1995

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

Ahmad Mahmoud Al-Ajlouni

Iowa State University

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

by

Ahmad Mahmoud Al-Ajlouni

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemistry

Approved:

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F|Charge of Major Work

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For the Major Department

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For the Graduate College

Iowa State University
Ames, Iowa

1995
Kinetics and mechanisms of oxidation of organic and inorganic substrates by transition metal oxo complexes

Ahmad Mahmoud Al-Ajlouni

Major Professor: James H. Espenson
Iowa State University

Epoxidation of olefins by H₂O₂ as catalyzed by methylrhenium trioxide, CH₃ReO₃, was investigated in semi-aqueous and organic solvents. Methylrhenium oxide activates H₂O₂ 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 10⁵ times more reactive than free H₂O₂. 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 peroxo oxygen has been proposed.

The kinetics and the mechanisms of oxidations of 1,2-diols, phenols and H₂O₂ by the pentaaquaoxochromium(IV) ion, CrO₂⁺ were studied in aqueous acidic solutions. Oxidation of vicinal diols with CrO₂⁺ involves a hydride abstraction from the α-position (primary and secondary 1,2-diols) or from the β-position (pinacol). Reactions of phenols with CrO₂⁺ produce the corresponding phenoxyl radicals in a rate-determining-step. The phenoxyl radicals are further oxidized by the superoxochromium(III), CrOO₂⁺, to produce quinones as final products. Oxidation of H₂O₂ with CrO₂⁺ produces CrOO₂⁺ in the presence and in the absence of O₂.
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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 O₂, H₂O₂, alkylperoxide, OX⁻ (X = Cl or I) and PhIO.

For many reasons, H₂O₂ is considered as the best source for an oxygen atom in epoxidation reactions. The amphoteric nature of H₂O₂ makes it more reactive and a better oxidant than O₂. It can be activated by basic and acidic catalysts, such as low- and high-valent transition metals. Heterolytic activation of H₂O₂ 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) H₂O₂ acts as an acid. Upon coordination, the nucleophilicity of the peroxo oxygens increases. Activation of H₂O₂ by high valent transition metal complexes increases the electrophilic character of the peroxo oxygens upon coordination.

Methylrhenium trioxide (MTO), CH₃ReO₃, has been found to activate H₂O₂ through formation of rhenium monoperoxide, A, and bisperoxide, B, having 1:1 and 2:1 ratios of peroxide to Re, respectively, eq 1.
In this work kinetic and mechanistic studies on the epoxidation of styrenes and aliphatic olefins by H₂O₂ 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 CD₃CN and CD₃OD, epoxides can be observed and isolated. The epoxide ring-opening to 1,2-diol is catalyzed by the CH₃ReO₃-H₂O₂ system. In 1:1 CH₃CN/H₂O 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.

\[
\begin{align*}
Cr(\text{VI}) + \text{RH} &\rightarrow Cr(\text{IV}) \quad \text{Cr(IV)} \rightarrow 2 \text{Cr(V)} + \text{RH} \rightarrow 2 \text{Cr(III)} \\
Cr(\text{VI}) + \text{RH} &\rightarrow Cr(\text{IV}) \quad \text{Cr(IV)} + \text{RH} \rightarrow \text{Cr(II)} \quad \text{Cr(II)} \rightarrow \text{Cr(III)} \\
&\quad + \text{Cr(V)} \rightarrow \text{Cr(III)}
\end{align*}
\]

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\text{2+} (here and elsewhere the coordinated water molecules are omitted), under aerobic conditions from reaction of Cr(II) ion with O\text{2}, eq 4, and in the absence of O\text{2}, from the reaction of TlOH\text{2+} with Cr(II) ion, eq 5.

\[
\begin{align*}
\text{Cr}^{2+} + \text{O}_2 &\rightarrow \text{CrOO}^{2+} \rightarrow \text{CrOO}^{2+} \rightarrow 2\text{CrO}^{2+} \\
\text{Cr}^{2+} + \text{TlOH}^{2+} &\rightarrow \text{CrO}^{2+} + \text{Tl}^+ + \text{H}^+
\end{align*}
\]
The pentaaquaoxochromium(IV) ion, CrO$_2^{2+}$, 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$_2^{2+}$. It has been found that CrO$_2^{2+}$ 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$_2^{2+}$ 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$_2$O$_2$ by CrO$_2^{2+}$ 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$_2^{2+}$. Oxidation of pinacol by CrO$_2^{2+}$ 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 phenoxy radical 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$_2^{2+}$ involves hydrogen atom abstraction from the O-H group of the phenol by CrO$_2^{2+}$ in a rate-determining step. Formation of a phenoxy radical from reaction of a phenol with CrO$_2^{2+}$ was directly observed. The final products are benzoquinones (major) and biphenols (minor).
It has been known that \( \text{H}_2\text{O}_2 \) reacts with \( \text{HCrO}_4^- \) to give oxodiperoxochromium(VI), \( \text{Cr(O(O}_2)2 \) in acidic solutions, which then decomposes to \( \text{Cr(III)} \) and \( \text{O}_2 \) via a \( \text{Cr(III)} \)-superoxyl radical intermediate. This \( \text{Cr(III)} \)-superoxyl radical intermediate is the superoxochromium(III), \( \text{CrOO}^{2+} \), which has been recently characterized. This study has shown that \( \text{CrOO}^{2+} \) also forms from reaction of hydrogen peroxide with \( \text{CrO}^{2+} \) in the presence and in the absence of \( \text{O}_2 \).

**Dissertation organization** The dissertation consists of five chapters. The first two present the epoxidation of styrenes and alkyl-substituted alkenes by \( \text{H}_2\text{O}_2 \) catalyzed by \( \text{CH}_3\text{ReO}_3 \). 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 \( \text{H}_2\text{O}_2 \) by \( \text{CrO}^{2+} \). 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, CH₃ReO₃, catalyzes the oxidation of styrenes by hydrogen peroxide. Kinetic studies by three methods were carried out in acidic CH₃CN/H₂O (1:1 v/v) solutions. The catalytically-active species are the mono-peroxide, CH₃Re(O)₂(O₂), A, and the bis-peroxide, CH₃Re(O)(O₂)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 ρ = -0.93 ± 0.05. In CD₃CN, 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 CH₃CN/H₂O, 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), which heterolyze the peroxides by way of an electron deficient peroxometal.\textsuperscript{2c}

Nucleophilic olefins are the most reactive towards metal-peroxo complexes. The oxygen transferred to the olefin comes exclusively from the peroxo group,\textsuperscript{1a,4} and epoxidation is mostly stereoselective.\textsuperscript{5,6} In protic solvents 1,2-diols and β-methoxy alcohols are obtained.\textsuperscript{7} Alkyl substituted styrenes are more prone to oxidative cleavage than are aliphatic olefins.\textsuperscript{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:\textsuperscript{2,12}

2. Olefin binding, followed by insertion into the M-O bond to form a five-membered peroxometallacycle intermediate, eq 1:\textsuperscript{1a}
(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\(_3\)ReO\(_3\), 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\(_2\)S\(^20\) at rates 10\(^4\)–10\(^6\) times those of free hydrogen peroxide.
The catalytic epoxidation of olefins by hydrogen peroxide using CH$_3$ReO$_3$ as a catalyst in tert-butyl alcohol has been reported,\textsuperscript{21} although no detailed kinetic studies were reported. Others have suggested that only B is active in the epoxidation of olefins.\textsuperscript{15} In the oxidations of most other species, however, both A and B react, A usually somewhat faster.\textsuperscript{16-20} Indeed, we have demonstrated that the same holds for styrenes.

Scheme I-1. Formation of CH$_3$Re(O)$_2$(O$_2$), A, and CH$_3$Re(O)(O$_2$)$_2$, B and their reactions with a styrene.

A kinetic study of catalytic epoxidation of a series of styrenes by CH$_3$ReO$_3$–H$_2$O$_2$ has been carried out in acidic CH$_3$CN/H$_2$O 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 H₂O₂ and MTO. These rhenium peroxides react independently with the styrene. Similar catalytic systems have been observed and studied before.¹⁴,¹³ Four different methods have been used to determine the rate constants k₃ and k₄ 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 trioxide¹⁴ was purified first by sublimation, then by recrystallization from CH₂Cl₂/hexane and finally by a second sublimation. Solutions of CH₃ReO₃ in water or in CH₃CN 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% H₂O₂ (Fisher) and standardized daily by iodometric titration.


1H NMR spectra were obtained with a Nicolet 300 MHz spectrometer referenced to (CH₃)₄Si. A Magnum GC/MS spectrometer was used for GC/MS results.

**Kinetics**

The kinetic studies were carried out in CH₃CN/H₂O (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 H₂O₂ (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.

\[
\text{Abs}_t = \text{Abs}_\infty + (\text{Abs}_0 - \text{Abs}_\infty)e^{-k_1t}
\]  

**(2)**

**Products**

Epoxides were formed in CD₃CN without added acid or water. To an NMR tube containing the styrene (0.2 M) and CH₃ReO₃ (0.01 M), 0.25 M H₂O₂ 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$_3$CN) was added dropwise to a flask containing CH$_3$ReO$_3$ (0.1–1 mmol) and H$_2$O$_2$ (12 mmol) in 1:1 CH$_3$CN/H$_2$O 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$_2$Cl$_2$, were dried over MgSO$_4$, and crystallized from CH$_2$Cl$_2$/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$_2$O$_2$ in the presence and in the absence of CH$_3$ReO$_3$ 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 peroxy-rhenium(VII) species, A and B

The equilibrium and rate constants of Scheme I-1 are given in Table I-1. 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$_3$ReO$_3$ with hydrogen peroxide, Scheme I-1$^a$

<table>
<thead>
<tr>
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<th>Forward Rate Constants (L mol$^{-1}$ s$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$k_1 = 32.5^b$</td>
<td>$k_{-1} = 3.0^b$</td>
<td>$K_1 = 10.8^b$</td>
</tr>
<tr>
<td></td>
<td>$k_2 = 1.05^c$</td>
<td>$k_{-2} = 0.008^c$</td>
<td>$K_2 = 136^b$</td>
</tr>
</tbody>
</table>

$^a$In 0.1 M HClO$_4$, CH$_3$CN/H$_2$O (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.

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

The rate equation was derived by means of the steady-state approximation for [A] and [B]. With the mass balance expression, $[\text{Re}]_T = [\text{CH}_3\text{ReO}_3] + [A] + [B]$, the rate of the reaction can be expressed as follows (see Appendix, page 49, for the complete derivation):

$$v = \frac{k_1[\text{Re}]_T[\text{Styrene}][\text{H}_2\text{O}_2]}{k_{-1} + k_3[\text{Styrene}] + k_1[\text{H}_2\text{O}_2] + \left\{ \frac{k_1k_2[\text{H}_2\text{O}_2]^2}{1 + (k_4/k_{-2})[\text{Styrene}]} \right\}} \quad (4)$$
Figure I-1. Typical absorbance-time data at 295 nm for β-methoxystyrene (2.0 mM) with H₂O₂ (50 mM) at 25 °C in 0.1 M HClO₄, CH₃CN/H₂O (1:1 v/v), in the presence and absence of CH₃ReO₃.
Under conditions in which \([A]\) is much greater than \([B]\) (\([H_2O_2] \leq 2.0 \text{ mM}\)) 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.

\[
v = \frac{k_1k_3[Re]_T[Styrene][H_2O_2]}{k_1 + k_3[Styrene] + k_1[H_2O_2]} \tag{5}
\]

**Kinetics with variable \([Re]_T\)**

Values of the initial rate \((v)\) were calculated from experiments in which \([Re]_T\) varied over a range of 0.05–1.0 mM. Hydrogen peroxide and \(\beta\)-methoxystyrene were held constant at 50 mM and 4.0 mM, respectively. As shown in Figure 1-2, the initial rates showed a linear dependence on \([Re]_T\) 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 1a**

The reaction of \(\beta\)-methoxystyrene was studied at constant concentrations of \(\text{CH}_3\text{ReO}_3\) and \(\beta\)-methoxystyrene of 2.0 and 3.0 mM, respectively. To minimize \([B]\), the variable concentration of hydrogen peroxide was kept \(\leq 2.0 \text{ mM}\), 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:

\[
v_i = \frac{1}{b \Delta \epsilon_{\lambda}} \times \frac{\Delta Abs}{\Delta t} \tag{6}
\]
where $\Delta \varepsilon$ is the difference in the molar absorptivities of the reactants and the products at wavelength $\lambda$, and $b$ the optical path length. The dependence of $v_i$ on $[\text{H}_2\text{O}_2]$, 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 $\beta$-methoxystyrene (4.0 mM) by $[\text{H}_2\text{O}_2]$ (50 mM) varies linearly with $[\text{Re}]_T$ in 0.1 M HClO$_4$/CH$_3$CN/H$_2$O (1:1 v/v) at 25°C.
Figure I-3. The initial rate of oxidation of β-methoxystyrene (3.0 mM) with $[\text{H}_2\text{O}_2]$ fits eq 5 at low $[\text{H}_2\text{O}_2]$ (involving only A) at $[\text{Re}]_T = 2.0$ mM.
Initial rates with involvement of A and B, Method Ib

Kinetic measurements were carried out with a constant $[\text{Re}]_T$ of 1.0 mM and a constant concentration of $\beta$-methoxystyrene of 2.0 mM. The concentration of $\text{H}_2\text{O}_2$ 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:

![Graph](image)

**Figure I-4.** Variation of the initial rate of oxidation of $\beta$-methoxystyrene (2.0 mM) with $[\text{H}_2\text{O}_2]$ fits eq 7 under conditions involving both A and B, at $[\text{Re}]_T = 1.0$ mM.
$k_3 = 14.2 \pm 0.5 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_4 = 15.7 \pm 0.75 \text{ L mol}^{-1} \text{ s}^{-1}$, and $k_2 = 0.008 \pm 0.001 \text{ s}^{-1}$. From $K_2$ and $k_2$, we obtained $k_2 = 1.05 \text{ L mol}^{-1} \text{ s}^{-1}$. 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 [\(= \text{CH}_3\text{Re(O)}_2(\text{O}_2), k_3\)] and B [\(= \text{CH}_3\text{Re(O)O}_2(\text{H}_2\text{O}, k_4\)] \(^a\) by various methods \(^b\)

<table>
<thead>
<tr>
<th>Styrene</th>
<th>$k_3 / \text{M}^{-1} \text{s}^{-1}$</th>
<th>$k_4 / \text{M}^{-1} \text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph CH =CH$_2$</td>
<td>0.11 ± 0.02(II)</td>
<td></td>
</tr>
<tr>
<td>PhCH$_3$CH =CH$_2$</td>
<td></td>
<td>0.12 ± 0.01(II)</td>
</tr>
<tr>
<td>H$_3$C=CH =CH$_2$</td>
<td>0.38 ± 0.06(III)</td>
<td>0.19 ± 0.01(III)</td>
</tr>
<tr>
<td>H$_3$C-CH =CH$_2$</td>
<td>0.38 ± 0.02(II)</td>
<td></td>
</tr>
<tr>
<td>H$_3$C=CH$_3$CH =CH$_2$</td>
<td></td>
<td>0.13 ± 0.05(III)</td>
</tr>
</tbody>
</table>
Table I-2. Continued.

