REDOX INTERACTIONS BETWEEN Cr(VI) AND SUBSTITUTED PHENOLS: KINETICS, PRODUCTS, AND MECHANISM

Michael Sidney Elovitz
B.S. Columbia University
in the City of New York, NY
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The dissertation "Redox interactions between Cr(VI) and substituted phenols: kinetics, products, and mechanism" by Michael Sidney Elovitz has been examined and approved by the following Examination Committee:

William Fish, Thesis Advisor
Associate Professor

James K. Hurst
Professor

Carl D. Palmer
Assistant Professor

Paul G. Tratnyek
Assistant Professor

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ABSTRACT

Redox Interactions Between Cr(VI) and Substituted Phenols: Kinetics, Products, and Mechanism

Michael Sidney Elovitz, Ph.D.
Oregon Graduate Institute of Science & Technology, 1993
Supervising Professor: William Fish

Redox interactions between Cr(VI) and 14 substituted phenols were investigated under conditions typical of waste mixtures at contaminated sites. Cr(VI) reduction occurred on time scales from minutes to months. The reaction was first-order with respect to concentrations of both Cr(VI) and phenol and the rate increased with solution acidity. The rates at a fixed pH are accurately predicted by an empirical expression,

$$-d[\mathrm{Cr(VI)}]/dt = k_{\mathrm{ArOH}}[\mathrm{Cr(VI)}][\mathrm{ArOH}]$$

where k_{ArOH} is a function of $[\mathrm{H}^+]$. This rate law is useful for estimating the characteristic time scales for Cr(VI) reduction, and is readily incorporated into contaminant transport models.

The mechanisms of Cr(VI)/phenol interactions in aqueous solution were characterized by kinetic analysis and measurements of reaction products and transient intermediates. The proposed mechanism predicts reaction rates over a wide range of solution conditions and is consistent with the observed products. The reaction initiates via a pre-oxidative equilibrium formation of chromate-ester between $\mathrm{HCrO_4^-}$ and undissociated ArOH. Ester intermediates were directly observed. The subsequent rate-limiting redox decomposition of the ester proceeds via an inner-sphere electron transfer. The overall rate dependence on $[H^+]$ can be explained by three parallel redox pathways involving zero (dominant at $pH \geq 5$), one (dominant at $2 < pH < 4$), and two protons (dominant at $pH \leq 2$). The overall rate expression is:

$$\begin{aligned} \text{Rate} &= \{k_0 + k_1[H^+] + k_2[H^+]\}[\text{ester}] \\ &= \{k_0 + k_1[H^+] + k_2[H^+]\}K_e[HCrO_4^-][ArOH] \end{aligned}$$

Reaction rates correlate with phenol half-wave oxidation potentials ($E_{1/2}$) and Hammett-type substituent parameters. Unstable Cr intermediates (Cr(IV) and Cr(V)) were not observed and their suppression by scavengers had no effect on overall rates. Significant oxidation products indicated both one- and two-electron pathways, with the latter predominant. Overall, Cr(VI) did not significantly mineralize the phenols and instead yielded phenols with oxidized substituents, oxygen additions, and many coupled products and polymers some of which resembled congeners of benzofurans and dibenzo-*p*-dioxins.

CHAPTER 1

Introduction

I.A. The Problems of Waste Mixtures

Among the vast array of landfills, dumps, and contaminated sites, few are adequately characterized as single-component systems. Whether legally or illegally dumped, the wastes and by-products of municipal and industrial activities often are complex mixtures of numerous compounds. This is especially true of landfills and industrial contamination sites where wastes from different sources or operations have been dumped together. Even in situations where the disposed waste consists of a single constituent, interactions with naturally occurring compounds in the environment or with other nearby wastes can create complicated mixtures whose behavior can differ markedly from the parent compounds. Consequently, remediation schemes based on the properties of the individual, isolated compounds may be severely inappropriate for the actual waste mixture.

In general, waste mixtures are highly susceptible to biotic and abiotic reactions that can dramatically alter the properties of the parent compounds. Processes including precipitation, sorption, dissolution, neutralization, hydrolysis, and oxidation-reduction (redox) reactions may act individually or, more often, in combination, to alter the physical and chemical nature of the mixture. Because of their dramatic effect on the characteristics of contaminants, redox reactions have received significant attention in recent years. These reactions often are biologically mediated, but abiotic redox reactions are also important. Redox reactions between two components in a waste mixture can create a complicated system of partially and fully oxidized and reduced compounds. Alternatively, naturally occurring materials may act as redox active partners with a waste component. Natural organic matter, for example, can serve as a reductant, while *in situ* mineral and inorganic species can act as either an oxidizing or a reducing agent for anthropogenic waste compounds. Coupling the many plausible reactions with typical environmental considerations of biotic or abiotic controls and aerobic or anaerobic conditions leads to a multiplicity of environmentally significant redox reactions.

I.B. Redox Reactions at Contaminated Sites

The multi-component systems common at contamination sites engender a wide variety of electron transfer reactions which in turn prompts various approaches for characterizing the redox status of the system. Biologically mediated degradation of organic substrates is a driving force for most redox reactions. Aerobic biodegradation is dominant in surface waters and shallow, phreatic groundwater systems. However, sediments and deep groundwaters receive negligible oxygen from the atmosphere. Such systems develop anaerobic conditions which may subsequently drive a series of redox reactions utilizing native Fe, Mn, nitrate, and sulfate as electron acceptors. In a natural, unperturbed system these reactions often occur over a large spatial scale creating gentle chemical gradients. In a perturbed contamination site, specific oxidants in the waste such as hexavalent chromium or permanganate may dominate the redox reactivity of natural or contaminant reductants. Unlike the natural system, a perturbed system frequently has large contaminant concentrations confined to small, demarcated plume areas, resulting in large chemical gradients. Redox reactions at these sites can generate drastic changes in the toxicity and mobility of the plume over relatively short distances.

Three approaches have been employed by contaminant hydrologists and geochemists to describe redox systems: equilibrium, redox capacity, and specific-reaction approaches. Because many reaction couples can occur simultaneously, the equilibrium approach is advantageous in that a single redox intensity parameter such as E_H or pe describes, in principle, the equilibrium status of all redox active species in the system. This approach is analogous to using pH to describe a system's acid-base chemistry.

Unfortunately, unlike acid-base chemistry, environmental redox reactions are typically slow or irreversible, and consequently, complete equilibrium is rarely achieved [Hostettler 1984; Stumm 1984]. As such, intensity parameters may, at best, provide an indication of the direction in which the system has a potential to move. The limitations of the intensity approach has been discussed previously [Lindberg et al. 1984, Hostettler 1984, Stumm 1984].

Another scheme advocates the use of redox capacity calculations or measurements to assess the redox status of a system. These approaches closely parallel calculations and measurements of alkalinity and pH buffering capacities for acid-base chemistry, and is likewise based on the assumption of chemical equilibrium of the reaction couples. Calculation of total oxidative and reductive capacities is based on *a priori* knowledge of the principal electroactive species and their concentrations. Alternatively, redox capacity can be measured directly with total oxidative or reductive digestions under harsh conditions that drive the redox the system to completion (e.g.; Walkley-Black method [Bartlett 1991]). The first approach is practical for applications to relatively unchanging systems composed of a manageable number of readily measurable electoactive components. Identification and quantification of all important species, however, poses a serious limitation for many environmental systems. In general, digestion measurements represent the maximum redox capacity achievable if the system were to reach a completely oxidized or reduced equilibrium state. However, because redox processes are relatively slow and final equilibrium is rarely achieved, digestion-derived capacity measurements tend to overestimate the actual redox capacity.

A promising alternative is to adopt a specific-reaction based approach that has been used successfully to elucidate reactions involving hydrolysis, photolysis and other reactions of organic compounds. The reaction-based strategy focuses on specific, pertinent reactions of the target compound. This strategy entails: 1) identifying key reactions of the compound of interest, 2) characterizing each specific reaction individually, 3) quantifying the rates, stoichiometries, and orders of reaction, and 4) determining the variables such as pH, and temperature effects that control the reaction rates.

Application of a reaction-based scheme avoids the assumption of chemical equilibrium inherent in the intensity and capacity schemes. In addition, a reaction-based approach yields practical information about the rates at which a parent compound is transformed. It can serve as a basis for understanding the changing transport properties of reactants and products, and, it allows chemical reaction time scales to be related to transport time scales. One obvious necessity for applying approaches that depend on reaction kinetics is the availability of kinetic data. Unfortunately, as research into redox chemistry has traditionally followed the needs and approaches of industrial chemistry and engineering, data concerning redox reactions at relatively dilute, mildly acidic conditions typical of a contaminant plume are scant, partially because the experiments take so long to complete. Herein lies the impetus for research in this area.

I.C. Statement of Intended Research and Rationale for Experimental System.

The need of abiotic redox reaction data between co-contaminants under environmentally significant conditions was the original motivation for the research addressed in this thesis. In particular, a detailed wet-chemical investigation of the kinetics and the mechanisms of the reaction of Cr(VI) with substituted phenolic compounds was made under controlled laboratory conditions. The choice of the model system satisfied the desire to study the redox reactions between a common inorganic oxidant and a class of organic reductants typical of contamination sites containing waste mixtures. Such reactions constitute an important class of abiotic redox processes and several other studies of various redox systems have been reported in the recent years. For example, Stone and co-workers have studied redox reactions between manganese dioxide and phenols [Stone 1987]. Voudrias and Reinhard [1986] reviewed several investigations of the oxidation of organic compounds by metal-substituted clays. However, in none of these studies was the inorganic oxidant itself a priority pollutant.

In the several years since this thesis project first began, the environmental relevance of this model system has become increasingly apparent. Chromium contamination has become a major concern throughout the United States. A recent volume of *Environmental Health Perspectives* (vol. 92, 1991) was devoted to the topic of chromium contamination and risk assessment. At the national ACS conference in April 1992, six talks concerning chromium contamination were delivered in the symposium on oxidation-reduction transformations of inorganic and organic species in the environment. In addition, interest in phenolic compounds as electroactive species in the environment has flourished within this same time period. Numerous papers have been published detailing abiotic, bio-mediated, and photochemical redox interactions of phenols in the environment

Hence, given the fact that both phenols and Cr(VI) are reactive species in the environment, the principal questions concerning their potential interactions are: 1) do they react in such a way as to critically alter their transport and toxicity properties, 2), do they react on environmentally relevant timescales, and 3), what are the reaction conditions that affect the reaction rates? It is hoped, therefore, that the results presented in this thesis will make a significant contribution towards answering these questions and improve our understanding of the redox processes affecting the behavior of Cr(VI) and phenols in the environment such that more accurate assessments of their toxicities and mobilities can be made.

I.D. Thesis Overview.

The following chapters of this thesis comprise the experimental results and discussions of this thesis work on the redox interactions of Cr(VI) and substituted phenols as well as a background review chapter of pertinent literature relating to this subject.

Chapter 2 is the background review chapter and is meant to be a short summary of the principal literature that guided me throughout this research. The review emphasizes the literature concerning Cr(VI) oxidation of hydroxylated organics, phenol oxidations, and other relevant systems. Although most of the references are cited in the subsequent research chapters, some are not and I hope that their inclusion in Chapter 2 will help guide the reader to some additional references that may spark some scientific inquiry as they did for me.

Chapters 3 and 4 encompass the bulk of my experimental results and discussion. The research itself consisted of two stages. The first stage focussed on the kinetics of Cr(VI)/phenol redox interactions. The results identify the overall rates of these reactions and characterize the factors governing the reaction rates under conditions that might be encountered in the environment. In addition, we were able to describe the reaction kinetics by a relatively simple empirical rate expression suitable for a transport model. The second stage consisted of a mechanistic study and interpretation of the kinetics from the mechanistic model. These chapters are written as research papers with the intent to submit them for publication in *Environmental Science and Technology* as a two-paper series. As such, the style of Chapters 3 and 4 reflect the standard format of ACS journal publications.

In Chapter 5, the overall conclusions of this work are summarized. Considerations of the scientific benefits of this work are given in the context of environmental chemistry and engineering. While this research provides a careful examination of the kinetics and mechanism of Cr(VI)/phenol redox interactions, the postulation of a suitable mechanism for a complex chemical reaction is just that, a postulate. And, as with most research, the answers to original questions is accompanied by unexplained loose ends, the discovery of new questions, and insight into future experiments. Chapter 5, therefore, includes some suggestions for future experiments and the impact their results could have on the conclusions advanced thus far. While the mechanism itself is subject to future scrutiny, the experimental data collected over the course of this project are a valid data set that can be used to validate any future mechanistic interpretations. A summary of selected experimental data collected are included in the Appendices.

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CHAPTER 2

Background

II.A. Relevance of Research

The redox interactions of Cr(VI) and phenols were investigated because of the significant environmental problems presented by these two compounds and because of the distinct potential for Cr(VI)/phenol interactions in the environment. Chromium can exist in oxidation states ranging from -2 to +6 but typically is stable in the environment only in its trivalent (Cr(III)) and hexavalent (Cr(VI)) forms. The two oxidation states exhibit very different toxicities and mobilities. Cr(III) is relatively insoluble and inert in aqueous systems existing usually as the hexa-aquo trivalent ion or its hydrated forms, as a sorbed cation, or as a hydroxide/oxide solid [Early and Cannon 1965]. Cr(III) exhibits little or no toxicity. In contrast, Cr(VI) usually occurs as the highly soluble chromate anions ($HCrO_4^-$ or CrO_4^{2-}) that exhibit acute and chronic toxicity to humans and other organisms. Studies have shown rapid bioaccumulation of Cr(VI) in fish [van de Putte et al. 1981; Stary et al. 1982; Nishihara et al. 1985], and a variety of adverse biological effects including impaired metabolism and decreased tissue energy reserves have been observed [Arillo et al. 1982; Ghosh and Chatterjee 1985]. At low concentrations (1 ppm) it is toxic to bacteria [Natl. Acad. Sci. 1974]. The USEPA has set the maximum permissible level of total Cr in drinking water at 50 ppb (μg-Cr/kg) [EPA 1983]. In addition, Cr(VI) acts as a carcinogen and a mutagen. It has been well known that Cr(VI) in aerosols and dusts causes lung cancer in exposed workers [Mancuso and Hueper 1951; Mancuso 1951; Waterhouse 1975] and links between cell mutations and exposure to dilute solutions of chromate have been demonstrated [Hatherill 1981].

