cr^{2+} is involved as an intermediate.

Kinetic isotope effect. A further guide to the mechanism is found in the kinetic isotope effect (kie). We suggest that this is a primary kie for D_2O_2 *versus* H_2O_2. The kie need not necessarily arise from D_2O_2, however, in that both the solvent and the coordinated water molecules are also deuterated given the design of the experiment. On the one hand, the kie appears to be far too large to be attributed to the cumulative secondary kie's of water molecules coordinated to the oxochromium(IV) ion. On the other, if it is instead a primary kie of a coordinated water molecule, we have been unable to construct a mechanism that would facilitate the facile conversion of reactants to products. Thus we postulate that the H–OOH bond is indeed centrally involved in the activation step.

The proposed mechanism

The moderate primary kie ($k_H/k_D = 3.6$) supports the proposed oxygen-hydrogen bond breaking in the rate-controlling step. Also, the low value of $\Delta H^{\ddagger}$ is indicative of the coordination of H_2O_2 to chromium prior to hydride (or hydrogen atom) abstraction. The molecular orbital analysis has shown that such coordination would lower the activation energy for hydride abstraction by the oxo ligand.[28]

Scheme V-1. Mechanism of oxidation of H_2O_2 by CrO^{2+}.



A mechanism consistent with all the data is presented in Scheme V-1. A rapidly-formed CrO^{2+}–H_2O_2 complex is proposed to undergo rate-controlling intramolecular hydride (or hydrogen atom) transfer. This yields $(HO)CrO_2^+$, which upon protonation becomes $CrOO^{2+}$. This mechanism agrees with the previous work on catalyzed disproportionation and oxidation of H_2O_2 by high valent transition metal complexes[9,11] and on the oxidation of alcohols by CrO^{2+}.[24]

Formation of $CrOO^{2+}$ from reduction of $HCrO_4^-$

The decomposition of the $OCr(O_2)_2$ compound (i.e., CrO_5) formed in the H_2O_2–$HCrO_4^-$ reaction is not completely understood. It decomposes at low temperatures (≤ 0 °C) in 3-6 M $HClO_4$ to yield the polynuclear peroxochromium(III) species, CrO_2Cr^{4+} and $CrO_2CrO_2Cr^{5+}$.[10] On the other hand, the decomposition of CrO_5 at room temperature was proposed[11] to yield a trivalent chromium(III) complex with a coordinated peroxyl radical. In the notation of these authors it was written as $Cr^{III}(O_2\bullet)^{2+}$. This intermediate reacts rapidly with CrO_5 and finally yields Cr^{3+}, H_2O_2 and O_2, eq 11.

$$Cr^{III}(O_2\bullet)^{2+} + CrO_5 + 4H^+ \longrightarrow 2\,Cr^{3+} + 2\,H_2O_2 + O_2 \qquad (11)$$

Additional experiments on the previously-studied oxidation of H_2O_2 with $HCrO_4^-$ were also carried out in this work under the same conditions used for the H_2O_2–CrO^{2+} reaction. In our hands the reaction yielded $CrOO^{2+}$. This suggests that it and the proposed $Cr^{III}(O_2\bullet)^{2+}$ are identical. Assuming that they are, one wonders why a different, polynuclear product was formed at 0 °C .[11] We considered the possibility that the reported CrO_2Cr^{4+}, formally a dimer of the oxochromium (IV) ion, might dissociate at room temperature into two molecules of CrO^{2+}, eq 12. This would then be followed by reaction 9 and yield $CrOO^{2+}$. According to this interpretation the reaction yields different products at 0 °C and 25 °C because of the temperature effect on the equilibrium of eq 12.

$$CrO_2Cr^{4+} \xrightleftharpoons{K_{eq}} 2CrO^{2+} \qquad (12)$$

As attractive as this proposal may sound, it had to be discarded, because our experiments with the μ-peroxo complex CrO_2Cr^{4+}, prepared as in the published report,[10] does not yield measurable amounts of CrO^{2+} at 25 °C. It is possible that the use of high concentrations of reactants in reference 11 is the reason for the formation of different products.