<table>
<thead>
<tr>
<th>Styrene</th>
<th>$k_3 / M^{-1} s^{-1}$ (Method)</th>
<th>$k_4 / M^{-1} s^{-1}$ (Method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph-$\ce{C=CH}$</td>
<td>$0.47 \pm 0.02$ (II)</td>
<td></td>
</tr>
<tr>
<td>trans-Ph-$\ce{CH=CH(CH_3)}$</td>
<td>$0.51 \pm 0.07$ (III)</td>
<td>$0.22 \pm 0.02$ (III)</td>
</tr>
<tr>
<td>cis-Ph-$\ce{CH=CH(CH_3)}$</td>
<td>$0.74 \pm 0.08$ (III)</td>
<td>$0.28 \pm 0.01$ (III)</td>
</tr>
<tr>
<td>Ph-$\ce{CH=CH(CH_3)_2}$</td>
<td>$1.00 \pm 0.17$ (III)</td>
<td>$0.70 \pm 0.04$ (III)</td>
</tr>
<tr>
<td>Ph-$\ce{CH=CH-CH_2OH}$</td>
<td>$0.14 \pm 0.01$ (II)</td>
<td></td>
</tr>
<tr>
<td>trans- Ph-$\ce{CH=CH(CH_3)}$</td>
<td>$0.73 \pm 0.07$ (Ib)</td>
<td>$0.40 \pm 0.03$ (Ib)</td>
</tr>
<tr>
<td>trans- H$_3$CO-$\ce{CH=CH}$</td>
<td>$0.67 \pm 0.12$ (III)</td>
<td>$0.63 \pm 0.01$ (II)</td>
</tr>
<tr>
<td>trans- H$_3$CO-$\ce{CH=CH(CH_3)}$</td>
<td>$2.79 \pm 0.05$ (Ib)</td>
<td>$0.80 \pm 0.03$ (Ib)</td>
</tr>
<tr>
<td>Ph-$\ce{CH=CH(OCH_3)}$</td>
<td>$14.2 \pm 0.5$ (Ib)</td>
<td>$15.7 \pm 0.8$ (Ib)</td>
</tr>
</tbody>
</table>

$^a$ In CH$_3$CN /H$_2$O (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 \([\text{H}_2\text{O}_2] > 0.5 \text{ M}\), the absorbance-time values followed first-order kinetics. Indeed, at high \([\text{H}_2\text{O}_2]\), 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. \(k_2[\text{H}_2\text{O}_2] >> k_4[\text{Styrene}]\). 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:

\[
v = k_4[B][\text{Styrene}] = k_4[\text{Re}]_T[\text{Styrene}] = k_\psi[\text{Styrene}]
\]  

(7)

A series of experiments was done with constant \([\text{H}_2\text{O}_2] = 0.5-1 \text{ M}\) and \([\text{Styrene}] = 2-5 \text{ mM}\), with \([\text{Re}]_T\) varied from 0.3–3 mM. The solutions of \(\text{CH}_3\text{ReO}_3\) and \(\text{H}_2\text{O}_2\) were allowed to equilibrate with B for 3–5 min. before adding the styrene. The rate constants \(k_\psi\) from eq 2 varied linearly with \([B] = [\text{Re}]_T\) 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 \([\text{H}_2\text{O}_2]\), 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 \([B] = [\text{Re}]_T\) is valid throughout the reaction. The values of \(K_1\) and \(K_2\) are such that when \([\text{H}_2\text{O}_2] > 0.5 \text{ M}\), \([\text{CH}_3\text{ReO}_3]_{eq}\) and \([A]_{eq}\) are less than 2% of \([B]_{eq}\) (i.e., \([B]_{eq} \sim [\text{Re}]_T\)).

To ensure that \([\text{H}_2\text{O}_2]\) and \([B]_{eq}\) remain essentially constant during the reaction, styrenes were used at ~2–5 mM, very low relative to \([\text{H}_2\text{O}_2]\). Furthermore the experimental observation of pseudo-first-order kinetics under these conditions was confirmed by kinetic simulations using KINSIM.24
Figure 1-5. The pseudo-first-order rate constants for the oxidation of 5.0 mM styrene and 4-vinylstyrene with [H₂O₂] (0.8 M) vary with B (\( \equiv [\text{Re}]_T \)) are fitted by eq 8, \( k_4 = k_4[B] \).

The values of \( k_4 \) obtained by methods I and II are in a good agreement, Table I-2, except for \textit{trans}-4-propenylanisole, \( 0.80 \pm 0.03 \) (I) and \( 1.20 \pm 0.03 \) (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:

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

Helping to attain this condition, for all except β-methoxystyrene, is the finding \( k_1 \gg k_3 \) and \( k_2 > k_4 \). In addition to that, \([H_2O_2]\) was at least ten times more than \([\text{Styrene}]\). 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:

\[ v = (k_3[A]_{eq} + k_4[B]_{eq}) \times [\text{Styrene}] = k_w[\text{Styrene}] \] (9)

The validity of eq 9 in which \([A]_{eq}\) and \([B]_{eq}\) 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 \([\text{Re}]_T\) of 1–2 mM and constant \([\text{Styrene}]\) 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 \([\text{Styrene}]\). As in Method II, the solutions of CH3ReO3 and H2O2 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 \( k_w = k_3[A]_{eq} + k_4[B]_{eq} \). In some cases, where the reactions were relatively slow, the initial reaction rates were calculated from the initial stage only.
The observed rate constants, $k_{\psi}$, were then calculated from the initial rates, $k_{\psi} = \frac{v_i}{[\text{Styrene}]}$. The concentrations of $[A]_{eq}$ and $[B]_{eq}$ for each $[\text{H}_2\text{O}_2]$ and $[\text{Re}]_T$ were calculated from the equilibrium constants, $K_1 = 10.8 \text{ L mol}^{-1}$ and $K_2 = 136 \text{ L mol}^{-1}$. 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, $[A]_{eq}$ and $[B]_{eq}$. An equation with single independent variable can also be used by dividing $k_\psi$ by $[A]_{eq}$ (eq 10) or $[B]_{eq}$.

$$\frac{k_\psi}{[A]_{eq}} = k_3 + k_4 \frac{[B]_{eq}}{[A]_{eq}}$$  \hspace{1cm} (10)

Plots of $k_\psi/[A]_{eq}$ against $[B]_{eq}/[A]_{eq}$ 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 $\beta$-methoxystyrene with $A$ obtained under these two conditions agreed, $k_3 = 14.6 \pm 0.4$ and $14.2 \pm 0.5$ 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 $PR_3$ or $R_2S$. Method III is permissible especially when $k_3 < k_1$ and $k_4 < k_2$, and $[H_2O_2] >> [Styrene]$, which is true except for $\beta$-methoxystyrene.
Figure I-7. A plot of $k_{\text{obs}}/[A]_{\text{eq}}$ against $[B]_{\text{eq}}/[A]_{\text{eq}}$ for the oxidation of 2-methyl-1-phenyl-1-propene (1.0 mM) by A and B at $[\text{Re}]_T = 1.0$ mM, and $[\text{H}_2\text{O}_2]$ 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, $[A]_{\text{eq}}$ and $[B]_{\text{eq}}$, 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:

<table>
<thead>
<tr>
<th>( T/°C )</th>
<th>3.3</th>
<th>8.0</th>
<th>14.5</th>
<th>20.0</th>
<th>25.0</th>
<th>30.0</th>
<th>37.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_4/\text{L mol}^{-1}\text{s}^{-1} )</td>
<td>0.133</td>
<td>0.195</td>
<td>0.273</td>
<td>0.398</td>
<td>0.626</td>
<td>0.75</td>
<td>1.18</td>
</tr>
</tbody>
</table>

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

Products

In CH\(_3\)CN/H\(_2\)O acidic solutions. The reactions of \( \beta \)-methoxystyrene and \textit{trans}-4-propenylanisole with CH\(_3\)ReO\(_3\)-H\(_2\)O\(_2\) in CH\(_3\)CN/H\(_2\)O at 0.1M HClO\(_4\) showed that epoxidation of 1.0 equivalent of styrene required 1.0-1.2 equivalents of H\(_2\)O\(_2\). This slight mismatch is consistent with the known slow decomposition of the catalytic system, CH\(_3\)ReO\(_3\)-H\(_2\)O\(_2\), to HReO\(_4\), CH\(_3\)OH and oxygen.\(^{22}\)

\(^1\text{H}-\text{NMR experiments showed that the initial product from reaction of the styrenes with CH}_3\text{ReO}_3\text{-H}_2\text{O}_2\text{ was the styrene oxide. In the presence of aqueous acid, the epoxide ring opened, yielding 1,2-diol and other minor products. In CH}_3\text{CN/H}_2\text{O, the final product was the 1,2-diol. The catalytic reactions of 0.5 M styrene, 4-methoxystyrene and \textit{trans}-4-propenylanisole with H}_2\text{O}_2\text{ (0.6 M) in the presence of 2–20 mM CH}_3\text{ReO}_3\text{ 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.}\n
\textbf{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 chromatropic acid analysis. $^2^3$ $^1$H NMR experiments showed that the same products also resulted from the reaction of β-methoxystyrene with $m$-chloroperoxybenzoic acid in CD$_3$CN/D$_2$O (1:1 v/v) containing 0.1 M HClO$_4$.

In CD$_3$CN. The stereochemistry of these reactions was studied in CD$_3$CN 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$_3$ReO$_3$-H$_2$O$_2$ system gives the cis epoxide; likewise, trans-β-methylstyrene is converted to the trans epoxide, Figure 1-8.

**Epoxide ring opening**

In CD$_3$CN, in the absence of acid, styrene oxide reacts with CH$_3$ReO$_3$ in both the presence and absence of H$_2$O$_2$ to yield a Re(VII) compound with a bound diol, eq 11. Its $^1$H–NMR spectrum in CD$_3$CN showed six signals: $\delta$ 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$_3$ReO$_3$ and the 1,2-diol.
Figure I-8. $^1$H NMR spectra, in CD$_3$CN, of cis- and trans-$\beta$-methylstyrene epoxide formed from reactions of cis- and trans-$\beta$-methylstyrene, respectively, with H$_2$O$_2$/CH$_3$ReO$_3$ catalytic system. The scale in the bottom is for both $^1$H NMR spectra.
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$_3$ReO$_3$ and not from reaction of phenyl-1,2-ethanediol with CH$_3$ReO$_3$. Under the same conditions, phenyl-1,2-ethanediol (0.10 M) and CH$_3$ReO$_3$ (0.05 M) in CD$_3$CN did not yield any Re-diol adduct even after two days. In CH$_3$CN/H$_2$O (1:1 v/v), 0.10 M HClO$_4$, addition of CH$_3$ReO$_3$ 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$_3$ReO$_3$.