Phenols are ubiquitous in the environment, owing their presence both to natural and to anthropogenic sources. As environmental contaminants, their most common health risk is as eye, nose, throat, and skin irritants. Many phenols, however, exihibit toxic effects at low concentrations [Buikema et al. 1979] and eleven of them appear on the USEPA list of priority pollutants [USEPA 1979]. Phenolic compounds are relatively reactive and are commonly used in industrial processes. Furthermore, phenolic moieties are a major constituent of natural organic and humic matter [Thurman 1986]. Whether from anthropogenic or natural sources, the widespread presence of phenols in the environment warrents attention regarding their reactivity in natural waters and thus makes them an excellent class of compounds from which to choose model reactants.

An important consideration for choosing Cr(VI) and phenols for the target reactions is the actual observance of such interactions in the environment. The occurrence of waste mixtures containing hexavalent chromium and phenolic derivatives is common in a number of industries. The wood products industry throughout the U.S. utilizes large quantities of creosotes, cresols, chlorophenols, and Cr-Cu-As (chromated copper arsenate, CCA) for wood treatment. These compounds may leach out of the wood and mingle together or otherwise be dumped together as process wastes. The South Cavalcade Street Superfund site (Houston, Tx) is an example of such a wood treatment contamination site [USEPA 1988]. The leather tanning industry uses many of the same compounds (phenol, chlorophenol, Cr(VI) salts) as tanning agents. An abandoned disposal site in Middlesex County, Massachusetts contains several thousand kilograms of rotting hides buried along with large quantities of chromate tanning liquors [Mass. DEQE 1981]. Although tanneries are a declining industry in the U.S. there is still very much a problem at abandoned tannery disposal sites.

In addition to these industrial settings where Cr(VI) and phenolic compounds necessarily coexist, many other types of disposal sites engender potentially reactive mixtures of hexavalent Cr and organic compounds. Cr(VI) derivatives are commonly used as anticorrosives and as oxidizing agents while phenolic compounds are used in disinfectants, scouring agents, food antioxidants, and herbicides. This creates a strong potential for very diverse and complex mixtures to develope when these wastes are dumped together. For example, a detailed analysis of a contaminated aquifer in Woburn, Massachusetts revealed over 40 organic pollutants including cresols, phenol and nitrophenol in well samples, as well as Cr(VI) and nine other heavy metals [Cook and DiNitto 1982]. Even when organic co-contaminants are not mixed with Cr(VI), the chromium is likely to react with the phenolic components of natural soil organic matter. The reduction of Cr(VI) by soil organic matter is an important process at sites contaminated by inorganic plating wastes and ore tailings.

A large subsurface plume of Cr(VI) at the United Chrome Products Superfund site at Corvallis, Oregon [Keely and Boatang 1987] and the recent acknowledgment of severe chromium contamination stemming from former ore processing in Jersey City, New Jersey [Bueke et al. 1992] may be harbingers of the future problems chromium will present in the environment.

II.B. General Chromium Redox Chemistry

Cr(III) is generally considered inert and relatively insoluble in the aqueous environment [Earley and Cannon 1965]. In its pure dissolved form it is usually associated with six waters of hydration and exhibits extremely slow exchange of ligands [Earley and Cannon 1965, Morel 1983]. However, aqueous Cr(III) sorbs strongly to oxide surfaces [MacNaughton 1975; Bartlett and Kimble 1976; Huang and Wu 1977; Davies and Leckie 1980; Leckie et al. 1980; James and Bartlett 1983a,b; Honeyman 1984; Rai et al. 1986, 1988; Zachara et al. 1987]. Under certain conditions, Cr(III) sorption to mineral oxide surfaces can lead to a slow but important oxidation of Cr(III) to Cr(VI). Bartlett and James [1979] and James and Bartlett [1983b] have found that in the case of manganese dioxide (ß-MnO_2, pyrolusite) the Mn apparently acts as an oxidizing agent and a surface catalyst driving the conversion of Cr(III) to Cr(VI) at $pH > 7.3$. Adding tannery sludge to a MnO_2 rich soil, they were able to oxidize Cr(III). In effect, Cr(VI) was created from "inert" Cr(III). This may represent an important pathway of environmental Cr cycling in mildly to strongly alkaline systems.

Cr(VI) exists primarily as five different species in aqueous solution: chromate ion (CrO_4^{2-}, dominant above pH 6.4), bichromate ion ($HCrO_4^-$, dominant at $pH < 6$), dichromate ion ($Cr_2O_7^{2-}$, dominant for $[Cr(VI)] > 0.05$ M), and at very low pH, chromic acid (H_2CrO_4) and acid dichromate $HCr_2O_7^-$. In the environment Cr(VI) is commonly found in only three of these forms: CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$. (These three forms will be referred to collectively as Cr(VI) and specific ions will be properly identified when necessary). An important consequence of Cr(VI) speciation in aqueous systems is the dramatic differences in oxidizing strength of the various species. Chromate, CrO_4^{2-}, for example, has little or no oxidizing power, and dichromate, $Cr_2O_7^{2-}$, has little oxidizing power in comparison with $HCrO_4^-$ [Benson 1976]. At moderate acidities where $HCrO_4^-$ and H_2CrO_4 are dominant forms, Cr(VI) is a strong oxidant and is capable of oxidizing both inorganic compounds and numerous classes of organic compounds. Reactions of Cr(VI) with organic compounds have been studied extensively. Most published literature concerning oxidation via Cr(VI) derivatives has approached the subject from a synthetic organic chemistry perspective, aiming to devise and optimize reaction pathways for aldehyde and organic acid production. Typically, this calls for extremely acidic conditions where the Cr(VI) oxidizing power is greatest (97% acetic acid is common), high temperatures, and high Cr(VI) concentrations. From an environmental standpoint, such conditions are perhaps possible very near a waste source (e.g.; a chrome-plating bath), but in general they are unrepresentative of environmental conditions typically encountered in surface and sub-surface waters. Given some of the peculiarities of Cr(VI) oxidations, namely acid catalysis at high acid concentrations, and decreased reaction rates due to Cr(VI) dimerization, it may be inappropriate to extrapolate these synthetic experimental systems to less acidic and more dilute conditions that would prevail as a plume spreads through an aquifer.

II.C. Redox Chemistry of Cr(VI)

Cr(VI) is a standard oxidizing agent in chemical analysis and synthesis, and consequently electron transfer mechanisms involving Cr(VI) have been studied to a large degree. The reader is referred to several reviews of Cr(VI) redox chemistry with inorganic and organic compounds [Beattie et al. 1972, Benson 1976, Stewart 1964, Wiberg 1965]. Cr(VI) is an unusual oxidant in that reduction of Cr(VI) to the stable Cr(III) oxidation state requires a transfer of three electron-equivalents[1]. With the exception of tri-molecular or higher order reaction mechanisms, the transfer of more than two electron-equivalents usually requires more than one concerted reaction step[2]. In the case of Cr(VI) reduction, chromium presumably must pass through intermediate, unstable oxidation states of Cr(IV) or Cr(V) before formation of the stable Cr(III) oxidation state. Depending on the reductant, either a one- or two-equivalent transfer reaction step is possible for the initial redox step. It may be possible to characterize the resulting transient intermediates, Cr(V) and Cr(IV) respectively, from which the number of electron-equivalents transferred in the initial oxidation can be inferred. Several reaction schemes have been proposed for the reduction of Cr(VI) to Cr(III). The following sections are a brief overview of the relevant reaction schemes. The review is divided into two broad categories, one-equivalent and two-equivalent reductions, as they refer to the initial step in the reduction of Cr(VI) to either Cr(IV) or Cr(V).

II.C.1. One-Equivalent Reductions: An Overview

The general mechanism for a one-equivalent reduction of Cr(VI) proposed by King and co-workers [Tong and King 1960, Espenson and King 1963] consists of a sequence of three one-equivalent transfer steps:

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[1] Beattie and Haight, Jr. [1972] describe oxidation/reduction processes in terms of either a one- or two-equivalent transfers. The concept of an "equivalent" is usually defined as the formal number of electrons accepted by an oxidant or given off by a reductant. In more practical terms an equivalent transfer is not always an electron transfer. Acceptance by an oxidant of one electron is equivalent to acceptance of a hydrogen atom. Likewise, the acceptance of two electrons is equivalent to acceptance of a hydride ion. Additionally, the acceptance of two electrons is also the same as the loss or donation of an oxygen atom, hence the familiar term "oxidation". Therefore, redox processes of either one- or two-equivalent transfers, can occur by electron, atom, or ion transfer.

[2] Three electron transfer reactions have been reported in certain systems such as the cooxidation of isopropyl alcohol and oxalic acid by chromic acid [Hasan and Rocek 1972a, 1972b, 1973]

$$\begin{array}{lll} \mathrm{Cr(VI) + Red = Cr(V) + Ox} & & k_{65}, k_{56} \\ \mathrm{Cr(V) + Red = Cr(IV) + Ox} & & k_{54}, \mathrm{k}_{45} \\ \mathrm{Cr(IV) + Red = Cr(III) + Ox} & & k_{43}, k_{34} \end{array}$$

with the assumptions: 1) steady-state [Cr(V)] intermediate

2) the Cr(IV) → Cr(V) reaction is negligible

i.e., k_{45}[Cr(IV)][Ox] is small as a result of:

i) k_{45} very small

ii) [Cr(IV)] very small

Though the reductant may be organic or inorganic, most published work concerning one-equivalent reactions has involved inorganic reductants. The complete rate law may be written as

$$-d[\mathrm{Cr(VI)}]/dt = \frac{k_{65}k_{54}[\mathrm{Cr(VI)}][\mathrm{Red}]^2}{k_{45}[\mathrm{Red}] + k_{56}[\mathrm{Ox}]}$$

[King et al. 1960,1963]

Limiting cases of reactions will exist where terms drop out leaving simplified empirical rate laws. This would be the case for a pseudo-first-order situation where [Red] » [Ox] resulting in a rate expression of the form

$$\mathrm{rate} = k_{65}[\mathrm{Cr(VI)}]$$

a simple first-order rate expression.

One of the most important features of the step-by-step nature of one-equivalent reductions of Cr(VI) is the potential to the track the involvement of intermediate Cr(IV) and Cr(V) species since the role of these species may have a significant influence on the rate of Cr(VI) reduction. In reference to the one-equivalent reaction scheme outlined above, numerous studies have shown that the second reaction step, the reduction of Cr(V) to Cr(IV) is the rate limiting step [Beattie and Haight, Jr. 1972]. This step apparently involves an expansion of the chromium coordination sphere from four to six, a process which requires more energy than the initial Cr(VI) to Cr(V) step which involves no change in the coordination number.

Most of the original evidence for the existence of intermediate redox states of chromium was obtained from induced oxidations of inorganic ions by Cr(VI) [Wiberg 1965] . Two of the most frequently used examples for investigating the role of Cr(IV) and Cr(V) are the induced oxidation of iodide (I^-) and manganous ion (Mn(II)).

At low reactant concentrations and low acidity ($pH \geq 3$), the oxidation of I^- by Cr(VI) proceeds at a very slow rate. With the addition of Fe(II), however, I^- is rapidly oxidized to iodine. Because the oxidation of I^- by Fe(III) is also slow under these conditions, one of the intermediate chromium species is responsible for oxidizing I^-, whereas Cr(VI) and Fe(III) are not. Based mainly on stoichiometric arguements, it was established that Cr(V) was the active chromium species responsible for the induced oxidation of I^- [Wiberg 1965].

In a similar manner as I^-, Mn(II) and Ce(III) act as excellent scavengers of specific Cr species. Though direct oxidation of Mn(II) by Cr(VI) is thermodynamically unfavorable at $pH > 0$, oxidation proceeds readily in the presence of other reducing agents [Beattie and Haight, Jr. 1972]. Induced oxidations of Mn(II) by Cr(VI) are specific for reactions in which Cr(IV) is a principal reaction intermediate. That is, Mn(II) reacts with Cr(IV) while Cr(VI) is unaffected [Watanabe and Westheimer 1949]. Mn(II), therefore, acts an effective scavenger of Cr(IV):

$$\mathrm{Cr(IV)} + \mathrm{Mn(II)} \rightarrow \mathrm{Cr(III)} + \mathrm{Mn(III)}$$

Ce(III) similarly serves as a Cr(IV) scavenger [Beattie and Haight, Jr. 1972].

The ability of I^- and Mn(II) to scavenge chromium species of specific oxidation states that form during the reduction of Cr(VI) provides a useful probe for the existence of Cr(V) or Cr(IV). As will be discussed below, induced oxidations of Mn(II) in two-equivalent reductions of Cr(VI) have been very helpful in elucidating Cr(VI)/organic reactions.

II.C.2. Two-Equivalent Reductions

As there are many reagents that can generate a single-step two-equivalent reduction of Cr(VI) to Cr(IV), a complete review here would be too lenghty (Beattie and Haight, Jr.

[1972] give an excellent review). As with one-equivalent transfer reactions, the reductant can be either organic or inorganic. Since this thesis focusses on the reduction of Cr(VI) by phenols, the following section emphasizes the mechanisms relevant to the interaction of Cr(VI) with a hydroxylated organic compounds.

A review of the oxidation of hydroxylated organics is not complete without mention of the work by Westheimer and his co-workers. The studies made by his group were the first major steps in defining the Cr(VI) oxidation of aliphatic alcohols and of Cr(VI) oxidations of many organic compounds in general. Through extensive research on Cr(VI) oxidation of isopropyl alcohol, Westheimer showed the following characteristics of these reactions: 1) a Cr(VI) ester is a pre-oxidation intermediate, 2) a carbon-hydrogen bond cleavage of a hydride abstraction is rate limiting, 3) the reaction rate increases with increased acidity, and 4) Cr(IV) and Cr(V) are reaction intermediates with Cr(IV) being the product of the first step of the reaction. The reaction kinetics demonstrate first-order dependence on the concentration of both Cr(VI) and alcohol. In acidic solution ($[H^+] \geq 0.2$ M) the reaction rate is proportional to $[H^+]^2$, and at lower acidities (*ca.* 0.1 - 0.01 M) the rate appproaches a first-order dependence on $[H^+]$. When the reaction is carried out in the presence of excess Mn(II), the reaction rate is reduced approximately 50% due to the purported scavenging of Cr(IV) by Mn(II).