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22. The formula for the oxochromium(IV) ion is written in several places as the pentaaqua ion, which we believe but have not proved it to be. The superoxochromium(III) ion, $(H_2O)_5CrOO^{2+}$, has been shown to be a chromium(III) species with an η^1–superoxide ion. (We write its formula as shown in this paper, lest the notation $(H_2O)_5CrO_2^{2+}$ be confused for an oxo complex.) Because of the reactions that CrO^{2+}, $CrOOH^{2+}$, and $CrOO^{2+}$ undergo, we *assume* that they are all six-coordinate. The noncomittal

notation CrO^{2+} has been used except in circumstances where the specification of the solvation is helpful.

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26. The range of k_{dec} given represents the value at the concentrations of oxochromium(IV) ion that were used. The decomposition pathway is a minor component under these conditions; thus we have no clear proof that the decomposition pathway has a first-order dependence on $[CrO^{2+}]$. Indeed, there is some indication that the order of the decomposition reaction with respect to $[CrO^{2+}]$ is > 1.

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GENERAL SUMMARY

Epoxidation of Olefins by hydrogen peroxide as catalyzed by methylrhenium trioxide. Methylrhenium trioxide, CH_3ReO_3 (MTO), activates heterolytically hydrogen peroxide through formation of 1:1 and 2:1 peroxide-rhenium adducts, **A** and **B**, respectively. MTO is an efficient and selective catalyst for the epoxidation of olefins by hydrogen peroxide ($k_{cat}/k_{uncat} > 10^5$). It does not catalyze hydride or hydrogen atom abstraction reactions, or involve radical pathways. It can be used over a wide temperature range, below and above room temperature. Unlike other transition metal peroxo complexes, the reactivities of the catalytic species are not inhibited by the presence of basic ligands or solvents, such as alcohols or water. The rates, however, enhance with the solvent polarity and water concentration.

Both, the monoperoxo-Re(VII), **A**, and diperoxo-Re(VII), **B**, species are active with very similar activity. They transfer oxygen atom to olefins in semi-aqueous acidic and organic solvents to yield epoxides. In organic solvents the epoxide undergoes slow ring-opening catalyzed by CH_3ReO_3-H_2O_2 system. In semi-aqueous solutions at pH 1, the epoxide hydrolyzes rapidly to 1,2-diol catalyzed by the acid. The epoxidation reactions are stereospecific. The rate constant for the epoxidation of an olefin by the active species, **A** or **B**, increases with the olefin nucleophilicity and slightly sensitive to the steric hindrance on the olefinic carbons. The general mechanism for the epoxidation of olefins by **A** (or **B**) involves concerted-external nucleophilic attack of the electron-rich olefin on the electropositive peroxy oxygen of **A** (or **B**).

Oxidation of 1,2-diols, phenols and hydrogen peroxide by pentaaquaoxochromium(IV) ion. Pentaaquaoxochromium(IV) ion, CrO^{2+}, is a strong oxidizing agent (Cr(IV)/Cr(III), ca. 1.5-1.7 V). It functions as either a one-electron or a two-electron oxidant. Although CrO^{2+} decomposes to Cr(III) and Cr(VI) species, it stable enough ($t_{1/2}$ = 30 s in 1 M $HClO_4$) to use as a bulk reagent in mechanistic studies. CrO^{2+} oxidizes various 1,2-diols by hydride abstraction. Oxidations of primary and secondary 1,2-diols involve α-hydride abstraction by CrO^{2+} in a rate-determining step. In the case of pinacol (tertiary diol), CrO^{2+} abstracts hydride from the β-carbon. The final products from oxidation of glycol and pinacol by CrO^{2+} in acidic aqueous solutions are formaldehyde and acetone, respectively.

Reaction of a phenol with CrO^{2+} undergoes hydrogen atom abstraction from the O-H group leading to the corresponding phenoxyl radical in a rate-determining step. The radical is rapidly oxidized by the superoxochromium(III) ion, $CrOO^{2+}$, to benzoquinones, or coupled and further oxidized to yield biphenoquinone intermediates. In aqueous acidic solutions these intermediates hydrolysis or react slowly with the phenol to give biphenols.

Oxidation of hydrogen peroxide by CrO^{2+} gives the superoxochromium(III) ion, $CrOO^{2+}$ under aerobic and anaerobic conditions. The mechanism involves a reversible binding of H_2O_2 to CrO^{2+} followed by hydrogen atom or hydride abstraction by CrO^{2+} in a rate-determining step. One-electron (hydrogen atom abstraction) or two-electron (hydride abstraction) oxidation of H_2O_2 by CrO^{2+} are nondistinguishable in this case.

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