**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$_3$ReO$_3$...
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$_3$ReO$_3$-H$_2$O$_2$ in tert-butyl alcohol catalytic ring opening of epoxides to 1,2-diols also occurs.$^{21}$ In dry organic solvents, such as CH$_2$Cl$_2$ and THF, 1,2-diols react with CH$_3$ReO$_3$ to form Re-diol chelate complexes, eq 12.$^{25}$

\[
\text{CH}_3\text{Re} = \text{O} \quad + \quad \begin{array}{c}
\text{HO} \\
\text{OH} \\
\text{C} \\
\text{C}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{CH}_3 \\
\text{Re} = \text{O} \\
\text{C} \quad \text{O} \\
\text{C}
\end{array}
\]

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 $^1$H-NMR from the reaction of styrene oxide with CH$_3$ReO$_3$ suggest formation of the Re-diol adduct rather than a Re-epoxide adduct. Here the Re-diol chelate complex was observed only in CD$_3$CN in the absence of acid. Under
the conditions for the kinetics, CH₃CN/H₂O, 0.1 M HClO₄, CH₃ReO₃ 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 CH₃ReO₃-H₂O₂. The epoxide ring-opening is catalyzed by the acid (0.10 M HClO₄) rather than by CH₃ReO₃. The reaction of 1,2-diols with Re(VII) is inhibited by water since d⁰ 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 CH₃ReO₃-H₂O₂ increases with the amount of water in the solution, consistent with the higher values of k₁, k₁, k₂, and k₂, in H₂O.¹⁶,¹⁹ There is also an effect on the catalytic steps: the rate constants for trans-4-propenylanisole are k₄ = 1.1 L mol⁻¹ s⁻¹ in 1:1 CH₃CN/H₂O, 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 k₄ is 0.021 L mol⁻¹ s⁻¹ in methanol, compared to 0.11 in 1:1 CH₃CN/H₂O. 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 relative 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 study¹⁷ of the oxidation of anilines by the CH₃ReO₃/H₂O₂ 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 \( \text{Re}^{\text{VI}} \) binds to \( \text{CH}_3, \text{oxo}, \) 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 \( \text{M(O}_2\text{)}_2\text{HMPT} \) (HMPT = hexamethyolphosphoric triamide; \( \text{M} = \text{Mo} \) and \( \text{W} \)) have shown that the diperoxo is more reactive than the monoperoxo when \( \text{M} = \text{W} \). In the case of \( \text{Mo} \) 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 \( \text{trans}-4\text{-propenylanisole} \) 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 \( 4\text{-vinylanisole} \), \( k_3/k_4 = 1.3 \).

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: \( \text{Br}^- \), \( \text{ArNMe}_2 \), \( \text{R}_2\text{S} \), and \( \text{Ar}_3\text{P} \), for example. This might at first seem surprising, in that \( \text{CH}_3\text{ReO}_3 \) is the product of \( A \), whereas \( A \) itself is formed when \( B \) reacts; clearly the two products, \( \text{CH}_3\text{ReO}_3 \) 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 \( \text{H}_2\text{O}_2/\text{H}_2\text{O} \) by which they differ; that is, \( K_1 \) is only 10.6 L mol\(^{-1}\), or \( \Delta G_1^\circ = -6 \text{kJ mol}^{-1} \). Both \( A \) and \( B \) contain \( \text{Re}(\eta^2\text{-O}_2^{2-}) \), 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 \( \sim 150 \) 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, $\sigma^+$ (but not $\sigma$) gave a good correlation, Figure I-9, with $\rho = -0.93 \pm 0.05$. The correlation with $\sigma^+$ implies a

![Graph showing Hammett correlation](image)

**Figure I-9.** The Hammett correlation of $k_d$ for the oxidation of styrenes by B against $\sigma^+$. The reaction constant is $\rho = -0.93$. 
direct interaction through resonance between the substituent and the reaction site. The relatively small negative value of \( \rho \) 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 \( \sigma^+ \). The latter study proposed nucleophilic attack of one of the olefinic carbons \( (\alpha \text{ or } \beta) \) 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\(_3\)ReO\(_3\)-H\(_2\)O\(_2\) we propose for A the mechanism diagrammed in Scheme 1-2.

**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. 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.

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 $-106 \text{ J mol}^{-1} \text{ K}^{-1}$ 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). An allyl alcohol binds the metal through its OH group, 5, before oxygen transfer. In addition, this binding leads to selective epoxidations.
Our results for cinnamyl alcohol and \textit{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 \textit{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$_2$OH. 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$_3$ReO$_3$/H$_2$O$_2$, however, the reactivity increases with the [H$_2$O] present in the solutions.
The substituents effects on the C-C bond cleavage

Expoxides are the initial products from these reactions. Expoxides 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:

\[
\begin{align*}
\text{PhCH(OCH_3)OCH_3} + \text{H}^+ \rightarrow & \text{PhCH(OCH_3)OH} + \\
& \text{PhCH(OCH_3)OCH_3} + \\
& \text{H}_2\text{O} \rightarrow & \text{HCHO} + \text{CH}_3\text{OH} + \text{H}_2\text{O}.
\end{align*}
\]

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. In the presence of basic ligands, such as pyridines, only the epoxide is formed at 25 °C in
almost quantitative yield. In the absence of acid, using only CD$_3$CN as solvent, the epoxide was detected by $^1$H NMR. It reacted slowly with the water introduced with the 30% H$_2$O$_2$ 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 or proceed by nucleophilic attack of one of the olefinic carbon atoms on the peroxo oxygen, as in the third mechanism, are partially or completely nonstereospecific. The radical mechanism has been proposed for epoxidation of allyl alcohols by V(O)(O$_2$)(pic)(H$_2$O)$_2$.1b

CONCLUSION

Epoxidation rates catalyzed by d$^0$ early transition element peroxo complexes increase in the following, Ti(IV) < V(V) < Mo(VI). Tungsten(VI) complexes are the best, but water or a polar solvent retards the reaction. Rhenium(VII) may be the most active catalyst among these d$^0$ early transition metals. Herrmann et al have claimed that CH$_3$ReO$_3$ is the best catalyst for epoxidation of olefins by H$_2$O$_2$; they state: "Among the epoxidation catalysts, only Groves' manganese/porphyrin systems can successfully compete with CH$_3$ReO$_3$ in terms of yields and turnover numbers (TON)." The sources of oxygen in these reactions, however, are PhIO, KHSO$_5$ or very high [H$_2$O$_2$] (> 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.\textsuperscript{2} Furthermore, non-selective catalysts, such as (Por)M=O; M = Fe\textsuperscript{3,30} or Mn\textsuperscript{2,31} lead to further oxidation of the epoxides by C–C bond cleavage and hydride or hydrogen atom abstraction pathways. Although the CH\textsubscript{3}ReO\textsubscript{3}–H\textsubscript{2}O\textsubscript{2} catalyst decomposes slowly under certain conditions,\textsuperscript{32} CH\textsubscript{3}ReO\textsubscript{3} is a good catalyst for epoxidation of olefins. It is easy to prepare and handle, soluble and active in H\textsubscript{2}O and most organic solvents. Methylrhenium trioxide activates H\textsubscript{2}O\textsubscript{2} heterolytically and achieves high reactivity ($k_{\text{cat}}/k_{\text{uncat}} \sim 10^5$) 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\textsubscript{3}ReO\textsubscript{3} can be used, efficiently, over a wide temperature range, below and above room temperature.

REFERENCES


32. Methylrhenium trioxide in the presence of low $[\text{H}_2\text{O}_2]$ ($[\text{H}_2\text{O}_2]/[\text{CH}_3\text{ReO}_3] < 10$) decomposes slowly. Its stability increases with increasing $[\text{H}_2\text{O}_2]$. The product seems inactive compared with A and B.
APPENDIX: DERIVATION OF THE RATE LAW FOR REACTIONS OF A STYRENE WITH A AND B

\[
\begin{align*}
\text{rate} &= -\frac{d[\text{St}]}{dt} = (k_3[A] + k_4[B]) [\text{St}] \\
\text{Steady state approximation on } B \text{ and } A :- \\
\frac{d[B]}{dt} &= k_2[H_2O_2][A] - k_2[B] - k_4[B][\text{St}] = 0 \quad (1) \\
[B] &= \frac{k_2[H_2O_2][A]}{k_2 + k_4[\text{St}]} \quad (2) \\
\frac{d[A]}{dt} &= k_1[H_2O_2][\text{Re}] + k_2[B] + k_4[B][\text{St}] - k_1[A] - k_2[H_2O_2][A] - k_3[A][\text{St}] = 0 \quad (3) \\
- \text{ Add eq 1 to eq 3 :-} \\
\frac{d[A]}{dt} - \frac{d[B]}{dt} &= k_1[H_2O_2][\text{Re}] - k_1[A] - k_3[A][\text{St}] = 0 \quad (4) \\
- \text{ The mass balance of the catalyst :-} \\
[\text{Re}] &= [\text{Re}]_T - [A] - [B]
\end{align*}
\]
- Substitute [B] from eq 2 into eq 5:

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

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

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

- \([A]_{ss}\) from eq 7:

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

- and \([B]_{ss}\) from eq 2 and eq 8:

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

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

\[
\text{rate} = \frac{k_1[H_2O_2][\text{Re}]_T[\text{St}]\left\{ k_3 + \frac{k_2k_4[H_2O_2]}{k_{-2} + k_4[\text{St}]} \right\}}{k_{-1} + k_3[\text{St}] + k_1[H_2O_2] + \frac{k_1k_2[H_2O_2]^2}{k_{-2} + k_4[\text{St}]}} \tag{10}
\]
CHAPTER II. KINETICS AND MECHANISM OF THE EPOXIDATION OF ALKENES BY H₂O₂, CATALYZED BY METHYLRENETHIUM 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 H₂O₂ as catalyzed by methylrhenium trioxide, CH₃ReO₃ (MTO), were carried out in 1:1 CH₃CN/H₂O at pH 1 and in methanol. Reactions of alkenes with the bis-peroxide, CH₃Re(O)(O₂)₂, B, were studied by ¹H NMR (in methanol-d₄), thermometric and spectrophotometric (in CH₃CN/H₂O) techniques. The epoxidation reactions in CD₃OD (or CH₃OH) are about one order of magnitude slower than in CH₃CN/H₂O 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 peroxo oxygen of B.
INTRODUCTION

Epoxides are useful intermediates for the preparation of a wide variety of products. The epoxide ring is highly reactive and may be ring-opened with different nucleophilic and electrophilic reactants. 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. The reaction of epoxides with alcohols provides glycol ethers, used as polar solvents.

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. 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. The electrophilic character of H\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{2} some of these species, such as Ti\textsuperscript{IV} and V\textsuperscript{V}, catalytically decompose H\textsubscript{2}O\textsubscript{2}. Mo\textsuperscript{VI} and W\textsuperscript{VI} complexes have been reported as the best catalysts among these. Heterolytic activation of H\textsubscript{2}O\textsubscript{2} by early transition metal complexes to achieve high reactivity and selective oxygen transfer has posed a challenge.

Methylrhenium trioxide, CH\textsubscript{3}ReO\textsubscript{3} (MTO), activates H\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{2} in semi-aqueous and organic solvents, such as alcohols, at low and moderately high temperatures with very high activity and
Recent studies on olefin epoxidation by H$_2$O$_2$/MTO catalytic system in tert-butanol have suggested that only the bis-peroxide, B, is active toward epoxidation of olefins.

Both peroxo species A and B are active toward oxygen transfer to other organic and inorganic substrates, such as anilines, PR$_3$, R$_2$S, Br$^-$ and Cl$^-$.Recently, 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. 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.

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.
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.\textsuperscript{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: \textit{NMR} (in methanol-d\textsubscript{4}), \textit{thermometric} and \textit{spectrophotometric} (in 1:1 CH\textsubscript{3}CN-H\textsubscript{2}O 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\textsubscript{3} and methanol-d\textsubscript{4} (Cambridge Isotope Laboratories) were used without further purifications. In semi-aqueous solutions the pH was maintained by HClO\textsubscript{4} stock solutions prepared by diluting 70\% HClO\textsubscript{4} (Fisher).
Methylrhenium trioxide, MTO, was prepared by a recently published method.\textsuperscript{15} It was purified first by sublimation then by recrystallization from CH\textsubscript{2}Cl\textsubscript{2}/hexane and finally by a second sublimation. Solutions of MTO (0.01-0.20 M) were prepared in CD\textsubscript{3}OD (NMR method) or in CH\textsubscript{3}CN (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\textsubscript{4}: 239 nm (ε 1900 L mol\textsuperscript{-1} cm\textsuperscript{-1}) 270 nm (ε 1300 L mol\textsuperscript{-1} cm\textsuperscript{-1}).\textsuperscript{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.** \textsuperscript{1}H NMR spectra were obtained with a VXR 300 MHz spectrometer referenced to (CH\textsubscript{3})\textsubscript{4}Si. The kinetic reactions were carried out in methanol-d\textsubscript{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\textsubscript{2}O\textsubscript{2}] = 0.5 M. The alkene (0.05-0.1 M) and the catalyst (1-50 mM) were of lower concentrations. The \textsuperscript{1}H NMR spectrum was recorded at 2-10 min increments 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.

\[
Y_t = Y_\infty + (Y_0 - Y_\infty) \exp(-k_y t)
\]

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$_3$CN/H$_2$O (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$_2$O$_2$ and the catalyst, MTO, (50-80 mL) and another contains the alkene (10-20 mL) were prepared in 0.1 M HClO$_4$-CH$_3$CN/H$_2$O 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:

$$T_t = T_0 + \Delta T_r + \Delta T_T$$

where $T_0$ is the temperature at time = 0, $\Delta T_r$ is the temperature changes due to the reaction and $\Delta T_T$ 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). Under the above conditions, the changes in temperature due to the reaction, $\Delta T_r$, is also first-order kinetics. So the pseudo-first-order rate constants, $k_{\psi_r}$, 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.
\[ T_t = T_\infty + (T_0 - T_\infty \pm C_T) e^{-k_T t} \pm C_T e^{-k_T t} \]  