Westheimer, and later Wiberg and co-workers [1969a,1969b,1971,1974], proposed several two-stage mechanisms for the redox interactions of Cr(VI) and isopropanol. The first stage, a pre-oxidation equilibrium process, consists of a rapid formation of chromate mono- and diesters with the alcohol. This first reaction step, a rapid, reversible esterfication susceptible to acid catalysis, occurs with no change in oxidation state. The second stage consists of the actual oxidation steps and includes the rate determining step. The following sets of reactions were proposed:

preoxidation equilibria:

$$R_2CHOH + HCrO_4^- + H^+ = R_2CHOCrO_3H + H_2O \qquad \text{(monoester)}$$

$$R_2CHOCrO_3H + HCrO_4^- + H^+ = (R_2CHO)_2CrO_2H + H_2O \qquad \text{(diester)}$$

oxidation steps:

$$\text{mono- and diester} \rightarrow R_2C{=}O + Cr(IV)$$

I.

$$R_2CHOH + Cr(IV) \rightarrow R_2COH^{\bullet} + Cr(III) + H^+$$
$$R_2COH^{\bullet} + Cr(VI) \rightarrow R_2C{=}O + Cr(V) + H^+$$
$$R_2CHOH + Cr(V) \rightarrow R_2C{=}O + Cr(III)$$

II.

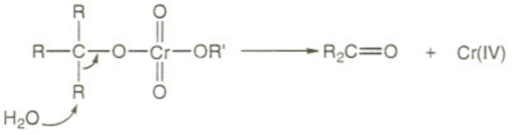
$$Cr(IV) + Cr(VI) \rightarrow 2\,Cr(V)$$
$$2\,(\,Cr(V) + R_2CHOH \rightarrow R_2C{=}O + Cr(III)\,)$$

III.

$$2\ Cr(IV) \rightarrow Cr(V) + Cr(III)$$
$$Cr(V) + R_2CHOH \rightarrow R_2C{=}O + Cr(III)$$

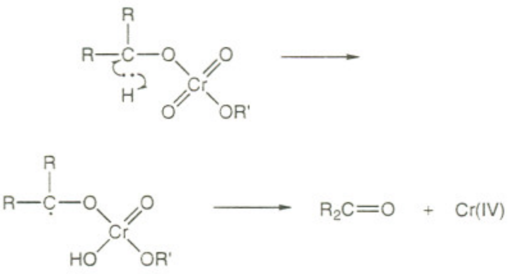
If the two-stage theory is correct, then the final oxidation must proceed by a pathway that is consistent with the chromate ester decomposition. Wiberg [1969a,b] proposed the following mechanisms:

Mechanism A



Mechanism B

Mechanism C



Whether a heterolytic (A or B) or homolytic (C) cleavage occurs, for oxidation of 1° or 2° alcohols, the cleavage of the C–H bond α to the hydroxy group is thought to be rate determining. Isotope effects on the order of $k_H/k_D = 6.0$ [Wiberg and Schafer 1969a,b] substantiated this conclusion. Thus, according to the proposed reaction scheme, rates of oxidation of 1° and 2° alcohols will depend on the stability of the chromate ester and the ease of an α carbon-hydrogen bond cleavage.

From the detailed study of Cr(VI) oxidation of 1° and 2° alcohols, it became well established that many Cr(VI) oxidation-reduction reactions proceed through a pre-oxidation equilibrium formation of a Cr(VI)-reductant complex. It was shown, for example, that aldehydes are oxidized in proportion to the concentration of their hydrated forms, which are capable of ester formation [Wiberg 1965]. Detection of Cr(VI) esters of tertiary (3°) alcohols ostensibly extended this general characterization of Cr(VI) oxidations to 3° alcohols as well. Richer et al. [1975] isolated chromate esters of 3° alcohols by an extraction technique. The reaction solution immediately turned red-orange, indicating the formation of the chromate ester. Upon exposure to light and air, the colored solution decomposed moderately quickly, forming a black-brown residue which was not analyzed.

Zeiss and Mathews [1956] sucessfully isolated chromate esters of simple 3° alcohols by a freeze-drying method. The esters of 3° alcohols, unlike those of 1° or 2° alcohols, are relatively stable and could be isolated by this technique. Visual confirmation of ester formation was described as the development of yellow or red color and subsequent decomposition resulting in a brown solid. The experimental evidence suggested that Cr(VI) esterfication and ligand replacement is a prerequisite to the redox reaction with subsequent redox steps proceeding in connection with an inner-sphere electron, atom, or ion transfer and decomposition of the ester complex.

Despite these reports of Cr(VI) esters with 3° alcohols, the general applicability of this reaction scheme has not been firmly established. Oxidations of several tertiary alcohols in acidic media were reported to proceed by a rate determining preoxidative dehydration of the alcohol to an olefin [Sager 1956, Rocek and Radkowsky 1968 (references therein)]. Thus, the compound undergoing oxidation was an olefin and not the tertiary alcohol itself. The reaction kinetics were independent of Cr(VI) concentration and were consistent with a rate determining dehydration.

Gold and Riley [1962] and Rao et al. [1977] countered these reports with Cr(VI)/ 3° alcohol kinetics that were first-order in chromic acid concentration, not zeroth-order. On the basis of acidity function correlation, Rao et al. proposed a pre-oxidation dehydration to a carbonium ion, followed by rapid oxidation:

$$(R)_3COH + H^+ = (R)_3C^+ + H_2O$$

$$(R)_3C^+ + Cr(VI) \rightarrow \text{Products}$$

Rocek and Radkowsky [1968] reported what they believed to be the first direct Cr(VI) oxidation of a tertiary alcohol. Since Sager and other workers found that 3° alcohol oxidation proceeded by an initial dehydration to an olefin followed by oxidation of the olefin, the authors chose 1-methylcyclobutanol as the reductant because of its very low dehydration rate. Relief of high ring strain would also add to the likelihood of a C–C oxidative bond cleavage. Oxidation was slow but proceeded 40 times faster than that predicted by dehydration kinetics. Furthermore, a first-order dependence on chromic acid concentration was observed, although the typical decrease in the second order rate constant connected with the bichromate dimerization equilibrium ($2\ HCrO_4^- = Cr_2O_7^{2-}$) was not observed. The authors concluded that the oxidation was an example of a direct oxidation and not an oxidation preceded by dehydration.

Stewart and Banoo [1969] reported that Cr(VI) oxidations of tri-aryl carbinols followed second-order kinetics, first-order each in oxidant and reductant concentrations. Tri-aryl carbinols which are resistant to dehydration underwent oxidative cleavage of an aryl group by means of a 1,2-aryl shift. The proposed mechanism involves a pre-oxidative esterfication step followed by a rate limiting aryl shift.

II.D. Oxidation of Phenols

The literature contains extensive discussions of the reaction of phenols with one-equivalent oxidizing agents including alkaline ferricyanide, ferric chloride, Fenton's reagent, and persulfate. In general, one-equivalent oxidations of phenols lead to the formation of unstable, reactive phenoxy radicals that can further react through various pathways including radical-radical coupling to create mono-, di-, and polymeric coupled phenols (Figure 2.1) [Waters 1961,1964,1971; Musso 1967; Chinn 1971; Bailey et al. 1983]. The principle pathways for one-equivalent phenol oxidations are fairly well established and the reader is referred to several reviews on this subject [Musso 1967; McDonald and Hamilton 1973; Altwicker 1967; Fieser 1930a,b].

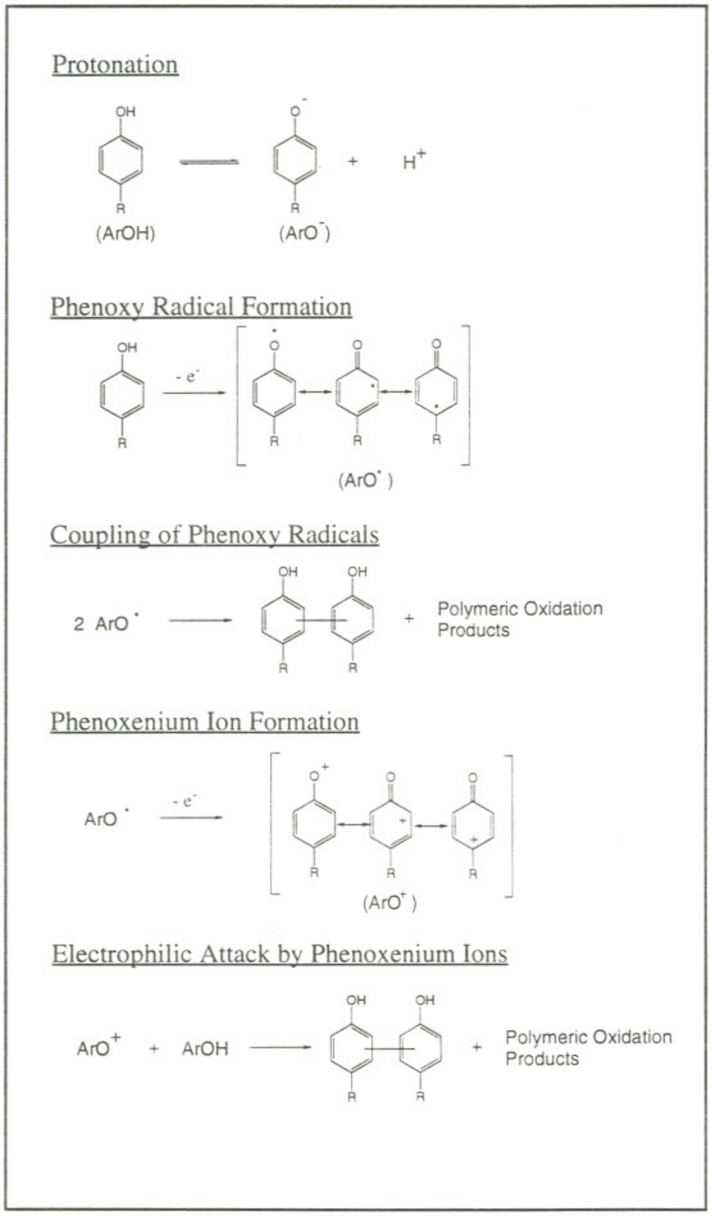


Figure 2.1. Oxidation pathways of substituted phenols. Adapted from Stone [1987].

Considerably less work has been done to elucidate the mechanisms of two-equivalent oxidations of phenols. Successive one-equivalent oxidations of a phenol to produce a phenoxy cation species has been proposed as a pathway when the oxidizing agent is strong and the acidity is high (Figure 2.1) [Waters 1971]. Because little detailed work has been done to examine phenol oxidations by oxidants capable of accepting two electron-equivalents, it is still not well established if a concerted two-equivalent transfer step occurs with phenol oxidation as it does for oxidation of 1° and 2° alcohols by Cr(VI).

Stabilization effects generated by the aromatic ring and ring substituents will likely have a

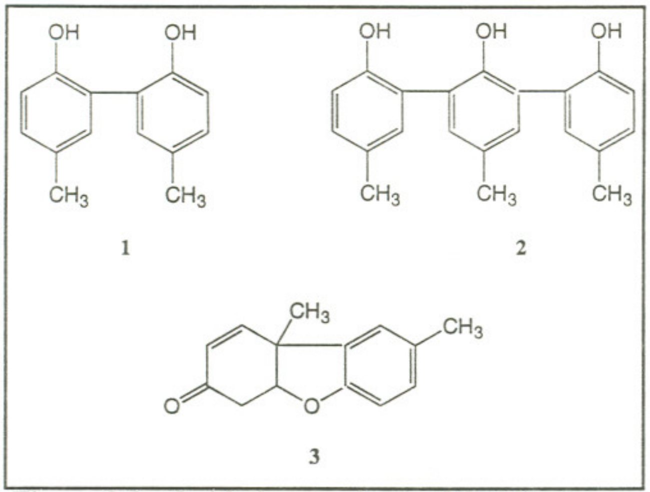


Figure 2.2. Oxidation products of Cr(VI) oxidation of 4-methylphenol. Tanaka et al. [1970].

major effect on the reactivity of the phenol. While investigating the product yields of Cr(VI) oxidation of *p*-cresol (4-methylphenol), creosol (2-methoxy-4-methylphenol), and homocatechol, Tanaka et al. [1970] found that the rate of Cr(VI) reduction increased in the order homocatechol > creosol > *p*-cresol which is in agreement with increasing electron density of the phenolic hydroxyl group. Analysis of the reaction products showed that the oxidation of *p*-cresol with dichromate gave a crystalline fraction (15% yield) composed of ortho-linked dimeric (2% yield) and trimeric (1% yield) cresols and dimeric ketone (12% yield) (compounds **1**,**2**, and **3** in Figure. 2.2). A major part of the reaction products (up to 60%) was a resinous fraction of "complicated products" that the authors presumed were products resulting from ring-cleavage. Addition of Mn(II) to the reaction mixture resulted in as much as triple the coupled (polymeric) products (**1**(13%), **2**(7%), **3**(21%), 41% total), and a 44% decrease in the unresolved complicated products. However, the reaction rate was unaffected by the presence of excess Mn(II). The changes in the proportion of products can be explained by the following set of reactions:

$$\mathrm{PhOH} + \mathrm{Cr(VI)} \rightarrow \mathrm{PhO}^{\bullet} + \mathrm{Cr(V)} \qquad (1)$$

$$\mathrm{PhOH} + \mathrm{Cr(VI)} \rightarrow \mathrm{Cr(IV)} + \text{complicated products} \qquad (1a)$$

$$\mathrm{PhO}^{\bullet} + \mathrm{PhOH} + (\mathrm{Cr(IV)} \text{ or } \mathrm{Cr(V)}) \rightarrow \text{complicated products} \qquad (2)$$

$$\mathrm{Mn}^{2+} + (\mathrm{Cr(IV)} \text{ or } \mathrm{Cr(V)}) \rightarrow \mathrm{Mn}^{3+} + (\mathrm{Cr(III)} \text{ or } \mathrm{Cr(IV)}) \qquad (3)$$

$$\mathrm{PhOH} + \mathrm{Mn}^{3+} \rightarrow \mathrm{PhO}^{\bullet} + \mathrm{Mn}^{2+} \qquad (4)$$

$$\mathrm{PhO}^{\bullet} + \mathrm{PhO}^{\bullet} \rightarrow \text{Dimer} \rightarrow \text{Trimer} \qquad (5)$$