**Spectrophotometric method.** The kinetic studies were carried out in 1:1 CH\textsubscript{3}CN/H\textsubscript{2}O 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\textsubscript{2}O\textsubscript{2}] (≥ 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\textsubscript{2}O\textsubscript{2} with β-pinene in methanol and 1:1 CH\textsubscript{3}CN/H\textsubscript{2}O solutions at pH 1 in the absence of the catalyst, MTO, were relatively very slow (k\textsubscript{cat} > 10\textsuperscript{5} k\textsubscript{uncat}), Figure II-1. It was not necessary to correct for the uncatalyzed reactions.
Figure II-1. Absorbance-time curves, at \( \lambda = 215 \) nm, for the reaction of \( \text{H}_2\text{O}_2 \) (0.4 M) with \( \beta \)-pinene (10 mM) in the presence and in the absence of the catalyst, \( \text{CH}_3\text{ReO}_3 \), in methanol at 25 °C.
Scheme II-1. Formation of the monoperoxorhenium(VII) complex, A, and the bisperoxorhenium(VII) complex, B, and their reactions with an olefin.

\[
\begin{align*}
\text{MTO} + \text{H}_2\text{O}_2 & \xrightleftharpoons[k_1]{k_{-1}} \text{A} + \text{H}_2\text{O}_2 \xrightleftharpoons[k_2]{k_{-2}} \text{B} \\
\text{MTO} + \text{olefin} & \xrightarrow{k_3} \text{MTO} + \text{Epoxide} \\
\text{A} + \text{olefin} & \xrightarrow{k_4} \text{A} + \text{Epoxide}
\end{align*}
\]

**Determination of the rate constants for the epoxidation reactions**

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

\[
\nu = \frac{d[\text{epoxide}]}{dt} = (k_3[A] + k_4[B]) [\text{olefin}] \tag{6}
\]

The total catalyst concentration, \([\text{Re}]_T\), is defined by \([\text{Re}]_T = [\text{MTO}] + [\text{A}] + [\text{B}]\). At high \([\text{H}_2\text{O}_2]\) the equilibrium is shifted to the formation of the bis-peroxide species, B. Considering the equilibrium rate constants (\(K_1 = 13\) and \(K_2 = 136\ \text{M}^{-1}\) in 0.1 M \(\text{HClO}_4-\text{CH}_3\text{CN/\text{H}_2\text{O}}\) (1:1 v/v)\),\(^9\) and \(K_1 = 261\) and \(K_2 = 814\ \text{M}^{-1}\) in \(\text{CH}_3\text{OH}\)\(^8\) in which \([\text{H}_2\text{O}_2] \geq 0.3\ \text{M}\), ([MTO] + [A]) < 3% of [B] (i.e. [B] ~ [Re]\(_T\)). To insure that [B] remain essentially constant during the reaction [H\(_2\)O\(_2\)] were at least five times more than the alkene concentration ([alkene] ≤ 0.1 M). Furthermore H\(_2\)O\(_2\) 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:

\[ \nu = k_4[B][\text{alkene}] = k_4[\text{Re}]_T[\text{alkene}] = k_\psi[\text{alkene}] \]  

(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 \([\text{H}_2\text{O}_2]\) was fixed at 0.5 M and so the amount of water introduced with \(\text{H}_2\text{O}_2\) (30% stock) was the same ([\text{H}_2\text{O}] \sim 1.5 \text{ M}, i.e. 2.7\%). Each experiment was also done with constant \([\text{alkene}] = 0.05-0.10 \text{ M}\) and constant \([\text{Re}]_T \sim [\text{B}] = 1 - 50 \text{ mM}\). The changes of the relative intensities of \(^1\text{H} \text{NMR alkene signal(s)} with time showed first-order kinetics, Figure II-2. The pseudo-first-order rate constants, \(k_\psi\), were obtained from fitting the relative intensity-time data to eq 3. The values of \(k_4\), Table II-1, were calculated from \(k_\psi\) 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 \(\text{R}-(+)\)-limonene, 1, by B were determined separately by following the relative intensities of the \(^1\text{H} \text{NMR peaks at 5.4 ppm (H}_a\) or at 4.6-4.8 ppm (H\(_b\) and H\(_c\)), respectively, with time.
The value of $k_\psi$ gave $k_4 = 0.235 \text{ L mol}^{-1} \text{ s}^{-1}$; the mathematics of this situation 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. $k_4 = k_\psi/[\text{Re}]_T = k_i + k_e$. The ratio of the products $[1i]/[1e] = 1.9$ is equal to the ratio of $k_i/k_e$. This measurement was carried out when only ca.

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$_2$O$_2$] = 0.5 M in CD$_3$OD at 25°C. The $^1$H NMR signal intensities were recorded for an olefinic proton of 1-octene at $\delta = 5.6$ ppm and trans-4-octene at $\delta = 5.4$ ppm.
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.

![Chemical reaction diagram]

**Thermometric method.** For each alkene, a series of experiments was done with $[\text{Re}]_T$ ($\sim [\text{B}]$) varied from 0.2-5.0 mM, and with constant $[\text{H}_2\text{O}_2] = 1.0$ M and $[\text{alkene}] = 10$-50 mM. Under these conditions $[\text{B}]$ 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 HClO₄, CH₂CN/H₂O (1:1 v/v) with [H₂O₂] = 1 M and [Re]ₜ = 0.45 and 0.75 mM.
Figure II-4. Variation of the pseudo-first-order rate constants, $k_{\psi}$, for the reaction of cyclohexene (solid circle) and norbornylene (open circle) with $[B] \sim [\text{Re}]_T$ in 0.1 M HClO$_4$, CH$_3$CN/H$_2$O (1:1 v/v). The slopes of the lines are $k_4$, eq 7.

The pseudo-first-order rate constants, $k_{\psi}$, varied linearly with $[\text{Re}]_T \sim [B]$, 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 $\leq 200$ nm. Some alkenes, such as R-(+)-limonene, 1, $\beta$-pinene, 2, and $\alpha$-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, H₂O₂ 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 [H₂O₂] ≥ 0.3 M and [alkene] = 5-20 mM with [Re]₀ (≈ [B]) varied between 0.2-5 mM were carried out in acidic CH₃CN/H₂O solutions. The solutions of H₂O₂ and CH₃ReO₃ 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]₀, Figure II-5. The values of the second-order rate constant, k₄, 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 CD₃OD (NMR method) and in CH₃OH (spectrophotometric method) at 25 °C. The rate constants were:

<table>
<thead>
<tr>
<th></th>
<th>k₄/L mol⁻¹ s⁻¹ in CH₃OH</th>
<th>k₄/L mol⁻¹ s⁻¹ in CD₃OD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>0.021 ± 0.001</td>
<td>0.019 ± 0.002</td>
</tr>
<tr>
<td>β-Pinene</td>
<td>0.38 ± 0.02</td>
<td>0.35 ± 0.01</td>
</tr>
</tbody>
</table>
Figure II-5. Variation of the pseudo-first-order rate constants, $k_p$, with $[B] \sim [\text{Re}]_T$ for the reaction of $\beta$-pinene (5 mM) with $\text{H}_2\text{O}_2$ (0.4 M) in 1:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ at pH 1 and 25 $^\circ$C. The data are fitted to $k_p = k_4[B]$, eq 7.
**Epoxide ring-opening and products**

In methanol-d$_4$. In organic solvents, such as acetonitrile and methanol, $^1$H NMR experiments have shown that reactions of alkenes with $\mathbf{B}$ give epoxides which then react with water introduced with H$_2$O$_2$ (30% stock) or produced during the reaction to yield 1,2-diols, eq 9.

\[
\begin{align*}
\text{\textsuperscript{3}R} & \quad \text{\textsuperscript{4}R} \\
\text{\textsuperscript{3}R} & \quad \text{\textsuperscript{4}R} \\
\end{align*}
\]

In CD$_3$OD, under the kinetic conditions, formation of the epoxide was faster than its hydrolysis to 1,2-diol. Since [H$_2$O] ($\sim 1.5$ 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$_2$O$_2$] = 0.5 M, the pseudo-first-order rate constant of the epoxidation step was $1.34 \times 10^{-3}$ s$^{-1}$. Under the same conditions the pseudo-first-order rate constant of the epoxide-ring opening of trans-4-octene oxide was $1.70 \times 10^{-4}$ 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$_2$O$_2$ and the catalyst.$^7b$

In semi-aqueous. In 1:1 CH$_3$CN/H$_2$O 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 $\text{CH}_3\text{Re(O)(O}_2\text{)}_2$, B, at 25 °C by various methods in two solvents.

<table>
<thead>
<tr>
<th>Olefin</th>
<th>$k_4$/ $\text{L mol}^{-1}\text{s}^{-1}$ (method)$^a$</th>
<th>$k_4$/ $\text{L mol}^{-1}\text{s}^{-1}$ (method)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>0.019 ± 0.001(N)</td>
<td>0.11 ± 0.01(S)</td>
</tr>
<tr>
<td></td>
<td>0.021 ± 0.002(S)</td>
<td></td>
</tr>
<tr>
<td>4-Methoxystyrene</td>
<td></td>
<td>0.62 ± 0.05(T)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.57 ± 0.04(S)</td>
</tr>
<tr>
<td>1-Methylcyclohexene</td>
<td>0.32 ± 0.01(N)</td>
<td>4.20 ± 0.16(T)</td>
</tr>
<tr>
<td>β-Pinene</td>
<td>0.35 ± 0.01(N)</td>
<td>3.63 ± 0.10(T)</td>
</tr>
<tr>
<td></td>
<td>0.34 ± 0.01(S)</td>
<td>3.88 ± 0.20(S)</td>
</tr>
<tr>
<td>α-Pinene</td>
<td></td>
<td>2.21 ± 0.15(S)</td>
</tr>
<tr>
<td>R-(+)-Limonene</td>
<td>0.15 ± 0.013(N)$^c$</td>
<td>2.79 ± 0.13(S)</td>
</tr>
<tr>
<td></td>
<td>0.09 ± 0.006(N)$^d$</td>
<td></td>
</tr>
<tr>
<td>Norbornylene</td>
<td>0.250 ± 0.001(N)</td>
<td>1.88 ± 0.04(T)</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>0.108 ± 0.003(N)</td>
<td>1.06 ± 0.02(T)</td>
</tr>
<tr>
<td>Methylene cyclohexane</td>
<td>0.096 ± 0.001(N)</td>
<td>0.97 ± 0.06(T)</td>
</tr>
<tr>
<td>2,3-Dimethyl-2-butene</td>
<td>1.33 ± 0.03(N)</td>
<td>8.93 ± 0.55(T)</td>
</tr>
<tr>
<td>2-Methyl-2-pentene</td>
<td>0.260 ± 0.007(N)</td>
<td>3.92 ± 0.04(T)</td>
</tr>
<tr>
<td>Olefin</td>
<td>$k_4$ / L mol$^{-1}$ s$^{-1}$ (method)$^a$</td>
<td>$k_4$ / L mol$^{-1}$ s$^{-1}$ (method)$^b$</td>
</tr>
<tr>
<td>----------------------------</td>
<td>------------------------------------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>2-Methyl-1-pentene</td>
<td>0.061 ± 0.001(N)</td>
<td>0.55 ± 0.06(T)</td>
</tr>
<tr>
<td>Cis-3-Hexen-1-ol</td>
<td>0.106 ± 0.008(N)</td>
<td></td>
</tr>
<tr>
<td>Trans-3-Hexen-1ol</td>
<td>0.039 ± 0.001(N)</td>
<td></td>
</tr>
<tr>
<td>Trans-4-Octene</td>
<td>0.048 ± 0.003(N)</td>
<td>0.253 ± 0.003(T)</td>
</tr>
<tr>
<td>1-Octene</td>
<td>0.0126 ± 0.001(N)</td>
<td>0.098 ± 0.021(T)</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>0.0124 ± 0.0002(N)</td>
<td></td>
</tr>
<tr>
<td>3,3-Dimethyl-1-Butene</td>
<td>0.0087 ± 0.0003(N)</td>
<td></td>
</tr>
<tr>
<td>5-Hexen-2-one</td>
<td></td>
<td>0.066 ± 0.003(S)</td>
</tr>
<tr>
<td>4-Hexen-3-one</td>
<td></td>
<td>0.0038 ± 0.0003(S)</td>
</tr>
<tr>
<td>Allyl alcohol</td>
<td>0.0033 ± 0.0002(N)</td>
<td></td>
</tr>
<tr>
<td>Allyl phenyl ether</td>
<td>0.0052 ± 0.0001(N)</td>
<td></td>
</tr>
<tr>
<td>2-Buten-1,2-diol</td>
<td></td>
<td>0.0326 ± 0.0004(S)</td>
</tr>
<tr>
<td>Cis-1-Bromopropene</td>
<td></td>
<td>0.012 ± 0.001(S)</td>
</tr>
<tr>
<td>Trans-1-Bromopropene</td>
<td></td>
<td>0.0051 ± 0.0003(S)</td>
</tr>
</tbody>
</table>
Table 1. continued

<table>
<thead>
<tr>
<th>Olefin</th>
<th>$k_4$ / L mol$^{-1}$s$^{-1}$ (method)$^a$</th>
<th>$k_4$ / L mol$^{-1}$s$^{-1}$ (method)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Chloro-2-methyl-propene</td>
<td>0.0160 ± 0.0005 (N)</td>
<td></td>
</tr>
<tr>
<td>1-Bromo-2-methyl-propene</td>
<td>0.0098 ± 0.0003 (N)</td>
<td></td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>&lt; 0.001 (S)</td>
<td></td>
</tr>
<tr>
<td>1,4-Dicyano-2-butene</td>
<td>&lt; 0.001 (S)</td>
<td></td>
</tr>
<tr>
<td>Acrylnitrile</td>
<td>&lt; 0.001 (S)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ In CD$_3$OD at 25 °C, by NMR method (N) (or spectrophotometric method (S)); $^b$ In CH$_3$CN/H$_2$O (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$_3$ReO$_3$ (MTO) catalyzes oxygen transfer from H$_2$O$_2$ to inorganic and organic substrates, such as PR$_3$, R$_2$S, Br$^-$ and Cl$^-$ $^{9-12}$, (including epoxidation of styrenes)$^6$ much effort was devoted to defining separately the reactivity of A (the monoperoxo-rhenium(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. [H₂O₂] was in large excess relative to [alkene] and [Re]₇.