Cr(VI) may act as a one-equivalent oxidant forming a phenoxy radical as in reaction (1). The phenoxy radicals combine to form dimers and trimers (reaction (5)). In the case of oxidation of phenols by Cr(VI), Tanaka concluded that the Cr(IV) or Cr(V) species caused C–C ring cleavage which could lead to yet additional pathways involving the cleaved products. A possible explanation apparently not entertained by the authors is that the complicated products were ring-coupled oligomers. In either case Mn(II) scavenges Cr(IV) and Cr(V) ions and prevents them from inducing the putative ring cleavage or polymerization that yields complicated products. In addition, Mn(II) is oxidized to Mn(III) via its Cr(IV)/Cr(V) interactions (reaction (3)) and is itself capable of one-equivalent oxidation of phenols. Thus, in the presence of Mn(II), one mole of Cr(VI) acts indirectly as three one-equivalent oxidants,

$$\mathrm{Cr(VI)} + \mathrm{PhOH} \rightarrow \mathrm{PhO^{\bullet}} + \mathrm{Cr(V)}$$

$$2\ \mathrm{Mn^{2+}} + \mathrm{Cr(V)} \rightarrow 2\ \mathrm{Mn^{3+}} + \mathrm{Cr(III)}$$

$$2\ \mathrm{Mn^{3+}} + 2\ \mathrm{PhOH} \rightarrow 2\ \mathrm{Mn^{2+}} + 2\ \mathrm{PhO^{\bullet}}$$

Although Tanaka et al. only superficially examined the kinetics of the reaction, it is apparent from the lack of a Mn(II) effect and the inferred initial reduction of Cr(VI) to Cr(V) that some differences exist between the Cr(VI) oxidations of simple aliphatic alcohols and phenols.

II.E. Recent Investgations of Phenol Oxidations in Environmental Systems.

In recent years, several studies have investigated the kinetics of the oxidation of phenolic compounds by various environmentally relevant oxidants. Faust and Hoigné [1987] measured the rates of DOM-sensitized (DOM: dissolved organic matter) photooxidations of various alkylphenols and found the reaction time scales were on the order of minutes to months under typical environmental conditions. Reaction rates were first-order in phenol concentration and, within the pH range studied (pH 7.1 - 8.3), the oxidation rate was independent of pH.

Tratnyek and Hoigné [1991] examined the oxidation of phenols by singlet oxygen and found first-order rate dependence with respect to the concentrations of the oxidant ($^1O_2$) and the phenol reductant. The authors point out that in aqueous solution, phenols can exist as either a neutral phenol or its deprotonated phenolate anion form. The pK_a values of phenols generally range from 7 - 11 and hence, significant amounts of the deprotonated phenol can exist in solution depending on the pH. In this manner phenols are distinctly different from aliphatic alcohols whose pK_a values are typically greater than 14. From thermodynamics, the phenolate species is a stronger reductant than the neutral phenol form due to the relatively higher electron density in the outer electron shell. Reaction rates may thus depend on the concentration of a particular species which in turn depend on the system acidity. In the pH range examined by Tratnyek and Hoigné (*ca.* pH 6 - 12) the reaction rate demonstrated an inverse dependence on the acidity. Assuming two possible oxidation pathways can exist, one involving the undissociated phenol and the other the phenolate species, the inverse dependence on [H^+] was linked to changing phenol speciation with changing acidity. As [H^+] increases, the proportion of phenol in the more reactive deprotonated form decreases, and the reaction rate is diminished. Hence, for oxidation of unsubstituted phenol by $^1O_2$, the phenolate species was found to be approximately 2 orders of magnitude more reactive than the protonated phenol. Comparison of relative reactivities for 22 various substituted phenols showed a strong correlation between oxidation rates and electron density of the aromatic system brought about by substituent effects.

Stone [1987] investigated the reductive dissolution of manganese (III/IV) oxides by substituted phenols in aqueous solutions of pH 1 - 7. In contrast to the pH effects mentioned above, the rate of manganese dissolution increased with increasing proton concentration, but was not a simple function of [H^+]. Stone surmised that the reaction rate is affected at least in part by the degree of Mn(III/IV) surface protonation which is dependent upon the pH of the solution. The positive rate effect of increasing [H^+] suggests that at higher acidities, where essentially all the phenol is in the undissociated form, the reaction is more sensitive to the speciation of the oxidant as opposed to the phenol. Precise interpretation of the proton dependence was complicated by the heterogeneous nature of the manganese dioxide solid. That is, because the oxidizing agent was actually a mixture of two Mn oxidation states, the possibility of several different pathways and various degrees of oxidation creates a complex reaction scheme. Comparison of relative reactivities of the 10 substituted phenols studied showed the same general substituent effects observed by Tratnyek and Hoigné for $^1O_2$ oxidations. In general, reaction rates increased with increased electron-donating character of the substituent (as measured by Hammett σ constants).

The preceding background review represents a sampling of the literature pertaining to the redox chemistry of Cr(VI) and phenols. The majority of the literature cited above and in the following chapters are from what we environmental scientists might refer to as "fundamental chemistry" publications, and their environmental relevance may not be obvious at first glance. However, they were a continual source of scientific muse over the course of this thesis project guiding me in the design and interpretation of the experiments that are described below.

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CHAPTER 3

Redox Interactions of Cr(VI) and Substituted Phenols: Kinetic Investigation

Abstract

Redox transformations are an important process affecting the fate of Cr(VI) and organic co-contaminants such as phenols in the environment. This study focussed on the kinetics of the reduction of Cr(VI) to Cr(III) by substituted phenols in aqueous solution. Reactions were studied over varying reactant concentrations, pH, temperature, and ionic strength. At a given pH the reaction was first-order with respect to both the concentration of phenol reductant and the total concentration of Cr(VI) monomer species. Reaction rates were strongly pH dependent with rates increasing as much as 4 orders of magnitude from pH 5 to pH 1. The apparent reaction order with respect to [H^+] varied between *ca.* 0.4 and 2 over this same pH range, but also depended on the identity of the phenol. Comparison of the reactivities of 13 substituted phenols revealed a strong substituent effect. At pH 2, rates for the 13 phenols spanned 6 orders of magnitude with reactivity generally increasing with electron donating character of the substituent (methoxy > methyl > chloro, aldehyde > nitro), the substituent position (para, ortho > meta), and degree of substitution (tri- > di- > mono-substituted). The effect of substituents on reaction rates could be described by a linear correlation of the second-order rate constants (k_{ArOH}) with the phenol half-wave potential ($E_{1/2}$). The results of this study show that Cr(VI) is reduced by phenols over a wide range of conditions and that the rates of these reactions vary orders of magnitude

depending on solution conditions. Representative reaction half-lives fall within the time scales of major environmental transport processes and suggest that the kinetics of these interactions are of significant concern regarding assessments of chromium contaminated sites.

Introduction

Few hazardous waste sites can be adequately characterized as single-component systems. The complex mixtures of organic and inorganic materials are susceptible to chemical reactions that can alter the toxicity and mobility of the parent compounds. Transport models intended to predict the behavior of these systems rarely include abiotic oxidation-reduction (redox) transformations because little information is available about the kinetics and mechanisms of this important class of reactions. Redox processes utilizing inorganic oxidizing agents and organic reductants are an important class of industrial oxidation-reduction reactions. Widespread industrial use of redox-active compounds such as hexavalent chromium (Cr(VI)) and phenols has resulted in numerous instances in which these compounds have been released into the environment. Previous research on redox reactions of these compounds has focused on synthetic organic or industrial processes so few data are available for relatively dilute, mildly acidic conditions typical of an environmental system. In order to accurately predict the environmental fate of these waste components, more information is needed about the rates and mechanisms of reactions under environmentally relevant conditions.

The redox interactions of Cr(VI) and phenols were investigated because of the significant environmental problems presented by these two compounds and because of the distinct potential for Cr(VI)/phenol interactions in the environment. Cr(VI) is a common industrial oxidizing agent and has been increasingly recognized as a serious environmental contaminant *(1-3)*. Chromium is highly electroactive and its redox chemistry is a critical factor controlling its behavior in the environment. The two environmentally stable oxidation states of chromium, Cr(VI) and Cr(III), exhibit very different toxicities and mobilities. Cr(III) is relatively insoluble in aqueous systems and exhibits little or no toxicity *(4)*. In contrast, Cr(VI) usually occurs as highly soluble and highly toxic chromate anions ($HCrO_4^-$ or CrO_4^{2-}) *(5)*, and is a suspected carcinogen and mutagen *(6, 7)*.

Phenols are ubiquitous in the environment, owing their presence both to natural and to anthropogenic sources. As environmental contaminants, their most common health risk is as eye, nose, throat, and skin irritants. Many phenols, however, exhibit toxic effects at low concentrations *(11)* and eleven of them appear on the USEPA list of priority pollutants *(8)*. Phenolic compounds are relatively reactive and are commonly used in industrial processes. Furthermore, phenolic moieties are a major constituent of natural organic and humic matter. Whether from anthropogenic or natural sources, widespread presence of phenols in the environment warrants attention regarding their reactivity in natural waters and thus makes them an excellent class of compounds from which to choose model reactants.

An important consideration for choosing Cr(VI) and phenols for the target reactions was the frequency of which such interactions are observed in the environment. Mixtures of Cr(VI) and phenolic derivatives are found in the waste streams of several industries *(9, 10)*. The wood products industry utilizes large quantities of creosotes, cresols, chlorophenols, and Cr-Cu-As (chromated copper arsenate) for wood treatment *(12)*. Leather tanning facilities use many of the same compounds (phenol, chlorophenols, and Cr(VI) salts) as tanning agents *(13)*. Even when phenolic co-contaminants are not mixed with Cr(VI), Cr(VI) may react with the phenolic moieties comprising a major fraction of natural organic matter (NOM). NOM may be the primary electron source for Cr(VI) reduction in many soils and natural waters *(14, 15)*.

This study was aimed at elucidating the kinetics and mechanisms of redox reactions between Cr(VI) and substituted phenols. This paper, the first of two, reports on kinetic experiments measuring the effects of reactant concentration, pH, temperature, phenol structure, and ionic strength on the rates of reaction. The results obtained allow field-site investigations and modeling efforts to quantitatively incorporate redox transformation reactions into transport models when assessing the fate of Cr(VI) and phenols in the environment. The following companion paper reports on the phenolic oxidation products and the mechanistic pathways of Cr(VI)/phenol interactions.

Experimental Section

Materials. Aqueous solutions of Cr(VI) and organic reactants were freshly prepared for each experiment from pure reagents or concentrated stock solutions. Pure phenols (Aldrich) were analyzed for significant impurities by gas chromatography flame ionization detection (GC/FID) and were purified by recrystallization before use if necessary. $K_2Cr_2O_7$ (Aldrich, ACS primary standard) stock solution was the source of Cr(VI) for all experiments. Aqueous buffers ranging from pH 1.0 to 6.0 were prepared from phosphate buffer or phosphate and acetate buffer solutions adjusted with $HClO_4$ to within 0.01 pH units of the desired value. Ionic strength was maintained with addition of $KClO_4$. All solutions were prepared using ultrapurified water (Nanopure system, Barnstead).

Kinetic Experiments. Reactions were carried out over a wide range of Cr(VI), phenol and proton concentrations. For experiments with excess phenol, reactions were initiated by mixing a small volume of 0.5 M Cr(VI) stock solution into aqueous phenol solutions. Reaction progress was followed by analyzing small aliquots for Cr(VI) by a diphenylcarbazide (DPC) colorimetric procedure *(16)*. All Cr(VI) measurements were compared to standards prepared in buffers without phenol. Reactions with an excess of Cr(VI) were initiated by adding a small volume of concentrated phenol stock solution to aqueous solutions of Cr(VI). Time-course concentrations of phenol were determined by HPLC (Isco 2350/GP2360) using a RP column (Supelcosil 25-cm LC-18; Supelco). UV detection (Spectra-Physics 8440 Variable UV/VIS Detector) was performed at either 280 nm or at the specific λ_{max} of the compound when increased sensitivity was necessary. For experiments where the molar ratio of Cr(VI) and phenol did not satisfy an excess condition ("stoichiometric experiments") substrate concentrations were followed by HPLC, and Cr(VI) concentrations by both DPC and HPLC with detection of Cr(VI) at 280 or 350 nm.

Reactions were carried out in glass vials with screw caps containing Teflon liners. All kinetic experiments were maintained at a constant temperature (15°, 25°, or 35°C (± 0.5 °C)) in a circulating water bath. Glassware was washed in 3 N HCl and rinsed thoroughly with purified water. Appropriate reaction blanks consisted of either Cr(VI) or the selected phenol without addition of the other reactant in pH buffer solutions in both clear and amber vials. The blanks showed no depletion of Cr(VI) or degradation of phenol over the course of the sampling period. Light-control reactions in amber vials showed no difference in reaction rates compared to clear vials, indicating the absence of light-induced side reactions. All reactions and corresponding blanks and controls were performed in duplicate or triplicate. The pH of the solution was measured with a micro combination electrode (Corning) at the beginning and end of each reaction. The pH change was less than 0.1 units in all cases indicating a sufficient buffer capacity.

Kinetic Analysis. Reaction kinetics were simplified in many cases by using one reactant concentration in large excess (20-500 fold) of the other and by maintaining constant pH with unreactive buffers. Under these conditions, the reaction kinetics were fixed with respect to the concentration of H^+ and the excess reactant (pseudo-zeroth-order conditions) thus isolating the rate dependence of the limiting reactant partner. In these experiments, pseudo-first-order rate constants, k_{exp}, were determined from the slope of plots of $\ln(C/C_o)$ as a function of time. Activity corrections due to secondary salt effects (ionic strength) were included for concentrations of charged species. Activity coefficients were calculated from the Davies equation, $\log \gamma_i = -0.5 z_i^2(\sqrt{I}/(1+\sqrt{I}) - 0.2I)$, where $I = 0.5\sum c_j z_j^2$ *(17)*.

Results and Discussion

Oxidation-Reduction Kinetics. The experiments revealed that Cr(VI) reacts relatively rapidly with phenolic compounds at moderately acidic pH values, causing reduction of Cr(VI) to Cr(III) and conversion of phenols to oxidized products. Reactions of Cr(VI) and excess phenol are characterized by a nonlinear reduction of Cr(VI) with time. The rate of Cr(VI) reduction, indicated by the slope of the reaction curve, decreases with time due to the depletion of Cr(VI) (Figure 3.1). Pseudo-first-order rate constants, k_{exp}, were determined from least-squares linear regression of first-order plots of ln[Cr(VI)] as a function of time. The linearity of the plots and statistical goodness-of-fit indicated the suitability of the first-order assumption (Figure 3.2).

The redox interactions of Cr(VI) and 4-methylphenol (4MP) comprised the primary focus of the kinetic investigations. Cr(VI) reduction rates, as quantified by k_{exp}, varied linearly with the concentration of excess 4MP, indicating that the reaction was first-order with respect to the reductant concentration (Figure 3.3). Thus, at a fixed pH the overall reaction could be characterized by a second-order rate expression

$$\text{rate} = k_{\text{ArOH}}[\text{Cr(VI)}][\text{4MP}] \tag{1}$$

where the second-order rate constant, k_{ArOH}, is defined as

$$k_{\text{ArOH}} = k_{\text{exp}} / [\text{4MP}] \tag{2}$$

Studies of Cr(VI) oxidation of primary and secondary alcohols *(18-29)* as well as tertiary alcohols *(30-32)*, aldehydes *(33-36)*, thiols *(37)*, and organic acids *(38)* have demonstrated a first-order dependence with respect to both Cr(VI) and the organic reductant, as was observed here for Cr(VI) and phenols. Oxidations of phenolic compounds by non-chromyl oxidants have likewise displayed a first-order dependence on the phenol concentration *(39,40,41)*. First-order dependencies of the oxidant and reductant are consistent among studies despite significant differences in the reactants, but overall, the observations of second-order kinetics suggest a bimolecular process in the rate limiting step.

The first-order dependence on [4MP] was verified in a second series of experiments with excess Cr(VI). For these "pseudo-zeroth-order" conditions with respect to Cr(VI), reaction progress was monitored by the loss of 4MP for several concentrations of excess Cr(VI). Plots of ln[4MP] vs. time were linear over at least three reaction half-lives (Figure 3.4). However, the observed rates in these experiments were not linearly proportional to total Cr(VI) concentration. The reaction rates, instead, increased less than the proportional increase in the initial Cr(VI) concentration (Figure 3.5). As discussed below, this phenomenon implies that 4MP reacts at different rates with different Cr(VI) species, and that the non-linear trend in k_{exp} is a reflection of changing Cr(VI) speciation. Proper interpretation of the kinetic data therefore depends on careful consideration of the active reactant species.

Cr(VI) Speciation Effects. Aqueous Cr(VI) exists as five species in this system: H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$, and $HCr_2O_7^-$. Previous reports have suggested that bichromate, $HCrO_4^-$, is the primary reactive species *(18,29,30,33,34)*, although this is not been conclusively established for all systems *(29,36,42,43)*. Our experiments with excess Cr(VI) indicate that a monomeric species (H_2CrO_4, $HCrO_4^-$, or CrO_4^{2-}) is the primary reactant with phenol. To achieve the necessary excess of [Cr(VI)] over [4MP] within the constraint of the analytical detection limit for 4MP, relatively high concentrations of Cr(VI) (0.01 - 0.5 M) were required. In this concentration range, dimerization according to the reaction

$$2\ HCrO_4^- = Cr_2O_7^{2-} + H_2O \qquad K_d = 35.5 \qquad (3)$$

becomes important. For acidic conditions (pH 0-6 where $HCrO_4^-$ is the dominant *monomeric* species) and $[Cr(VI)]_{tot} \geq 0.05$ M, the dimeric species $Cr_2O_7^{2-}$ and $HCr_2O_7^-$ become the dominant Cr(VI) forms. Because the dimerization equilibrium has a second-order dependence on $[HCrO_4^-]$, the relative concentrations of each species are not linearly proportional to $[Cr(VI)]_{tot}$, and the reaction rates are therefore expected to show a non-linear variation with $[Cr(VI)\ ]_{tot}$.

In the excess chromium experiments, $[Cr(VI)]_{tot}$ was essentially constant over the course of the reaction, so changes in Cr(VI) speciation during a reaction were minimal. Reaction rates could thus be compared with the essentially fixed concentations of each species. Plots of k_{exp} against concentrations of individual Cr(VI) species exhibited linear or nearly linear relationships with the monomeric species chromate (CrO_4^{2-}), bichromate ($HCrO_4^-$), and chromic acid (H_2CrO_4) (Figure 3.6). Values of the slopes in Figure 3.6 represent Cr(VI)-species-normalized second-order rate constants (the pseudo-first-order rate constant for 4MP oxidation normalized to specific Cr(VI) species concentrations). Given the uncertainty in published values of equilibria constants and calculated values of activity coefficients, exact speciation is uncertain so it is not possible to conclusively identify one Cr(VI) species as the primary reactive species simply from the goodness of fit. However, if we compare the Cr(VI)-species-normalized second-order rate constants for 4MP oxidation (calculated from the slopes in Figure 3.6) to the apparent second-order rate constant for Cr(VI) reduction (k_{ArOH}, calculated by eq 2), only the $HCrO_4^-$ normalized rate constant ($k_{HCrO_4^-}$) falls within the same order of magnitude as k_{ArOH} and in fact the two values are virtually identical for pH 1 and 2 (Table 3.1). This finding strongly suggests that $HCrO_4^-$ is the active Cr(VI) species and is consistent with previous reports.

For the majority of the experiments ionic strength was maintained at 0.1 M. In the excess Cr(VI) experiments above, because of the high concentrations of Cr(VI) used in several of the experiments, the ionic strength was as high as 0.64 M. It was therefore necessary to investigate the influence of ionic strength on the Cr(VI)/4MP oxidation rate in a system of excess Cr(VI). Additions of 0.1, 0.5, 1.0 and 2.0 N $NaClO_4$ or $KClO_4$ to reactions showed no significant effect on the reaction rate and therefore conclude that there is no distinct primary salt effect. Additional experiments were performed with additions of $CrCl_3$ to the reaction solution. The presence of Cr(III) had no inhibitory effect on the rate of Cr(VI) reduction.

Phenol Speciation Effects. There is also reason to suspect that phenol speciation would have an affect on the reactivity of the phenol as a reductant. The deprotonated anion form of a hydroxylated organic compound has frequently been observed to be more reactive as a reductant than the undissociated neutral form. Investigating a wide variety of phenolic compounds, Tratnyek and Hoigné have shown a reactivity difference of up to 2 orders of magnitude for oxidation by singlet oxygen *(40)* and up to 6 orders of magnitude for oxidation with chlorine dioxide *(44)*. For hexachloroiridate(IV) oxidation of phenol and 2,6-dimethylphenol, Cecil and Littler *(45)* showed that the phenolate species was 6 orders of magnitude more reactive than the phenol. The increased reactivity as reductant of the negatively charged species presumably reflects its higher redox potential. The anion has a higher electron density and hence a higher electron-donating potential. However, phenolate anions are unlikely to be important in the present study. The pK_a values of the phenols used here are typically ≥ 9.0, with the exception of 4-nitrophenol (7.16), vanillin (7.4) (see Table 3.6). Under the acidic conditions employed, solutions were poised at a pH five to nine orders of magnitude below the pK_a of the reactant phenol. Hence, for the pH range studied, concentrations of phenolate were minute (< 0.001 %) and the concentration of the undissociated phenol was essentially constant. At pH 5 values the phenolate anion would have to be at least five orders of magnitude more reactive, and at pH 2 eight orders of magnitude more reactive than the undissociated phenol to significantly affect the overall reaction.

Similarly, the possibility that the protonated phenol species, $ArOH_2^+$, contributes to the overall reactivity will depend on its concentration and reactivty. Values for the dissociation constant, $ROH_2^+ = ROH + H^+$; K_{diss}, for aliphatic alcohols have been estimated to be 10^3-10^5 M *(46)*, and a value of 3.63 M for phenol has been reported *(39)*. If we take this value for phenol to represent an order of magnitude approximation for the other phenols studied here, concentrations of the protonated phenol species would be 3 - 0.0003 % in our systems at pH 1 to 5 respectively. For conditions ≥ pH 3, the protonated species would have to be 4 orders of magnitude more reactive than the neutral phenol and probably contributes little to the overall system. At pH < 3 however, there is no a priori reason to discount significant contribution of reaction pathways involving $ArOH_2^+$. Overall, while parallel reaction pathways involving the phenolate or protonated phenol species are possible, within the pH range examined, changes in phenol speciation are small and there is no independent means of isolating the reaction rates of individual species. Moreover, because the concentration of the neutral phenol is nearly equal to the total concentration of phenol, results have been interpreted in terms of the concentration of total phenol.

pH Effect. Reaction rates displayed a pronounced dependence on the acidity of the solution. Half-lives of pH 1 reactions were on the order of seconds to minutes, while half-lives increased to hundreds of minutes at pH 3, and a month or more at pH 5 (Figure 3.7).

The empirical reaction order with respect to $[H^+]$ for a given initial concentration of oxidant and reductant can be derived from the slope of a plot of log k_{exp} (or log k_{ArOH}) versus log $[H^+]$. Log plots for reactions with excess phenols did not exhibit a linear relationship or simple order with respect to $[H^+]$ within the pH range studied (Figure 3.8). Comparing rates of reaction with Cr(VI) for a selection of substituted phenols also shows that the proton dependence is significantly different for each substitution. Plots of log k_{ArOH} versus pH for 4-methyl-, 4-methoxy-, and 2,6-dimethoxyphenol display a consistent trend of increasing rates with increasing $[H^+]$, but these plots, the slopes of which represent the empirical reaction order with respect to the proton, have varying degrees of curvature (Figure 3.8). At the lower end of the pH range examined (pH 1-2), the apparent reaction order with respect to $[H^+]$ approaches 2 for all three compounds. The reaction order decreases non-linearly with increasing pH approaching values of 0.18, 0.46, and 0.51 at pH 5 for 2,6-dimethoxy, 4-methoxy, and 4-methylphenol respectively.

These results elicit two observations about proton ivolvement in the reaction. First, while there is no inherent reason why the reaction order with respect to $[H^+]$ should be an integer value *(47)*, the pH dependence of the empirical reaction order suggests the presence of a rapid acid-base equilibrium involving the reactants, or the involvement of parallel reaction pathways involving different numbers of hydrogen ions. The effects of the former interpretation are only important in a pH-region close to the pK_a of the reactant in question, usually $(pK_a - 2) < pH < (pK_a + 2)$. For the pH-region studied, only the $HCrO_4^-/CrO_4^{2-}$ acid-base equilibrium

$$HCrO_4^- = H^+ + CrO_4^{2-} \qquad pK_a = 6.52 \qquad (4)$$

meets this general criterion, but only for pH > 4. Hence, an antecedent protonation and subsequent reaction of $HCrO_4^-$ may effect the apparent reaction order at higher pH, but it is not likely to be responsible for the changing proton dependence observed for pH 1 - 4. In this pH-region, parallel reaction pathways involving different numbers of protons is the most likely explanation of reaction order dependence.

Secondly, if $HCrO_4^-$ is the reactive Cr(VI) species, and the reactivity of the proton was associated with the Cr(VI) reactant alone, for example, in a pre-oxidation deprotonation of $HCrO_4^-$ (i.e., $HCrO_4^- = H^+ + CrO_4^{2-}$), a uniform pH dependence among the phenols would be expected. Consequently, the different empirical order curves we observed here imply that some or all the proton reactivity involves interaction with the phenolic reactant or a reaction intermediate.

The exact formulation of the proton dependence will inevitably rely on mechanistic considerations. Possible reaction mechanisms are discussed in detail elsewhere (Chapter 4), but one additional mechanistic aspect related to the role of the proton became apparent from the these rate studies. Because of the strong pH dependence of the Cr(VI)/phenol reactions, we explored the possibility of acid catalysis. Reactions were conducted with equimolar concentrations of Cr(VI) and 4MP in pH 1.0 solutions of H_3PO_4, H_2SO_4, HCl, and $HClO_4$ without additional buffer. The solutions containing the strong, completely dissociated acids HCl, H_2SO_4, and $HClO_4$ all reacted at the same rate (Figure 3.9). Reactions with H_3PO_4 proceeded more rapidly. H_3PO_4 is not completely dissociated at pH 1 and so has a higher concentration of total acid (approx. 1.4 M). Because the proton concentation is the same for both the strong acid and weaker acid systems, faster rates with the H_3PO_4 system must be due to general-acid catalyzing effects of the undissociated form of the Brønsted acid (H_3PO_4). At lower concentrations of total phosphate buffer (0.05 M), no general catalysis was observed. Reactions at pH 1 and pH 2 in $HClO_4$ showed no difference in rates with the addition of 0.05 M total phosphate. So while the reactions are subject to general-acid catalysis, lending a potentially important mechanistic detail, at the concentrations of phosphate buffer used in most experiments, general-acid catalysis was minimal and complications of accounting for the general-acid catalyzed pathways are moot.

Temperature Effects. The temperature dependence of Cr(VI) reduction in the Cr(VI)/4MP system was studied in the range 288 - 308 K. Reactions were conducted with an excess of reductant and a fixed pH. Pseudo-first-order rate constants, k_{exp}, were determned for pH 1.0, 2.0, and 3.0 and for t = 15°, 25°, 35°C. Activation enthalpy and entropy ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) were calculated from eq 5

$$k_{\text{exp}} = \frac{kT}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} \qquad (5)$$

by plotting ln (k_{exp}/T) versus $1/T$ *(48)* (Figure 3.10, Table 3.3). There are no representative values for the Cr(VI)/methylphenol system in the literature, but for comparison, activation parameters for similar systems are included in Table 3.4. Our values are consistent with those reported for other systems employing similar reaction conditions and kinetic analysis, and implies the operation of similar reaction pathways prior to and including the rate limiting step.