The advantages of using large excess [H₂O₂] 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, CH₃ReO₃/H₂O₂, is very stable in the presence of high [H₂O₂]. The mono-peroxide, A, which present in significant amount at low [H₂O₂] (< 0.1 M), decomposes irreversibly to CH₃OH and ReO₄⁻, eq. 10.

In the presence of high [H₂O₂], A reacts rapidly with H₂O₂ to give B and does not live long in the solution. Since the decomposition path, as shown in eq 10, increases with [OH⁻], the reaction were carried out in 0.1 M HClO₄ 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 CD₃OD. The rate constant for epoxidation of an olefin by B in CD₃OD or in CH₃OH
were essentially the same. The thermometric and the spectrophotometric methods were performed in 0.1 M HClO₄ - CH₃CN/H₂O (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 CH₃CN/H₂O at pH 1, the enthalpy of activation was determined: ΔH° = 42.8 kJ mol⁻¹. With that, a 0.6 °C increase will cause k₄ 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 CD₃OD (or CH₃OH) is 5-12 times slower than in 0.1 M HClO₄ - CH₃CN/H₂O (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.\textsuperscript{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$_2$OH or CH$_2$OPh, (relative to CH$_2$R) 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 acrylonitrile, 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 $\beta$-Pinene with B was about four-fold faster than reaction of methylenecyclohexane with B. $\beta$-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$_3$OD and CH$_3$CN/H$_2$O, 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

\[
\text{4} \quad \text{1} \quad \text{5}
\]

is about two times less reactive than trisubstituted 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-methyl-1-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.\textsuperscript{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 dimethyldioxirane is about 8 times larger than that of the trans isomer. 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 [H₂O] in the solution. The rate constants for epoxidation of para and meta substituted styrenes by B and dimethyldioxirane were correlated with σ⁺ and gave ρ = -0.92 and -0.90, respectively. Similar kinetic factors run throughout the entire series. Figure II-8 displays a plot of log k₄ (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.
Figure II-7. Correlation of the rate constants for the epoxidation of several olefins by B, in 1:1 CH₃CN/H₂O at pH 1, with those for dimethyldioxirane in acetone.

Mechanistic considerations

In the case of CH₃Re(O)(O₂)₂, B, two major modes of attack are possible:- a) external nucleophilic attack of the olefin on a peroxy oxygen¹⁹ 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
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. 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. In the case of high valent early transition metal peroxo complexes, group IV-VI, such intermediates have never been isolated. 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. Here the reactions are enhanced by the solvent polarity and the concentration of water. Furthermore allyl alcohols are epoxidized more readily by early transition metals peroxo complexes than normal olefins. An allyl alcohol binds the metal through its OH group prior to oxygen transfer. Our results on epoxidation of olefins by B in CH$_3$CN/H$_2$O and CD$_3$OD 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\textsuperscript{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).\textsuperscript{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 peroxo oxygens by different modes of attack leading to different transition states. The findings that cis- and trans-\(\beta\)-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 R2 and R3 (H or alkyl) do not affect the olefin attack.

REFERENCES


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

A paper published in Inorganic Chemistry

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ABSTRACT

Kinetic studies of the oxidation of 1,2-diols by pentaaqua(oxo)-chromium(IV) ion, \((\text{H}_2\text{O})_5\text{Cr}^{IV}=\text{O}^{2+}\), were carried out in dilute aqueous solutions of perchloric acid. These reactions yield the superoxochromium(III), \(\text{CrOO}^{2+}\), providing evidence that the two-electron reduction of \(\text{Cr}^{IV}\text{O}^{2+}\) to \(\text{Cr}^{2+}\) 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 \((k = 3.7 \text{ L mol}^{-1} \text{ s}^{-1})\). The kinetic isotope effect of the O-H hydrogens is negligible, \(k_{\text{H}}/k_{\text{D}} = 0.95-1.3\), whereas that for the C-H hydrogens is substantial, \(k_{\text{H}}/k_{\text{D}} = 3.7-4.8\). A two-equivalent mechanism is proposed, in which \(\text{CrO}^{2+}\) abstracts a hydride ion from an \(\alpha\)-position in the primary and secondary diols and from a \(\beta\)-position in pinacol.

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

\[
\begin{align*}
\text{R}^1\text{C}_1\text{OH} & \quad \xrightarrow{\text{H}^-} \quad \text{R}^1\text{C}_1\text{OH}^+ \\
\text{R}^2 & \quad \xrightarrow{\text{H}^+} \quad \text{R}^2\text{C}_1\text{OH}
\end{align*}
\]

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

\[
\begin{align*}
\text{R}^1\text{C}_1\text{OH} & \quad \xrightarrow{-1e, -H^+} \quad \text{R}^2\text{C} = \text{O} \\
\text{S} & \quad \xrightarrow{\text{Products}} \quad \text{C} = \text{O}
\end{align*}
\]

The limited data on the oxidation of diols7-10 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 O₂ to the corresponding ketone (eq 3).

\[
\begin{align*}
R^\prime & \quad R^\prime \cdot C-OH \\
\xrightarrow{\text{hv or } \Delta} R^\prime & \quad R^\prime \cdot C-O \cdot \\
\quad & \quad R^\prime \cdot C-OH \\
\xrightarrow{-H^+} R^\prime & \quad R^\prime \cdot C-OH \\
\quad & \quad R^\prime \cdot C-OH \\
-\text{H}^+ & \quad \text{Fe}^{\text{III}} \text{or } O_2 \\
R^\prime R^\prime & \quad \text{C}=O
\end{align*}
\]

The pentaaqua(oxo)chromium(IV) ion, \((\text{H}_2\text{O})_5\text{CrO}^{2+}\) (hereafter \(\text{CrO}^{2+}\)), is a powerful and reactive oxidant. It is sufficiently long-lived (\(t_{1/2} = 30 \text{ s in } 1.0 \text{ M HClO}_4 \text{ at } 25 ^\circ \text{C}\)) 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, and for the reaction of \(\text{H}_2\text{O}_2\), by \(\text{CrO}^{2+}\). The oxidation of phenols, however, involves a one-electron path, which leads to the formation of the corresponding phenoxy radical in the rate determining step. As such, the phenols are distinct from all the others.

In this section results from the study of the oxidation of diols by \(\text{CrO}^{2+}\) 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-\textit{d}_4 were used without purification. Pinacol was purified by sublimation under vacuum. The kinetic isotope effect (\textit{kie}) of the O-H bond was determined by conducting experiments in D\textsubscript{2}O and H\textsubscript{2}O. Deuterated pinacol (pinacol-\textit{d}_{12}) was prepared from acetone-\textit{d}_6 by a modification of a literature method.\textsuperscript{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.\textsuperscript{14}

Reactions

All the reactions were carried out in O\textsubscript{2}-saturated solutions. The perchloric acid concentration and the ionic strength (HClO\textsubscript{4} + LiClO\textsubscript{4}) were both 0.10 M except in experiments designed to study the effects of these variables. Solutions of Cr\textsuperscript{2+} (0.01 M) in dilute perchloric acid were prepared by the anaerobic reduction of Cr\textsuperscript{3+} with Zn/Hg. Injection of Cr\textsuperscript{2+} into an acidic aqueous solution saturated with O\textsubscript{2} gives rise
to CrO²⁺. Some CrOO²⁺ was also formed, eq 4-5, but it did not interfere. The saturated solutions of O₂ were prepared by bubbling O₂ through the solution for about 10 minutes. In a typical kinetic experiment CrO²⁺ was formed in situ by injecting 100 µL of 0.01 M Cr²⁺ ([Cr²⁺]final = 0.2 mM) into a 2-cm spectrophotometric cell filled with 5.0 mL of an O₂-saturated solution (1.26 mM at 25 °C) of 1.0-3.0 mM diol (excess). Under these conditions the reaction between Cr²⁺ and O₂ rapidly produced ~0.04 mM CrO²⁺ (~20% based on total Cr²⁺), which then reacted with the diol.

\[
\begin{align*}
\text{Cr(H₂O)₆}^{2+} + O₂ & \quad \text{slow} \quad \rightarrow \quad (H₂O)₅\text{CrOO}^{2+} \\
\text{Cr(H₂O)₆}^{2+} + (H₂O)₅\text{CrO}_₂^{2+} & \quad \text{rapid} \quad \rightarrow \quad (H₂O)₅\text{Cr}^{IV}O^{2+}
\end{align*}
\]

**Kinetic Measurements**

The kinetic data for the oxidation of diols by CrO²⁺ were collected by following the formation of the product, CrOO²⁺, at 290 nm (\(ε=3100 \text{ L mol}^{-1} \text{ cm}^{-1}\)), Figure III-1. The rate constant \(k_w\) of eq 6 was obtained by fitting the absorbance-time data to the first-order kinetic expression \(Abs_t = Abs_\infty + (Abs_0 - Abs_\infty)e^{-k_wt}\), where \(Abs = \text{absorbance.}

\[
\frac{d[\text{CrO}_2^{2+}]}{dt} = k_w[\text{CrO}^{2+}]
\]
Figure III-1. The UV-vis spectrum of the superoxochromium(III), CrO22+, in 0.1 M HClO4 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).

\[
\text{(H}_2\text{O})_5\text{Cr}^{IV}=\text{O}^{2+} + \text{diol} \rightarrow \text{(H}_2\text{O})_5\text{CrOO}^{2+} + \text{aldehydes/ ketones} \quad (7)
\]

Formation of CrOO$^{2+}$ (eq 7) which was detected by its absorption bands at 290 nm ($\varepsilon = 3100 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 245 nm ($\varepsilon = 7000 \text{ L mol}^{-1} \text{ cm}^{-1}$), 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 $k_\psi$ (eq 8) varied linearly with the diol concentration at constant ionic strength and acidity, yielding the second-order rate constants ($k_{\text{diol}}$). The values of the rate constants ($k_{\text{diol}}$) are summarized in Table III-1.

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

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 ($k_{\psi}$) 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.

<table>
<thead>
<tr>
<th>diol / alcohol</th>
<th>k(L mol^{-1} s^{-1})</th>
<th>k_H/k_D</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH_2(OH)CH_2(OH)</td>
<td>33 ±2</td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td>CH_2(OD)CH_2(OD)</td>
<td>28 ±3(^a)</td>
<td>1.2</td>
<td>this work</td>
</tr>
<tr>
<td>CD_2(OH)CD_2(OH)</td>
<td>8.9 ±0.5(^c)</td>
<td>3.7</td>
<td>this work</td>
</tr>
<tr>
<td>cis-1,2-(OH)C_6H_10</td>
<td>30 ±1</td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td>cis-1,2-(OD)C_6H_10</td>
<td>26 ±3(^b)</td>
<td>1.2</td>
<td>this work</td>
</tr>
<tr>
<td>trans-1,2-(OH)C_6H_10</td>
<td>57 ±1</td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td>[(CH_3)_2C(OH)]_2</td>
<td>3.7 ±0.2</td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td>[(CH_3)_2C(OD)]_2</td>
<td>3.9 ±0.7(^b)</td>
<td>0.95</td>
<td>this work</td>
</tr>
<tr>
<td>[(CD_3)_2C(OH)]_2</td>
<td>0.77 ±0.10(^c)</td>
<td>4.8</td>
<td>this work</td>
</tr>
<tr>
<td>CH_3OH</td>
<td>52.2 ±1.4</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>CD_3OH</td>
<td>15.1 ±1.7(^c)</td>
<td>3.5</td>
<td>5</td>
</tr>
<tr>
<td>CH_3CH_2OH</td>
<td>88.4 ±4.4</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>C_6H_5CH_2OH</td>
<td>56.0 ±3.5</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>(CH_3)_2CHOH</td>
<td>12.0 ±0.4</td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>

\(^a\) The rate constants 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 $k_{\text{dec}}$ 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 $k_{\text{dec}}$ (representing the rate of decomposition of CrO$_2^+$, but not necessarily the correct reaction order) with ionic strength, and not to a variation of $k_{\text{diol}}$. 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 $264 \pm 37$ K.
Table III-2. Activation Parameters for the Oxidation of Diols, Methanol and 2-Propanol by CrO^2+ in 0.1 M HClO₄ Solutions.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Activation parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Delta H^+ ) ((kJ,mol^{-1}))</td>
</tr>
<tr>
<td>cis-1,2-(OH)₂C₆H₁₀</td>
<td>43 ±3</td>
</tr>
<tr>
<td>trans-1,2-(OH)₂C₆H₁₀</td>
<td>51 ±5</td>
</tr>
<tr>
<td>(CH₃)₂CHOH</td>
<td>33 ±3²</td>
</tr>
<tr>
<td>[(CH₃)₂C(OH)]₂</td>
<td>57 ±5</td>
</tr>
</tbody>
</table>

² Reference 5.