Because the [H$^+$] term or its function is not explicitly included in the k_{exp} values, the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ must be taken as composite values for all reactions prior to and including the rate-limiting step *(46)*. As such, they may not describe the activation energy of an elementary reaction step. However, these values provide an opportunity to compare the thermodynamic effect of varying the system pH. It may be noted that all $\Delta S^\ddagger$ values are very similar and are independent of the initial proton concentration, whereas $\Delta H^\ddagger$ values increase with initial pH. One possibility for this behavior is the presence of specific acid catalysis. By definition, a catalyst lowers the activation energy of the reaction ($\Delta H^\ddagger$) without affecting the overall thermodynamics (i.e., $\Delta G^0_{\mathrm{rxn}}$) *(50)*. An alternative explanation of the apparent shift in $\Delta H^\ddagger$ is the already proposed hypothesis of parallel reaction pathways. Increasing activation energy associated with increasing pH is due to a gradual shift in the relative contribution of low energy and higher energy pathway(s). From the kinetic evidence alone, however, neither explanation can be adopted conclusively.

Stoichiometry. The overall stoichiometry of the Cr(VI)/phenol reaction is complicated by a possibly multi-step mechanism and a potential for side reactions involving primary reaction products, in particular phenoxy radical and cation species that will be discussed in the following chapter. To minimize the influence of side reactions, calculations were limited to data corresponding to approximately the first 50% of the reaction. For a 1:5 (mM) initial ratio of Cr(VI) to 4-methylphenol, the reaction stoichiometry Δ[Cr(VI)]/Δ[4MP] was calculated from the slope of plots of [Cr(VI)] versus [4MP]. The value of Δ[Cr(VI)]/Δ[4MP] was very close to 2/3. Reactions with 4-methoxyphenol displayed the same stoichiometry (for reactions conducted at equimolar initial concentrations). These results suggest that, on an average, each phenol molecule is oxidized by two electron equivalents for each Cr(VI) reduced to Cr(III). The net mean oxidation of the phenol could correspond to a single two-electron transfer, or to two succesive one-electron transfers. When equimolar initial conditions (5mM) of Cr(VI) and 4MP were used, a consistent 1:1 stoichiometry was observed within the initial 50+% of the reaction. A 1:1 stoichiometric ratio implies that each organic molecule is oxidized by an average of three electron equivalents, and therefore indicates products that are more oxidized than the reaction in which the ratio is 2:3. Apparently the five-fold decrease in the relative concentration of the organic leads to its more complete oxidation. Because the reaction is first-order in [Cr(VI)] and [phenol] for both extreme cases of excess oxidant and excess reductant, the net stoichiometry leading up to the activated complex associated with the rate-limiting πstep is probably a constant 1:1 ratio. Changes in the overall stoichiometry must therefore be due to reaction steps involving reaction intermediates that occur after the rate limiting step.

Empirical Rate Expression. The experimental results indicate a first-order dependence of both Cr(VI) and phenol concentrations and the order with respect to $[H^+]$ varied between 0.2 and 2. These findings are in accord with a second-order rate expression

$$-d[\mathrm{Cr(VI)}]/dt = k_{\mathrm{ArOH}}[\mathrm{Cr(VI)}]_m[\mathrm{ArOH}] \qquad (6)$$

where $[\mathrm{Cr(VI)}]_m$ and [ArOH] denote the total concentration of monomeric Cr(VI) and phenol respectively, and the empirical second-order rate constant, k_{ArOH}, is a function of pH. At a constant pH, eq 6 and a suitable value of k_{ArOH} will give a good prediction of the rate of chromate reduction. A empirical rate expression of this form is practical from a computational perspective. Its mathematical simplicity underscores the ease to which it can be incorporated into transport models. However, the dependence k_{ArOH} on pH is not easily fitted by a mathematical expression simpler than a third degree polynomial. The added complexity of a third degree polynomial for interpolating k_{ArOH} more or less negates the simplicity of the second-order rate expression (eq 6). It is clear that in order to accurately model the transformation rates of Cr(VI) and phenols, a more rigorous model that can account for the pH dependency is necessary. Derivation of a more sophisticated rate law based on mechanistic considerations will be considered in the following chapter.

Substituent Effects/Reactivity Correlation Analysis. The position and composition of ring substituents greatly affects the reactivity of aromatic compounds. We investigated the comparative reactivities of the three isomers of methylphenol to identify the effect of the methyl substituent position on the rates of Cr(VI) reduction. Experiments were carried out under pseudo-first-order conditions ([ArOH] in excess of [Cr(VI)]). Methylphenol isomers substituted at the 2 and 4 positions (ortho and para) exhibited similar reactivities and faster rates of reaction than did 3-methylphenol. For example, at pH 3 and initial [Cr(VI)] of 10 mM, about half of the Cr(VI) was reduced by 2-methylphenol or 4-methylphenol within two days, whereas in the same period less than 20% of the Cr(VI) was reduced by the 3-methylphenol (Figure 3.11). Reactions initiated at pH 5 showed a similar trend in reactivity. The 2- and 4-methylphenol isomers reduced Cr(VI) significantly faster than 3-methylphenol, which was virtually unreactive at pH 5. The greater reactivity of the para and ortho isomers suggest that resonance effects, whether by direct or indirect conjugation with the reaction center, play a more important role than field effects.

Investigations of the effects of structural variations on Cr(VI) reduction rates were expanded to include a total of 14 substituted phenols. Reactions with excess phenol were conducted at pH 2.0. Values of k_{exp} were calculated from first-order kinetic plots and second-order rate constants (k_{ArOH}) calculated as before, eq 2. Comparison of the second-order rate constants for the 14 phenols shows that k_{ArOH} values range approximately five orders of magnitude (Table 3.5). A general reactivity trend of methoxy-substituted > methyl-substituted > unsubstituted > chlorophenol > nitrophenol is evident. Reactivity also tended to increase with an increased degree of substitution.

Two considerations were made concerning activity correlation analysis. First, could a successful correlation be found that provided valid reactivity estimates for phenols not included in the study? Second, could the relationship provide any insight into the reaction mechanism? Correlations based on half-wave potentials ($E_{1/2}$) have been applied to several phenol-oxidation systems including oxidations by singlet oxygen *(40)* and

Mn(III,IV) *(47)*. Half-wave potentials are an experimentally derived redox parameter and are believed to represent the first one-electron oxidation potential of the phenol. Half-wave potentials were taken from Suatoni *et al.* *(54)* who reported $E_{1/2}$ values for 40 substituted phenols determined by anodic voltometry in 50% aqueous isopropanol buffered at pH 5.6 in 0.5 M acetate buffer. For the Cr(VI) system, application of $E_{1/2}$ as a predictor variable gave a good correlation (Figure 3.12, Table 3.5).

$$\log k_{\mathrm{ArOH}} = (-16.87 \pm 1.4)E_{1/2} + (6.25 \pm 0.73) \qquad (8)$$

$$(r^2 = 0.948;\ s = 0.44;\ n = 10)$$

With the exception of three outliers, a very good linear fit is achieved for 10 of our compounds with data ranging five orders of magnitude. This indicates a fairly robust data set and correlation that can be applied to compounds not included in this study. The three points not included in the regression line in Figure 3.12 are all di-ortho substituted phenols and their reactivities are all less than those predicted by their reported $E_{1/2}$. Assuming the hydroxyl group is the reaction center, di-ortho substitution may sterically hinder oxidation by Cr(VI) in such a way that is not reflected in its polarographic $E_{1/2}$ measurement. The possibility of steric effects needs to be examined further. Other correlations that potentially reveal mechanistic information were examined, but are presented in the following chapter.

Relevance to Environmental Systems

The results of this study show that phenolic compounds can reduce Cr(VI) to Cr(III) in aqueous solution under moderately acidic conditions. It is useful to examine the conditions under which these reactions occur in the field and thereby gain some sense of the environmental relevance and applications of these experiments. As discusssed in the introduction, phenols are common industrial chemicals and contamination sites containing both hexavalent chromium and phenolic derivatives are associated with a number of industrial activities. Many chromate-contaminated sites are characterized by high concentrations of contaminants and a high acidity (low pH) localized within one or more plume areas. These plumes often have steep chemical gradients, the spatial distribution of which depends on the constituent. For example, at the United Chrome Products site near

Corvallis, OR, a leaking chrome plating bath created a subsurface environment with highly elevated concentrations of chromium and a near-source pH of approximately 2 *(56)*. However the acidity plume is not spatially coincident with the chromate plume. The plume of high acidity is attenuated by the exchange capacity of the subsoil within tens of meters from the contaminant source while the chromium plume extends approximately a hundred meters down gradient and thereby occurs across a range from pH 2 to pH 7. At many sites the sources of Cr(VI) and phenol contaminants stem from related but spatially distinct industrial processes so the sources are likewise spatially separated and not initially mixed. During subsequent subsurface transport, Cr(VI) and phenol plumes can mix in varying proportions and under greatly varying pH conditions. An empirical rate expression is a useful tool for accounting for the Cr(VI)/phenol reaction at contaminated sites provided it adequately predicts the reaction rate over wide ranges of reactant concentrations and pH. The empirical rate law developed here (eq 6) is robust with respect to [Cr(VI)] and [ArOH] because of the unit order with respect to these reactants over a wide range of concentrations. In an environment in which the pH is well buffered and nearly constant, eq 6 yields reasonable estimates of Cr(VI)/phenol reaction rates for a wide range of solution concentration. However, because the reaction order with respect to $[H^+]$ appears to vary with pH, predictions of reaction rates across a large pH gradient may exhibit a greater degree of uncertainty.

Such complexities notwithstanding, we can use eq 6 and the experimentally determined rate constants to quantify the characteristic time scales of Cr(VI) reduction reactions and put them in the context of time scales of other environmental processes. For example, for concentrations of Cr(VI) and 4-methylphenol in the range of 0.1 M, eq 6 predicts reaction half-lives of 2.7 hours at pH 2 and 25 days at pH 5. For milli-molar concentrations of the same components, resultant half-lives increase to approximately 11 days and 7 years at pH 2 and 6 respectively. Reaction rates also depend strongly on phenol structure. For identical concentrations of mono-, di- and tri-substituted phenols, rates of reactions with a given concentration of Cr(VI) vary by as much as six orders of magnitude, depending on the composition and positioning of phenolic ring substituents (Table 3.5).

Figure 3.13 shows characteristic time scales for these reactions as well as for other environmental processes of interest. One can see that reaction time scales of the reduction of Cr(VI) by substituted phenols span a large range that encompasses the characteristic transport times of both surface and subsurface waters. Re-oxidation of Cr(III) to Cr(VI) is also possible within the time domain of reduction and transport processes.

Conclusions

The reduction of Cr(VI) with various phenolic compounds in aqueous solution follows a general rate law of the form $-d[Cr(VI)]dt = k_{ArOH}[Cr(VI)]_m[ArOH]$, where $[Cr(VI)]_m$ denotes the total concentration of monomeric Cr(VI), [ArOH] is the total concentration of phenol, and k_{ArOH} is dependent on pH. Although we were not able to quantitatively determine a proton dependence that is generally applicable to all phenols, we found evidence that the proton affects the rate by an interaction with the phenol or a reaction intermediate prior to, or probably during, the rate limiting step. Cr(III) does not inhibit the reaction which indicates it has no significant involvement in the rate limiting step. Substituent effects were found to be a major factor in the kinetics of Cr(VI) reduction, causing approximately 6 orders of magnitude difference in reaction rates. In general, compared to the un-substituted phenol, electron-donating substituents (methyl and methoxy groups) increase the reactivity while electron-withdrawing groups (chloro, nitro, and aldehyde) cause decreased reactivity of the phenol. The rates of Cr(VI) reduction correlated well with the half-wave potential ($E_{1/2}$) of the phenol reductant. This structure activity relationship allows at least a semi-quantitative estimate of Cr(VI) reduction rates by other phenol compounds. Our findings of the importance of substituent position and composition may be a useful starting point for detailed investigations of the active Cr(VI) reductant-moieties in natural organic matter. For example, such materials almost certainly contain phenol moieties substituted with methyl, methoxy and aldehyde groups *(57,58)*. Finally, by applying our empirical rate expression to a variety of solution conditions typical of sites contaminated with Cr(VI) and phenols we established characteristic reaction time scales. Cr(VI)/phenol interactions can be expected to occur on the time scales comparable to transport time scales in surface and subsurface waters.

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Table 3.1. Comparison of Apparent Second-Order Rate Constants for Cr(VI) Reduction by 4-Methylphenol and for 4-Methylphenol Oxidation by Cr(VI) at pH 1 and 2, t = 25 °C.

pH	k_{ArOH} ($\mathrm{M^{-1}s^{-1}}$)	$k_{\mathrm{exp}}/[\mathrm{HCrO_4^-}]$ ($\mathrm{M^{-1}s^{-1}}$)
1.0	$5.15 \pm 0.06 \times 10^{-2}$	$5.49 \pm 0.10 \times 10^{-2}$
2.0	$1.10 \pm 0.02 \times 10^{-3}$	$1.03 \pm 0.02 \times 10^{-3}$

Table 3.2. Second-order Rate Constants for Cr(VI) Reduction by 4-Methyl, 4-Methoxy, and 2,6-Dimethoxyphenol at Various Hydrogen Ion Concentrations and 25 °C.

pH	$[\mathrm{H^+}]$ (M)		k_{ArOH} ($\mathrm{M^{-1}\,s^{-1}}$)	
		4-methyl	4-dimethoxy	2,6-dimethoxy
1.00	1.33×10^{-1}	$5.15 \pm 0.06 \times 10^{-2}$		
1.98	1.39×10^{-2}		$2.16 \pm 0.03 \times 10^{-1}$	$4.35 \pm 0.1 \times 10^{-1}$
2.00	1.33×10^{-2}	$1.10 \pm 0.02 \times 10^{-3}$		
2.50	4.21×10^{-3}			$8.58 \pm 0.12 \times 10^{-2}$
2.98	1.38×10^{-3}	$1.21 \pm 0.01 \times 10^{-4}$	$1.59 \pm 0.01 \times 10^{-2}$	$5.40 \pm 0.04 \times 10^{-2}$
3.00	1.33×10^{-3}	$7.14 \pm 0.26 \times 10^{-5}$		
3.87	1.79×10^{-4}		$1.61 \pm 0.05 \times 10^{-3}$	$1.45 \pm 0.01 \times 10^{-2}$
4.85	1.81×10^{-5}	$4.57 \pm 0.04 \times 10^{-6}$	$5.82 \pm 0.05 \times 10^{-4}$	$7.28 \pm 0.08 \times 10^{-3}$
6.01	1.24×10^{-6}		$1.91 \pm 0.03 \times 10^{-4}$	$4.80 \pm 0.06 \times 10^{-3}$

Table 3.3. Activation Data for Cr(VI) Reduction by 4-Methylphenol at pH values of 1, 2, and 3. $[Cr(VI)]_o$ = 0.5 mM, [4MP] = 0.05 M, t = 15-35 °C.