**Reaction stoichiometry**

According to the expected stoichiometry, \([HCHO]_\infty/[CrO^2+]_0 = 2:1\), eq 9. The reaction of 40 \(\mu\)M CrO\(^2\)+ with 1 mM ethylene glycol yielded 66 \(\mu\)M 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 9.²⁷ A theoretical yield of 70 \(\mu\)M HCHO was calculated for this experiment by use of the program KINSIM.¹⁷
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\textsuperscript{2+}

The oxidation of pinacol by CrO\textsuperscript{2+} in 0.1 M HClO\textsubscript{4} in the presence of O\textsubscript{2} yielded CrOO\textsuperscript{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\textsuperscript{-1} and a slope of 3.7 ± 0.2 L mol\textsuperscript{-1} s\textsuperscript{-1} at 25°C, Figure III-4.

\begin{equation}
\begin{array}{c}
\text{HO} \\
\text{H}_3\text{C} - \text{C} - \text{C} - \text{CH}_3 \\
\text{CH}_3 \\
\text{OH} \\
\end{array}
\xrightarrow{\text{CrO}^2+ / \text{O}_2}
\begin{array}{c}
\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\text{C} = \text{O} \\
\end{array}
+ \text{CrOO}^2+
\end{equation}

(10)

The second-order rate constant is acid-independent in the range 0.1-1.0 M H\textsuperscript{+}. The \textit{kie} on deuteration of OH groups of pinacol (experiments in D\textsubscript{2}O) was again negligible \(k_\text{H}/k_\text{D} = 0.95\). On the other hand the \textit{kie} of the C-H (\(\beta\)) hydrogens, when pinacol-d\textsubscript{12} was oxidized, is significant, \(k_\text{H}/k_\text{D} = 4.8\), as given in Table III-1 and Figure III-4.

DISCUSSION

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

The one-equivalent reduction of CrO\textsuperscript{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\textsuperscript{2+} as a reactive intermediate, eq 11.

\begin{equation}
\begin{array}{c}
\text{(H}_2\text{O})_3\text{Cr}^{IV} = \text{O}^2+ + \text{SH}_2 \\
\end{array}
\xrightarrow{k_s}
\begin{array}{c}
\text{Cr(H}_2\text{O})_6^{2+} + \text{S} \\
\end{array}
\end{equation}

(11)
Figure III-4. Dependence of $k_w$ 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$_2^{2+}$ in 0.1 M HClO$_4$. 
In this work the intermediate Cr\textsuperscript{2+} was trapped by O\textsubscript{2} to yield CrOO\textsuperscript{2+} (eq 4). Therefore the formation of CrOO\textsuperscript{2+} from reduction of CrO\textsuperscript{2+} in the presence of O\textsubscript{2} can be taken as sound evidence for a two-electron mechanism.

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

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

The mechanism

It should be noted that this is exactly opposite to the findings for phenols, where there is no \textit{kie} for C-H bonds, but a marked \textit{kie} for O-H bonds. From this and other evidence, we inferred that phenols react by a one-equivalent mechanism.\textsuperscript{12b} Thus we propose for the diols a mechanism that is similar to the hydride abstractions from primary and secondary alcohols.\textsuperscript{5} This is shown for ethylene glycol and 1,2-cyclohexanediols in Scheme III-1.
Scheme III-1. Mechanism of oxidation of primary and secondary 1,2-diols by CrO$_{2}^{2+}$.

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.\textsuperscript{14} The intermediacy 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.\textsuperscript{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.\textsuperscript{18}

The oxidation of ethylene glycol by Fenton’s reagent involves hydrogen atom abstraction by HO$^{•}$ to yield a carbon-centered radical.\textsuperscript{19} This is then followed by the oxidation of the radical to hydroxyacetaldehyde or by rearrangement and reduction to acetaldehyde, eq 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-cyclohexanediols 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 \textit{trans}-1,2-cyclohexanediol is about twice as large as that for the \textit{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.

\textbf{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 \(k_{\text{ie}}\) on \(\beta\)-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 \(\text{cis-}1,2\)-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, \(\Delta H^\ddagger = 60 \pm 6 \text{ kJ mol}^{-1}\), lies between the values for the oxidation of pinacol by Cr(VI), \(\Delta H^\ddagger = 40.5 \text{ kJ mol}^{-1}\),\(^8\) and Os(VIII), \(\Delta H^\ddagger = 78 \text{ kJ mol}^{-1}\).\(^10\) 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\(_4\).

**\(\alpha\)-versus \(\beta\)-hydride abstraction**

There is a possibility of \(\beta\)-hydride abstraction from primary and secondary diols (or alcohols) by CrO\(^{2+}\) in these reactions. However, many alcohols, such as CH\(_3\)OH and C\(_6\)H\(_5\)CH\(_2\)OH, as shown in Table III-1, have no \(\beta\)-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\(_3\)CH\(_2\)OH and 1,2-diols which have both \(\alpha\)- and \(\beta\)-hydrogens, Table III-1. Finally the isokinetic plot of the activation parameters, \((\Delta H^\ddagger \text{ vs } \Delta S^\ddagger)\) 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.

REFERENCES


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, \((\text{H}_2\text{O})_5\text{CrO}_2^+\), in acidic aqueous solutions yields \(p\)-benzoquinone as a major product. Small amounts of the unstable \(4,4'\)-biphenooquinone 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 \(\text{CrO}_2^+\) 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, \(k_\text{H}/k_\text{D} = 14.7\), on deuteration of the hydroxylic hydrogen. There is, however, no kinetic isotope effect of deuteration of the C-H hydrogen, \(k_\text{H}/k_\text{D} = 1.0\). The rate constants of different meta-substituted phenols follow the Hammett relationship with \(p = -1.7\). The activation parameters are \(\Delta H^\ddagger = 15.2 \pm 1.5\) kJ mol\(^{-1}\) and \(\Delta S^\ddagger = -144 \pm 15\) J mol\(^{-1}\) K\(^{-1}\). We propose a mechanism according to which the phenols are first oxidized by one electron to the corresponding phenoxy radical; this occurs by hydrogen atom abstraction. The superoxochromium(III), \((\text{H}_2\text{O})_5\text{CrO}_2^{2+}\), which is also present in

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solution, then oxidizes the phenoxy 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 $\Delta H^\ddagger = 46 \pm 4 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -129 \pm 11 \text{ J mol}^{-1} \text{K}^{-1}$.

**INTRODUCTION**

Phenols are used as inhibitors of free radical autoxidations because of their facile reaction with alkylperoxyl radicals.\textsuperscript{1} The catalytic and noncatalytic activation of $\text{O}_2$ towards phenols by transition metals has therefore been studied extensively.\textsuperscript{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 phenoxy radical or its carbon-centered isomer.\textsuperscript{4-6}

\[
\text{OH} \quad \xrightarrow{-e^-,-H^+} \quad \text{O}^\cdots \quad \overset{\rightleftharpoons}{\text{H}} \quad \text{OH}
\]

(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 $\text{Mn(acac)}_3$ and $\text{Co(acac)}_3$, react by an outer-sphere mechanism.\textsuperscript{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.\textsuperscript{8} The hydroxoruthenium(III)
complex, \((\text{bpy})_2(\text{py})\text{Ru-OH}^{2+}\), 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. The outer-sphere path leads to the formation of a phenonium cation which then reacts with water to produce hydroquinone.

\[
\begin{align*}
\text{OH} & \quad \text{L}_5\text{Ru}^{\text{III}}\text{-OH}^{2+} & \quad \text{L}_5\text{Ru}^{\text{II}}\text{-OH}_2^{2+} \\
\text{O}^* & \quad \text{L}_5\text{Ru}^{\text{III}}\text{-OH}^{2+} & \quad \text{L}_5\text{Ru}^{\text{II}}\text{-OH}_2^{2+}
\end{align*}
\]

(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 \((\text{bpy})_2(\text{py})\text{Ru}^{\text{IV}}=\text{O}^{2+}\).

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

The chromyl or (pentaaqua)oxochromium(IV) ion, \((\text{H}_2\text{O})_5\text{CrO}^{2+}\), is a strong oxidizing agent. 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 \(\text{PPh}_3\).

The chromyl, \(\text{CrO}^{2+}\), is a flexible oxidant. It presents variety of mechanistic possibilities. It may function as an active species in catalytic reactions involving chromium and \(\text{O}_2\). From the point of view of the mechanistic chemist \(\text{CrO}^{2+}\) 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$_2^{2+}$ 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'-biphenooquinone, 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-butylyphenyl)propyl ammonium chloride, ArOH,
was synthesized by a published method.$^{12}$
The kinetic isotope effect $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ was determined by conducting experiments in $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$. 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 $\text{Cr}^{2+}$ (0.01 M) in dilute perchloric acid were prepared by the anaerobic reduction of $\text{Cr}^{3+}$ with Zn/Hg. In a typical kinetic experiment $\text{CrO}^{2+}$ was formed in situ by injecting 100 $\mu\text{L}$ of 0.01 M $\text{Cr}^{2+}$ into a spectrophotometric cell containing 5.0 mL of an $\text{O}_2$-saturated solution of the phenol. Under these conditions $\text{Cr}^{2+}$ and $\text{O}_2$ react rapidly to produce 0.04 mM $\text{CrO}^{2+}$ (~20% based on total $\text{Cr}^{2+}$), which then reacts with the phenol already present in solution. For anaerobic experiments the $\text{CrO}^{2+}$ was prepared by injecting $\text{Cr}^{2+}$ into a spectrophotometric cell that contained a 2-3 fold excess of air-free $\text{Tl}^{3+}$ 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\textsubscript{2}\textsuperscript{2+} were prepared by mixing Cr\textsuperscript{2+} and excess O\textsubscript{2} as previously described.\textsuperscript{10}

**Products identifications**

Chromium(II), 0.5 mL of 0.01 M, was injected into 10 mL of O\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} that contained 0.2 mM CrO\textsubscript{2}\textsuperscript{2+} and 0.2 mM phenol. The procedure was repeated ten times and all the solutions combined in a separatory funnel.\textsuperscript{13} The organic product(s) were extracted by CH\textsubscript{2}Cl\textsubscript{2} (2 \times 10 mL) and dried over MgSO\textsubscript{4}. Finally, the CH\textsubscript{2}Cl\textsubscript{2} was evaporated at room temperature. The yield of benzoquinone was determined by a spectrophotometric titration with a standard solution of Cr\textsuperscript{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, $\lambda_{\text{max}}$ 292 nm ($\epsilon$ $6.5 \times 10^3$ L mol\textsuperscript{-1} cm\textsuperscript{-1}) and 590 nm ($\epsilon$ $2.4 \times 10^2$ L mol\textsuperscript{-1} cm\textsuperscript{-1}).\textsuperscript{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\textsubscript{3} as solvent and referenced to tetramethylsilane.

**Kinetic measurements**

The kinetic data for the oxidation of phenols by CrO\textsubscript{2}\textsuperscript{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\textsubscript{2}\textsuperscript{2+}. The sequential first-order rate constants were calculated by fitting the kinetic trace to a biexponential function (eq 3).\textsuperscript{15}
\[ \text{Abs}_t - \text{Abs}_\infty = \alpha \exp(-k_f t) + \beta \exp(-k_s t) \]  \hspace{1cm} (3)

where

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

In these expressions \( \varepsilon_A, \varepsilon_I \) and \( \varepsilon_P \) 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, \( \text{i.e.} \varepsilon_A \sim \varepsilon_P \sim 0 \), the expression simplifies to:

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

**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 phenoxy radical ($\lambda_{\text{max}}$ 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.
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. This absorption band is typical for 4,4'-biphenoxyl radical, which is formed by the coupling of phenoxyl radicals followed by oxidation (eq 5). In aqueous solutions this species hydrolyses to other organic products. It also reacts with phenol to produce biphenol.

\[
\begin{align*}
2 \text{H} &\quad \text{[0x]} \\
\text{[0x]} &\quad \text{[0x]}
\end{align*}
\]

4,4'-biphenoxyl radical

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 (\( \varepsilon_{245} \sim 2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1} \)). 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 (\( \lambda_{\text{max}} \sim 390 \text{ nm} \)). The second-order 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\textsuperscript{2+} (~0.04 mM) in 0.1 M HClO\textsubscript{4} at 25 °C.
Figure IV-3. The UV-vis spectrum in H$_2$O/ 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$_2$Cl$_2$. *CDCl$_3$ peak. b) The FT-IR spectrum of the same sample.
The effect of the superoxochromium(III), CrO\textsubscript{2}O\textsuperscript{2+}

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

Kinetics

Build-up and disappearance of biphenooquinone intermediates. The reaction products, p-benzoquinone and 4,4'-biphenooquinone, 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'-biphenooquinone, 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\textsubscript{2}+. Similar absorption changes were observed for the other phenols used in this study. With the phenol in a large excess over CrO\textsubscript{2}+, the rate of the formation (fast stage) of 4,4'-biphenooquinone followed first-order kinetics. The subsequent absorbance decrease (slow stage) was found to depend on the concentration of the phenol RC\textsubscript{6}H\textsubscript{4}OH 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'-Biphenooquinone Intermediates (\(k_s\)).