$[H^+]$ (mol l^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	± s.d.	$\Delta S^\ddagger$ (J K^{-1} mol^{-1})	±s.d.
1.288×10^{-1}	35.0	1.6	-183.4	1.0
1.273×10^{-2}	42.3	1.1	-185.1	0.8
1.273×10^{-3}	54.9	1.7	-181.6	0.8

Table 3.4. Comparison of Activation Data for Cr(VI) Reduction Reactions by Compounds with Hydroxyl or Sulfhydryl Functional Groups.

Reductant	$\Delta H^\ddagger$ (kJ mol^{-1})	$-\Delta S^\ddagger$ (kJ K^{-1} mol^{-1})	Reference
4-methylphenol	35 - 54	181 - 185	this work
ethanol	49.0	120.2	29
isopropyl alcohol	53.2	107.7	29
benzyl alcohol	26.6	180.8	29
triphenylcarbinol	49.4	105.0	43
benzhydrol	24.7	155.2	43
glutathione	29	167	49

Table 3.5. Second-Order Rate Constants, pK_a Values, and Half-Wave Potentials ($E_{1/2}$) for Cr(VI) Reductions by Substituted Phenols.

compound	phenol derivative	k_{ArOH} ± s.d. (M^{-1} s^{-1})	pK_a [a]	$E_{1/2}$ (V vs. SCE)[b]
1	phenol	$2.63 \pm 0.06 \times 10^{-5}$	10.00	.633
2	4-methyl	$1.17 \pm 0.01 \times 10^{-3}$	10.28	.543
3	2,4-dimethyl	$9.37 \pm 0.08 \times 10^{-3}$	10.60	.459
4	3,4-dimethyl	$2.84 \pm 0.05 \times 10^{-3}$	10.36	.513
5	2,6-dimethyl	$1.23 \pm 0.01 \times 10^{-3}$	10.62	.427
6	2,4,6-trimethyl	$5.30 \pm 0.04 \times 10^{-3}$	10.86	.389 [c]
7	4-methoxy	$2.18 \pm 0.04 \times 10^{-1}$	10.21	.406
8	2,6-dimethoxy	$4.35 \pm 0.18 \times 10^{-1}$	9.63 [d]	.317
9	3,4-dimethoxy	3.75 ± 0.055	9.80 [d]	.392 [c]
10	3,5-dimethoxy	$2.54 \pm 0.02 \times 10^{-4}$	9.35	.605 [c]
11	2-methoxy-4-aldehyde	$1.12 \pm 0.01 \times 10^{-4}$	7.40	.597 [c]
12	2-methoxy-4-methyl	$3.84 \pm 0.02 \times 10^{-1}$	10.28	.371
13	4-chloro	$2.26 \pm 0.03 \times 10^{-5}$	9.41	.653
14	4-nitro	unreactive $< 10^{-7}$	7.16	.924

[a] pK_a values from refs 52 and 53 unless otherwise noted. [b] $E_{1/2}$ values from ref 54 at pH 5.6 in 50% aqueous isopropyl alcohol and 0.5 M acetate buffer. [c] $E_{1/2}$ values estimated from additivity of $\Delta E_{1/2}$ values (ref 54). [d] Value from ref 55.

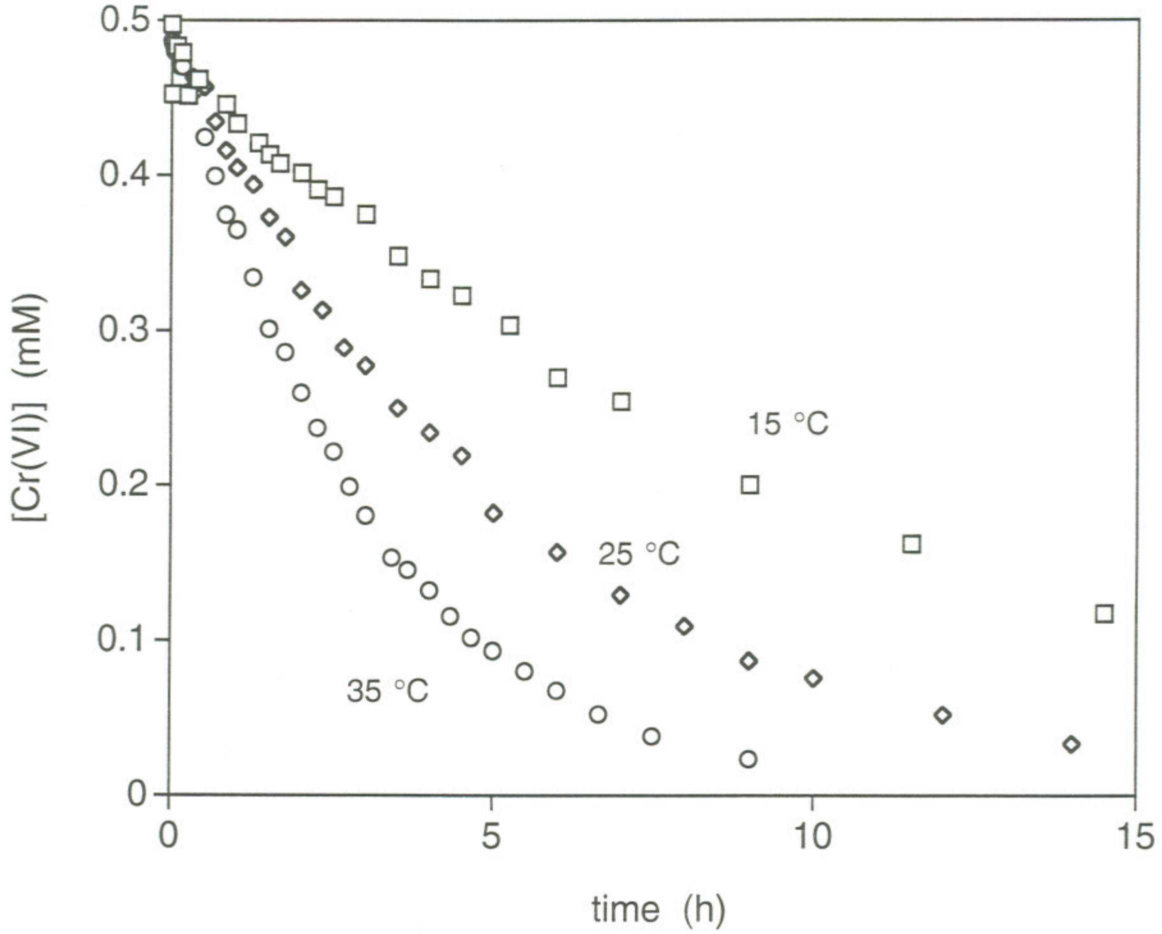


Figure 3.1. Reduction of Cr(VI) by 4-methylphenol at pH 2.0 showing concentration of Cr(VI) as a function of time for three reaction temperatures, 15, 25, and 35 °C. $[Cr(VI)]_o = 0.5$ mM; $[4MP] = 0.05$ M; $I = 0.1$ M.

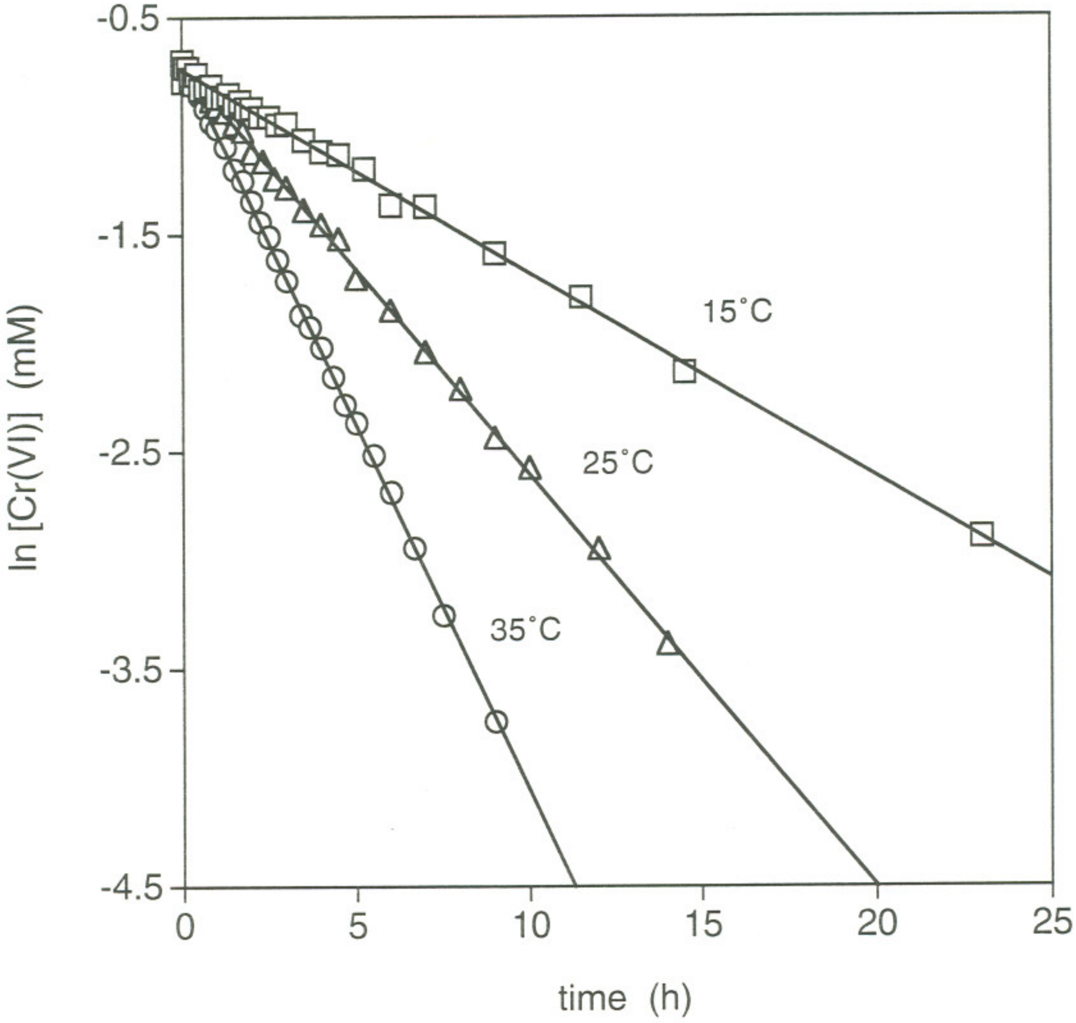


Figure 3.2. Pseudo-first-order rate plots of ln of the Cr(VI) concentration versus time for Cr(VI) reduction by excess 4-methylphenol for 15, 25, and 35 ˚C. Slopes of the lines are equal to the pseudo-first-order rate constants k_{exp}. Correlation coefficient, r^2, values from linear regression calculations were all > 0.999. Reactions were performed at pH 2.0 and $I = 0.1$ M. $[\text{Cr(VI)}]_o = 0.5$ M.

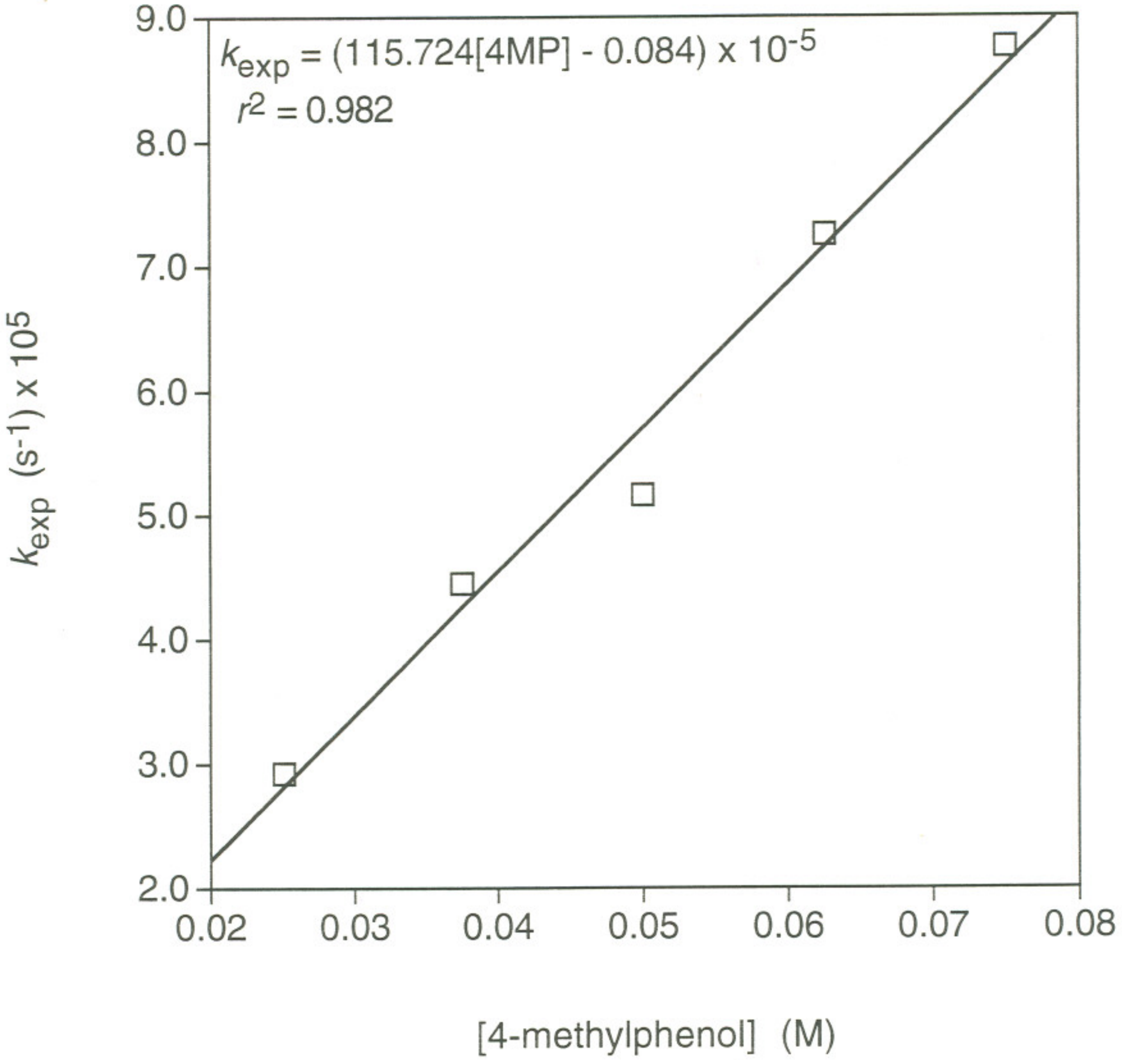


Figure 3.3. Linear plot of pseudo-first-order rate constants, k_{exp}, as a function of 4-methylphenol concentration for Cr(VI) reduction at pH 2.0 and 25 °C. $[Cr(VI)]_o$ = 0.5; [4-methylhenol] = 0.025, 0.0375, 0.05, 0.065, 0.075 M.