<table>
<thead>
<tr>
<th>Phenol</th>
<th>(k_f/\text{L mol}^{-1}\text{s}^{-1})</th>
<th>(k_s/10^{-3}\text{ s}^{-1})</th>
<th>(k_f^{\text{H}}k_f^{\text{D}})</th>
<th>(k_s^{\text{H}}/k_s^{\text{D}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_6)H(_5)OH</td>
<td>471(^a)</td>
<td>6.2(^a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_6)H(_5)OD</td>
<td>32(^b)</td>
<td>5.6(^b)</td>
<td>14.7</td>
<td>1.1</td>
</tr>
<tr>
<td>C(_6)D(_5)OH</td>
<td>465(^c)</td>
<td>4.6(^c)</td>
<td>1.0</td>
<td>1.3</td>
</tr>
<tr>
<td>3-CH(_3)-C(_6)H(_4)OH</td>
<td>645(^a)</td>
<td>11(^a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-CH(_3)-C(_6)H(_4)OH</td>
<td>1064(^a)</td>
<td>5.5(^a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-CH(_3)-C(_6)H(_4)OD</td>
<td>63(^b)</td>
<td>3.5(^b)</td>
<td>16.9</td>
<td>1.8</td>
</tr>
<tr>
<td>ArOH(^d)</td>
<td>240(^a)</td>
<td>5.0(^a)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Oxidation of the phenol in H\(_2\)O (0.1 M HClO\(_4\)) at 25 \(^\circ\)C in the presence of O\(_2\) ([CrO\(^{2+}\)]\~0.1 mM). The standard deviation of the rate constants was estimated as \(\leq 5\%\). \(^b\) Oxidation of RC\(_6\)H\(_4\)OD in D\(_2\)O. \(^c\) Oxidation of C\(_6\)D\(_5\)OH in H\(_2\)O. \(^d\) 2-Methyl-2-(4-hydroxyl-3,5-di-\text{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 \(\text{s}^{-1}\), 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.\textsuperscript{11}

**Kinetic isotope effects.** Large kinetic isotope effects ($k_H/k_D = 14.7$ for C$_6$H$_5$OH) were observed upon changing the solvent from H$_2$O to D$_2$O. They relate the rate constants for the reactions of C$_6$H$_5$OH with (H$_2$O)$_5$CrO$_2^+$ in H$_2$O to those for the reactions of C$_6$H$_5$OD with (D$_2$O)$_5$CrO$_2^+$ in D$_2$O. The oxidation of C$_6$D$_5$OH and C$_6$H$_5$OH by (H$_2$O)$_5$CrO$_2^+$ in H$_2$O 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.

<table>
<thead>
<tr>
<th>[HClO$_4$]/M</th>
<th>$k_f$/L mol$^{-1}$ s$^{-1}$</th>
<th>$k_s$/10$^{-3}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>514$^a$</td>
<td>4.1$^a$</td>
</tr>
<tr>
<td>0.06</td>
<td>504$^a$</td>
<td>5.0$^a$</td>
</tr>
<tr>
<td>0.10</td>
<td>471$^a$</td>
<td>6.2$^a$</td>
</tr>
<tr>
<td></td>
<td>635$^b$</td>
<td>11.5$^b$</td>
</tr>
</tbody>
</table>

$^a\mu = 0.10$ M. $^b\mu = 1.0$ 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, \( \log \left( \frac{k_X}{k_H} \right) = \rho \sigma \). The plot of \( \log(k_X/k_H) \) against \( \sigma \) is linear (Figure IV-6), with a slope \( \rho = -1.7 \pm 0.2 \).

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

<table>
<thead>
<tr>
<th>X</th>
<th>( \frac{k_X}{k_H} )</th>
<th>( \sigma^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CH₃</td>
<td>1.37</td>
<td>-0.06</td>
</tr>
<tr>
<td>OCH₃</td>
<td>0.760</td>
<td>0.10</td>
</tr>
<tr>
<td>CO₂H</td>
<td>0.244</td>
<td>0.35</td>
</tr>
<tr>
<td>CF₃</td>
<td>0.145</td>
<td>0.46</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.060</td>
<td>0.71</td>
</tr>
</tbody>
</table>

\( ^a \) 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 \( C₆H₅OH \) by \( CrO^{2+} \) yielded the activation parameters for the two stages. The values for the fast stage are \( \Delta H^\ddagger = 15.2 \pm 1.5 \text{ kJ mol}^{-1} \) and \( \Delta S^\ddagger = -144 \pm 15 \text{ J mol}^{-1} \text{ K}^{-1} \) and for the slow stage \( \Delta H^\ddagger = 46 \pm 4 \text{ kJ mol}^{-1} \) and \( \Delta S^\ddagger = -129 \pm 11 \text{ J mol}^{-1} \text{ K}^{-1} \).
Figure IV-6. A plot of \( \log(k_X/k_H) \) against \( \sigma \) for the reaction of meta substituted phenols with \( \text{CrO}^{2+} \) in 0.1 M \( \text{HClO}_4 \) at 25 °C. The slope \( \rho \) is \(-1.7 \pm 0.2\).
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 phenoxy radical, Scheme IV-1. Clear evidence for such one-electron process is provided by the direct observation of the stable phenoxy radical in the reaction of CrO$_2^+$ with ArOH. The large kinetic isotope effects in the reaction between CrO$_2^+$ and C$_6$H$_5$OH in H$_2$O versus C$_6$H$_5$OD in D$_2$O, ($k_H/k_D = 14.7$), and the absence of a kinetic isotope effect for C$_6$H$_5$OH in H$_2$O versus C$_6$D$_5$OH in H$_2$O, 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)$_2$Ru$^{IV}$=O]$^2^+$. On the other hand, oxidations of phenols by [(py)(bpy)$_2$Ru$^{III}$-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

\[
\text{OH} \quad \text{L}_5\text{Ru}^{III}\text{OH} \quad \rightarrow \quad \text{OH} \quad + \quad \text{L}_5\text{Ru}^{II}\text{OH}_2
\]  

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. 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. The reaction with phenol produces biphenol.
The role of $\text{CrOO}^{2+}$

Most of the three-electron oxidation of phenoxyl radicals to the major product, benzoquinone, seems to be carried out by $\text{CrO}_2^{2+}$, a natural impurity in solutions of $\text{CrO}^{2+}$ prepared from $\text{Cr}^{2+}$ and $\text{O}_2$. The role of $\text{CrO}_2^{2+}$ in the product-forming step(s) of eq 6 is demonstrated clearly by the decrease in the yield of benzoquinone with a decrease in $[\text{CrO}_2^{2+}]$. We infer that the oxidation of the phenoxyl radical by $\text{CrO}_2^{2+}$ is rapid, since the observed rate constants showed no dependence on the $\text{CrO}_2^{2+}$ concentration. In the absence of $\text{CrO}_2^{2+}$ the oxidation of the radical was presumably carried out by $\text{CrO}^{2+}$ itself, and in air-free experiments also by the $\text{Tl}^{3+}$ left over from the $\text{CrO}^{2+}$ preparation step.

\[
\begin{align*}
\text{H} & \text{O} \quad \text{CrO}_2^{2+} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{CrO}_2^{2+} \\
\end{align*}
\]

The oxidation of the phenoxyl radicals by $\text{CrO}_2^{2+}$ probably occurs by the coupling of phenoxyl radicals with $\text{CrO}_2^{2+}$ 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 $\text{CrOO}^{2+}$.
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 \( L_5\text{Co}^{III}O_2 \) \((L_5 = \text{bis}(3-(\text{salicylideneamino})-\text{propyl})\text{methylamine})\).\(^{22}\)

**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 2-benzoquinone in addition to the thermodynamically more stable 4,4'-biphenoquinone and \( p \)-benzoquinone. The UV-visible spectra showed that \( \text{CrO}^{2+} \) yields only the second pair of products. Also, the \( ^1\text{H} \) 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 \( \text{cm}^{-1} \) (\( \text{C} = \text{O} \)) of the same sample are also characteristic of \( p \)-benzoquinone (Figure IV-3). This selectivity of \( \text{CrO}^{2+} \) for the para position of the phenoxyl radical may be caused by the unfavorable steric effects of the \( \text{C} = \text{O} \) \( \pi \)-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 \( \sigma_m \) (Figure IV-6) indicates that all the phenols react with \( \text{CrO}^{2+} \) 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 \( \rho \) 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 phenoxy radical intermediate for example, Fe(bpy)$_3^{3+}$ has $\rho = -1.4$. Reactions involve two-electron transfer RDS were found, however, to have much higher structure constant values ($\rho > 4$).

**Activation parameters**

The enthalpy of activation for the first stage is low ($15.2 \pm 1.5 \text{ kJ mol}^{-1}$) suggesting the formation of the hydrogen bond between the oxo ligand of CrO$_2^{2+}$ and the acidic hydrogen of phenol prior to the proton-coupled electron transfer step as shown below.

![Diagram of hydrogen bond](image)

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 ($\Delta S^\ddagger = -144 \pm 15 \text{ J mol}^{-1} \text{ K}^{-1}$) agrees with the entropies of activation determined for the oxidation of hydroquinone by other oxidants. This is typical of a bimolecular reaction in the rate-controlling step. The decomposition of 4,4'-biphenoquinone has an enthalpy of activation of $\Delta H^\ddagger = 46 \pm 4 \text{ kJ mol}^{-1}$. 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'-biphenolquinones

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

REFERENCES


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.


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

A paper published in Inorganic Chemistry
Ahmad M. Al-Ajlouni, Andreja Bakac and James H. Espenson

ABSTRACT

Oxidation of hydrogen peroxide by (pentaaqua)oxochromium(IV), \((\text{H}_2\text{O})_5\text{CrO}_2^{2+}\), in aqueous acidic solutions (0.10-1.0 M \(\text{HClO}_4\)) yields the superoxochromium(III) ion, \((\text{H}_2\text{O})_5\text{CrOO}^{2+}\). The same product is obtained in both the presence and absence of oxygen. In 0.10 M \(\text{HClO}_4\) the second-order rate constant at 25 °C is 190 ± 10 L mol\(^{-1}\) s\(^{-1}\) in \(\text{O}_2\)-saturated solutions, and 172 ± 8 L mol\(^{-1}\) s\(^{-1}\) in \(\text{Ar}\)-saturated solutions, independent of acidity and ionic strength in the range 0.10-1.0 M \(\text{HClO}_4/\text{LiClO}_4\). In \(\text{D}_2\text{O}\) as solvent the rate constant is \(k_D = 53 ± 3\) 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 \(\Delta H^\ddagger = 25 ± 3\) kJ mol\(^{-1}\) and \(\Delta S^\ddagger = -116 ± 8\) J mol\(^{-1}\) K\(^{-1}\). A hydride transfer mechanism is suggested for the oxidation of \(\text{H}_2\text{O}_2\) by \(\text{CrO}_2^{2+}\). It involves the coordination of \(\text{H}_2\text{O}_2\) to \(\text{Cr(IV)}\) prior to the hydride abstraction step. The reaction of \(\text{HCrO}_4^-\) with \(\text{H}_2\text{O}_2\) under the same conditions also yields \((\text{H}_2\text{O})_5\text{CrOO}^{2+}\), which was identified by its characteristic UV spectrum. Possible mechanisms for these reactions are discussed.

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.

\[
\text{VO}_2^+ + \text{H}_2\text{O}_2 \rightarrow \text{V}(\text{O})(\text{O}_2)^+ + \text{H}_2\text{O} \tag{1}
\]

\[
\text{V}(\text{O})(\text{O}_2)^+ + \text{H}_2\text{O}_2 \rightarrow \text{V}(\text{O})(\text{O}_2)_2^- + 2\text{H}^+ \tag{2}
\]

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\(_2^-\):\(^6\)\(^a\)

\[
2 \text{VO}(\text{O}_2)^+ \rightarrow 2 \text{VO}^2^+ + \text{O}_2 \tag{3}
\]

\[
\text{VO}(\text{O}_2)^+ + \text{Co(H}_2\text{O})_6^{3^+} \rightarrow \text{VO}^2^+ + \text{O}_2 + \text{Co(H}_2\text{O})_6^{2^+} \tag{4}
\]
Oxidation-reduction pathways have been found for other high-valent metals including Fe, Co, Ni, Cu, and Ag. With coordination sites available, electron transfer involves M-OOH$^{n+}$ intermediates that rapidly yield O$_2$ or a superoxide adduct, eq 5. On the other hand, H$_2$O$_2$ is oxidized by (bpy)$_2$(py)-RuO$^{2+}$, which lacks a coordination site, by H-atom abstraction from non-coordinated H$_2$O$_2$, eq 6.

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

$$\text{(bpy)$_2$(py)Ru=O}^{2+} + H_2O_2 \rightarrow \text{(bpy)$_2$(py)RuOH}_2^{2+} + O_2$$ \hspace{1cm} (6)

The reaction of Cr(VI) with H$_2$O$_2$ first forms the oxodiperoxide CrO$_5$ ($K_f \approx 2 \times 10^8$ at 25 °C), eq 7. This is followed by the reduction of Cr(VI) by the peroxy group to yield Cr(III) and O$_2$ via a Cr(III)-peroxyl radical intermediate. 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$_2$.

$$\text{HCrO}_4^- + 2H_2O_2 + H^+ \overset{K_f}{\rightarrow} \text{CrO(O}_2)\text{O}_2 + 3H_2O$$ \hspace{1cm} (7)

Only one example of the reaction of H$_2$O$_2$ with Cr(IV) has been reported. The diperoxo Cr(IV) complex, Cr(O$_2$)$_2$(en)H$_2$O reacts with H$_2$O$_2$ to produce the oxodiperoxo Cr(VI) species, CrO(O$_2$)$_2$(en) ($k = 48$ L mol$^{-1}$ s$^{-1}$). In this reaction H$_2$O$_2$ oxidizes Cr(IV). However, in a different environment the reduction potentials
may be reversed and $\text{H}_2\text{O}_2$ may reduce $\text{Cr(IV)}$ to $\text{Cr(III)}$ or $\text{Cr(II)}$. An example of this type of chemistry was encountered in this work. We report the kinetics of oxidation of $\text{H}_2\text{O}_2$ by the hydrated oxochromium(IV) ion$^{22}$, $(\text{H}_2\text{O})_5\text{Cr}=$O$^{2+}$. This reaction is particularly striking in that it forms $\text{CrOO}^{2+}$ in the presence and absence of $\text{O}_2$.

EXPERIMENTAL SECTION

Reaction of $\text{H}_2\text{O}_2$ with $(\text{H}_2\text{O})_5\text{CrO}^{2+}$

Solutions of $\text{Cr}^{2+}$ (0.01 M) in dilute perchloric acid were prepared by anaerobic reduction of $\text{Cr}^{3+}$ with $\text{Zn/Hg}$. Injection of $\text{Cr}^{2+}$ into an acidic aqueous solution saturated with $\text{O}_2$ gives rise to $\text{CrO}^{2+}$, as described in more detail later. A fresh solution of $\text{CrO}^{2+}$ 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 $\text{Tl}_2(\text{SO}_4)_3$ were used without further purification. The kinetic isotope effect was determined by conducting experiments in $\text{D}_2\text{O}$ and $\text{H}_2\text{O}$ 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 $\text{CrO}^{2+}$ was formed in situ by injecting 100 $\mu$L of 0.01 M $\text{Cr}^{2+}$ (final $[\text{Cr}^{2+}] = 0.2 \text{ mM}$) into a spectrophotometric cell filled with an $\text{O}_2$-saturated (1.26 mM at 25 °C) solution containing at least 0.5 mM $\text{H}_2\text{O}_2$. Under these conditions $\text{Cr}^{2+}$ and $\text{O}_2$ react to produce $\sim 0.04 \text{ mM} \text{CrOO}^{2+} (\sim 20\%$ based on
total Cr\(^{2+}\)). This is then followed by the reaction of interest between H\(_2\)O\(_2\) 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 \(k_w\) of eq 8 was obtained by fitting the absorbance-time data to the first-order kinetic expression \(\text{Abs}_t = \text{Abs}_\infty - (\text{Abs}_0-\text{Abs}_\infty) \exp(-k_w t)\), where Abs = absorbance.

\[
\frac{d[\text{CrOO}^{2+}]}{dt} = k_w[\text{CrO}^{2+}]
\] (8)

**Reaction of H\(_2\)O\(_2\) with HCrO\(_4^-\)**

The oxidation of H\(_2\)O\(_2\) by HCrO\(_4^-\) was studied both in the presence and absence of O\(_2\). In each experiment a solution containing 3 \(\times\) 10\(^{-4}\) M HCrO\(_4^-\) was allowed to react with 2.0 mM H\(_2\)O\(_2\) in 0.1 M HClO\(_4\). The absorption spectra of the products were recorded at 200-400 nm.
RESULTS

Reaction of $\text{H}_2\text{O}_2$ with $\text{CrO}^{2+}$

In the presence of $\text{O}_2$, in the presence of $\text{O}_2$ the oxidation of $\text{H}_2\text{O}_2$ by $\text{CrO}^{2+}$ produces $\text{CrOO}^{2+}$ (eq 9) which was detected by its absorption bands at 290 nm ($\varepsilon = 3100 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 245 nm ($\varepsilon = 7000 \text{ L mol}^{-1} \text{ cm}^{-1}$).\(^{25}\) When $\text{H}_2\text{O}_2$ was in large excess over $\text{CrO}^{2+}$, the rate of formation of $\text{CrOO}^{2+}$ followed first-order kinetics, Figure V-1.

![Figure V-1](image)

**Figure V-1.** Absorbance change versus time at 290 nm for formation of $\text{CrO}_2^{2+}$ from reaction of $\text{H}_2\text{O}_2$ (M) with $\text{CrO}^{2+}$ ($\sim 0.05$ M) in 0.10 M perchloric acid at 25 °C.
The pseudo-first-order rate constants, Table V-1, varied linearly with H₂O₂ concentration at constant ionic strength, as expected from eq 9-10.

\[
\text{CrO}^{2+} + \text{H}_2\text{O}_2 \xrightarrow{k_9} \text{CrO}_2^{2+} + \text{H}_2\text{O} \tag{9}
\]

\[
\frac{-d[\text{CrO}^{2+}]}{dt} = (k_{\text{dec}} + k_9[\text{H}_2\text{O}_2])[\text{CrO}^{2+}] \tag{10}
\]

A plot of \(k_\psi\) vs. [H₂O₂] at 25.0 °C and 0.1 M ionic strength has a slope of \(k_9 = 191 \pm 10 \text{ L mol}^{-1} \text{ s}^{-1}\) in H₂O and \(53 \pm 3 \text{ L mol}^{-1} \text{ s}^{-1}\) in D₂O, 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 (\(k_\psi\)) for the oxidation of H₂O₂ and D₂O₂ by CrO²⁺ in 0.1 M HClO₄ at 25 °C.

<table>
<thead>
<tr>
<th>[H₂O₂]/ 10⁻⁴M</th>
<th>(k_\psi) / s⁻¹</th>
<th>[D₂O₂]/ 10⁻⁴Mᵃᵇ</th>
<th>(k_\psi) / s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>0.054ᵇ</td>
<td>5.0</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td>(0.058)ᶜ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>0.092ᵇ</td>
<td>8.0</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>(0.098)ᶜ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>0.162ᵇ</td>
<td>10</td>
<td>0.063</td>
</tr>
<tr>
<td>10.0</td>
<td>0.182ᵇ</td>
<td>13</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>(0.180)ᶜ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.0</td>
<td>0.228ᵇ</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃ In D₂O. ᵇ In the presence of O₂. ᵇ In the absence of O₂.
Figure V-2. The dependence of $(k_w)$ on the concentration of $\text{H}_2\text{O}_2$ in $\text{H}_2\text{O}$ (filled circles) and $\text{D}_2\text{O}_2$ in $\text{D}_2\text{O}$ (open circles) for the reaction of hydrogen peroxide with $\text{CrO}^{2+}$ 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 $k_{\text{dec}} = 0.01 - 0.03 \text{ s}^{-1}$ at 25.0 °C.\textsuperscript{26} The effects of the acidity and ionic strength on $k_\psi$ 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 $k_{\text{dec}}$ increases with ionic strength and that the second-order rate constant $k_\psi$ 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 $k_\psi$ for the reaction of H$_2$O$_2$ (0.50 mM) with CrO$^{2+}$ in 0.10 M perchloric acid at 25 °C. The sole source of the dependence is $k_{\text{dec}}$, eq 10.
Table V-2. The ionic strength dependence of $k_9$ and $k_{\text{dec}}$ in 0.1 M HClO$_4$ at 25 °C.$^a$

<table>
<thead>
<tr>
<th>Ionic strength/ M (HClO$_4$/LiClO$_4$)</th>
<th>$k_{\text{dec}}$/ s$^{-1}$</th>
<th>$k_9$/ L mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.009 ±0.001</td>
<td>191 ±10</td>
</tr>
<tr>
<td>0.4</td>
<td>0.018 ±0.001</td>
<td>182 ±13</td>
</tr>
<tr>
<td>0.6</td>
<td>0.023 ±0.002</td>
<td>184 ±9</td>
</tr>
<tr>
<td>1.0</td>
<td>0.029 ±0.003</td>
<td>188 ±12</td>
</tr>
</tbody>
</table>

$^a$ 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$_2$O$_2$ 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 $(k_\psi)$ on the concentration of $\text{H}_2\text{O}_2$ for the reaction of hydrogen peroxide with $\text{CrO}^{2+}$ in 0.10 M perchloric acid at different temperatures.
Reaction of HCrO$_4^-$ with H$_2$O$_2$

The oxidation of H$_2$O$_2$ 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 \( \text{CrO}^{2+} \) to \( \text{HCrO}_4^- \)

As an oxidant, \( \text{CrO}^{2+} \) is more reactive kinetically than \( \text{HCrO}_4^- \). Whereas it takes several hours to reduce dilute solution of \( \text{HCrO}_4^- \) by 2 mM methanol in 0.10 M \( \text{HClO}_4 \) at 25 °C, with \( \text{CrO}^{2+} \) the reaction is complete in 3 min.\(^{23}\) This is not surprising, in that \( \text{Cr(IV)} \) is thermodynamically more oxidizing than \( \text{Cr(VI)} \). Some of the relevant reduction potentials are: \( \text{Cr(VI)/Cr(V)} \), 0.55 V,\(^{27}\) \( \text{Cr(VI)/Cr(III)} \), 1.33 V; \( \text{Cr(IV)/Cr(III)} \), 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 \( \text{O}_2 \) (191 ± 10 L mol\(^{-1}\) s\(^{-1}\)) and \( \text{Ar} \) (172 ± 7 L mol\(^{-1}\) s\(^{-1}\)) are acceptably close to allow us to conclude that \( \text{O}_2 \) 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 \( \text{Tl}^{3+} \) and \( \text{Tl}^+ \), which are present only in the air-free experiments.

Activation parameters. The activation parameters were determined only in the presence of \( \text{O}_2 \). The large negative value of \( \Delta S^\ddagger \), \(-116 \ \text{J mol}^{-1} \ \text{K}^{-1} \), suggests a bimolecular rate-controlling step. The low value of \( \Delta H^\ddagger \), 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 \( \text{CrO}^{2+} \). 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$^{2+}$. 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$_2$O$_2$ both in the presence and absence of O$_2$. From these results we conclude that the source of oxygen in CrOO$^{2+}$ is H$_2$O$_2$ 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$_2$O$_2$ versus H$_2$O$_2$. The kie need not necessarily arise from D$_2$O$_2$, 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 \( \text{H}_2\text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \) by \( \text{CrO}^{2+} \).

\[
\text{(H}_2\text{O)}_5 \text{CrO}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{(H}_2\text{O})_5 \text{Cr}^{2+} \text{O}^2+ + \text{H}_2\text{O} + \text{H}_2\text{O}_2
\]
A mechanism consistent with all the data is presented in Scheme V-1. A rapidly-formed CrO\(^{2+}\)-H\(_2\)O\(_2\) 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\(_2\)O\(_2\) 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\(_2\)O\(_2\)-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\(_2\)Cr\(^{4+}\) and CrO\(_2\)CrO\(_2\)Cr\(^{5+}\).\(^10\) 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 peroxy radical. In the notation of these authors it was written as Cr\(^{III}\)(O\(_2\))\(^{2+}\). This intermediate reacts rapidly with CrO\(_5\) and finally yields Cr\(^{3+}\), H\(_2\)O\(_2\) and O\(_2\), eq 11.

\[
\text{Cr}^{III}(\text{O}_2)\text{Cr}^{2+} + \text{CrO}_5 + 4\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 2\text{H}_2\text{O}_2 + \text{O}_2 \quad (11)
\]

Additional experiments on the previously-studied oxidation of H\(_2\)O\(_2\) with HCrO\(_4^−\) were also carried out in this work under the same conditions used for the H\(_2\)O\(_2\)-CrO\(^{2+}\) reaction. In our hands the reaction yielded CrOO\(^2+\). This suggests that it and the proposed Cr\(^{III}(O_2)^{2+}\) 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\(_2\)Cr\(^{4+}\), 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.

\[
\text{CrO}_2\text{Cr}^{4+} \rightleftharpoons K_{\text{eq}} \text{ 2CrO}^{2+}
\]  

(12)

As attractive as this proposal may sound, it had to be discarded, because our experiments with the \(\mu\)-peroxo complex CrO\(_2\)Cr\(^{4+}\), 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.

REFERENCES


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, (H₂O)₅CrO₂⁺, has been shown to be a chromium(III) species with an η¹-superoxide ion. (We write its formula as shown in this paper, lest the notation (H₂O)₅CrO₂⁺ be confused for an oxo complex.) Because of the reactions that CrO²⁺, CrOOH²⁺, and CrOO²⁺ 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.


26. The range of $k_{\text{dec}}$ 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 $> 1$.


GENERAL SUMMARY

Epoxidation of Olefins by hydrogen peroxide as catalyzed by methylrhenium trioxide. Methylrhenium trioxide, CH₃ReO₃ (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 peroxy 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 CH₃ReO₃-H₂O₂ 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 peroxo oxygen of A (or B).
Oxidation of 1,2-diols, phenols and hydrogen peroxide by pentaaqua-oxochromium(IV) ion. Pentaaqua-oxochromium(IV) ion, CrO\(_2^+\), is a strong oxidizing agent (Cr(IV)/Cr\(_{\text{III}}\), ca. 1.5-1.7 V). It functions as either a one-electron or a two-electron oxidant. Although CrO\(_2^+\) decomposes to Cr\(_{\text{III}}\) and Cr\(_{\text{VI}}\) species, it is 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 phenoxy 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 biphensols.

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\(_2\)O\(_2\) 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\(_2\)O\(_2\) by CrO\(_2^+\) are nondistinguishable in this case.
ACKNOWLEDGMENTS

I would like to thank Professor James Espenson and Dr Andreja Bakac for their guidance and encouragement during my graduate career. I am also thankful to the members of my research group for their friendship and for sharing with me their own ideas and useful discussions. I am pleased to acknowledge informative discussion with Professor Walter Trahanovsky.

I would like to acknowledge my family for their support and love which give me direction and hope, and Natalia for her encouragement and help.

I would like to thank Jordan University of Science and Technology for offering me the opportunity to continue my graduate studies to obtain a Ph.D. degree.

The work in chapters I and II was supported by the U. S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences under contract W-7405-Eng-82. The work in chapters III, IV and V was supported by the National Science Foundation under Grant CHE 9007283. Some of the experiments were done with facilities of Ames Laboratory.