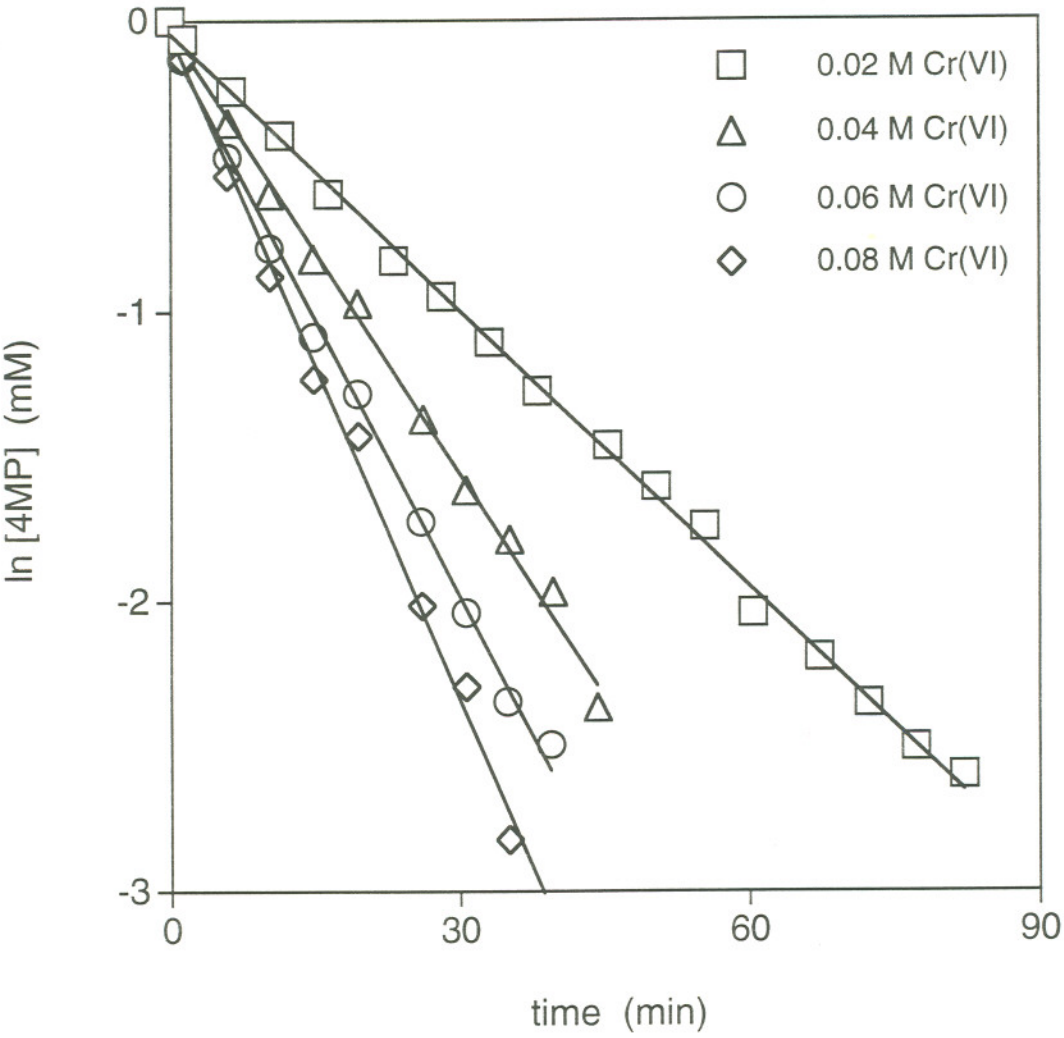


Figure 3.4. Pseudo-first-order linearization of 4MP oxidations of by various concentrations of excess Cr(VI). Reaction half-lives, $t_{1/2}$ (min) (calculated as ln $2/k_{\mathrm{exp}}$), and correlation coefficient r^2 were calculated from linear regression analysis. 0.02 M - 21.7, 0.998; 0.04 M - 13.6, 0.996; 0.06 M - 11.0, 0.996; 0.08 M - 9.1, 0.997. pH 1.0; 25 °C.

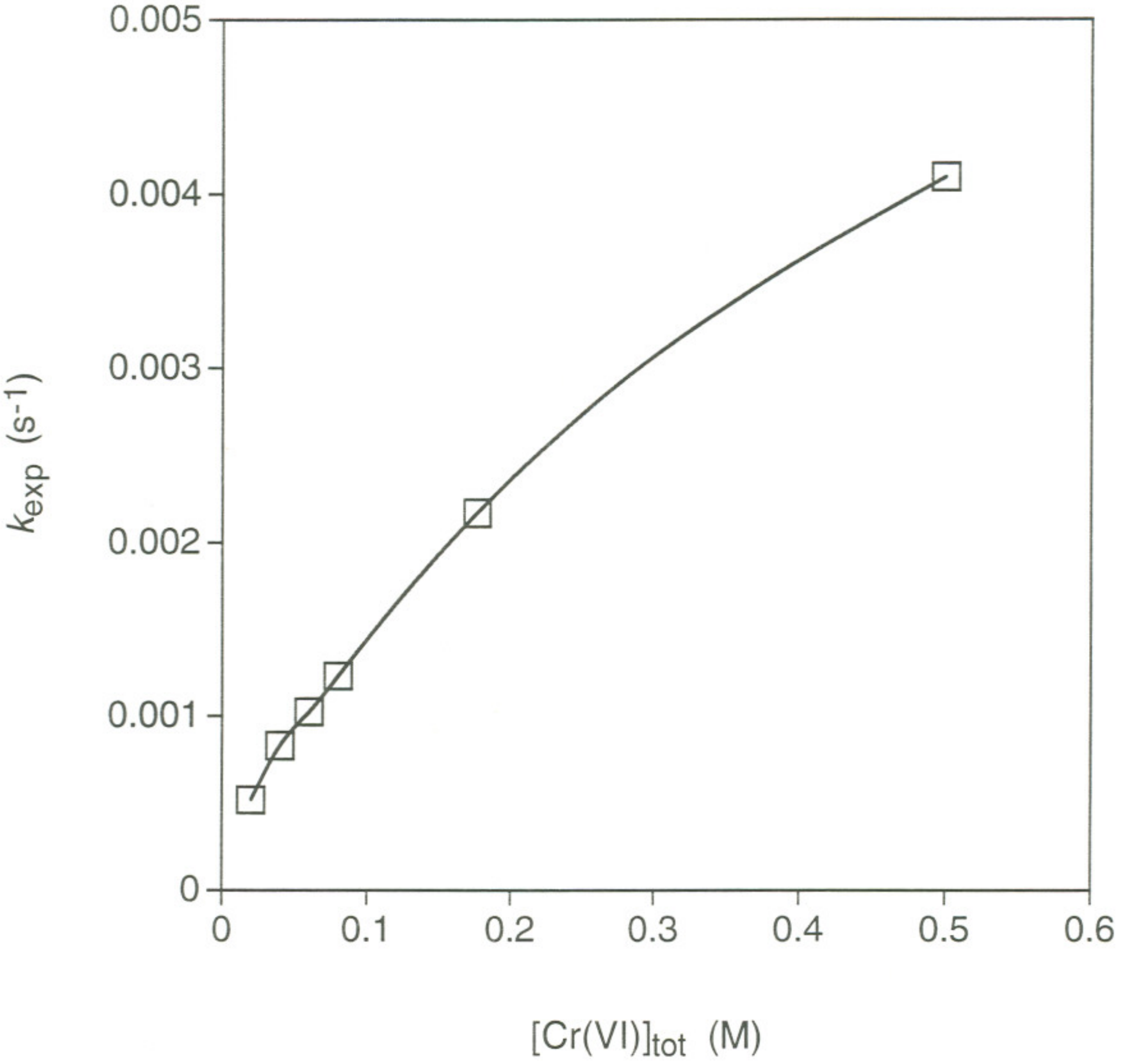


Figure 3.5. Dependence of the pseudo-first-order rate constant, k_{exp}, on the total Cr(VI) concentration for the oxidation of 4MP at pH 1.0 and 25 °C.

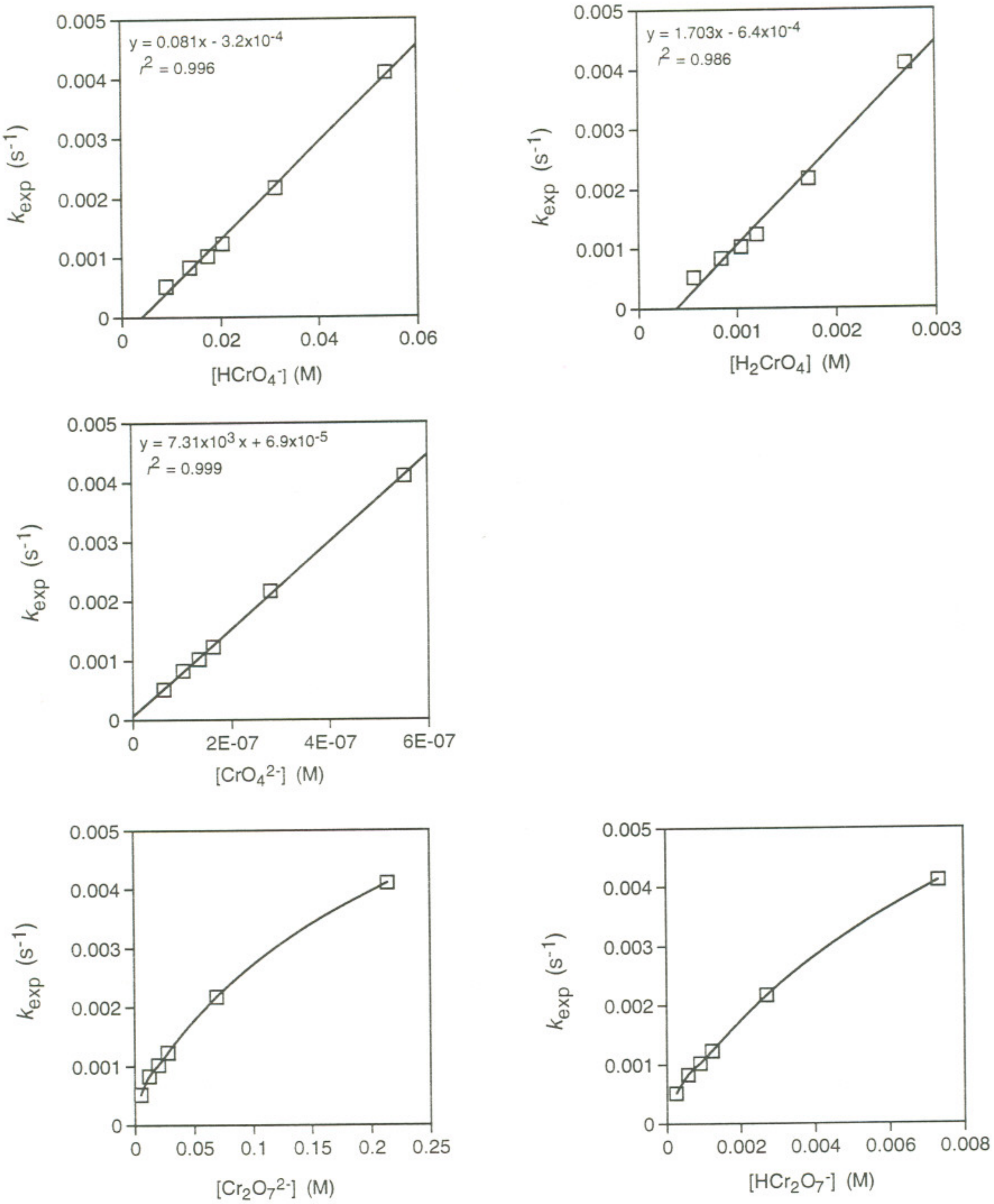


Figure 3.6. Plots of k_{exp} as a function of the concentration of individual Cr(VI) species $HCrO_4^-$, H_2CrO_4, CrO_4^{2-}, $Cr_2O_7^{2-}$, $HCr_2O_7^-$. Equilibrium constants for speciation calculations taken from ref 28 with activity corrections calculated from the Davies equation (ref 17).

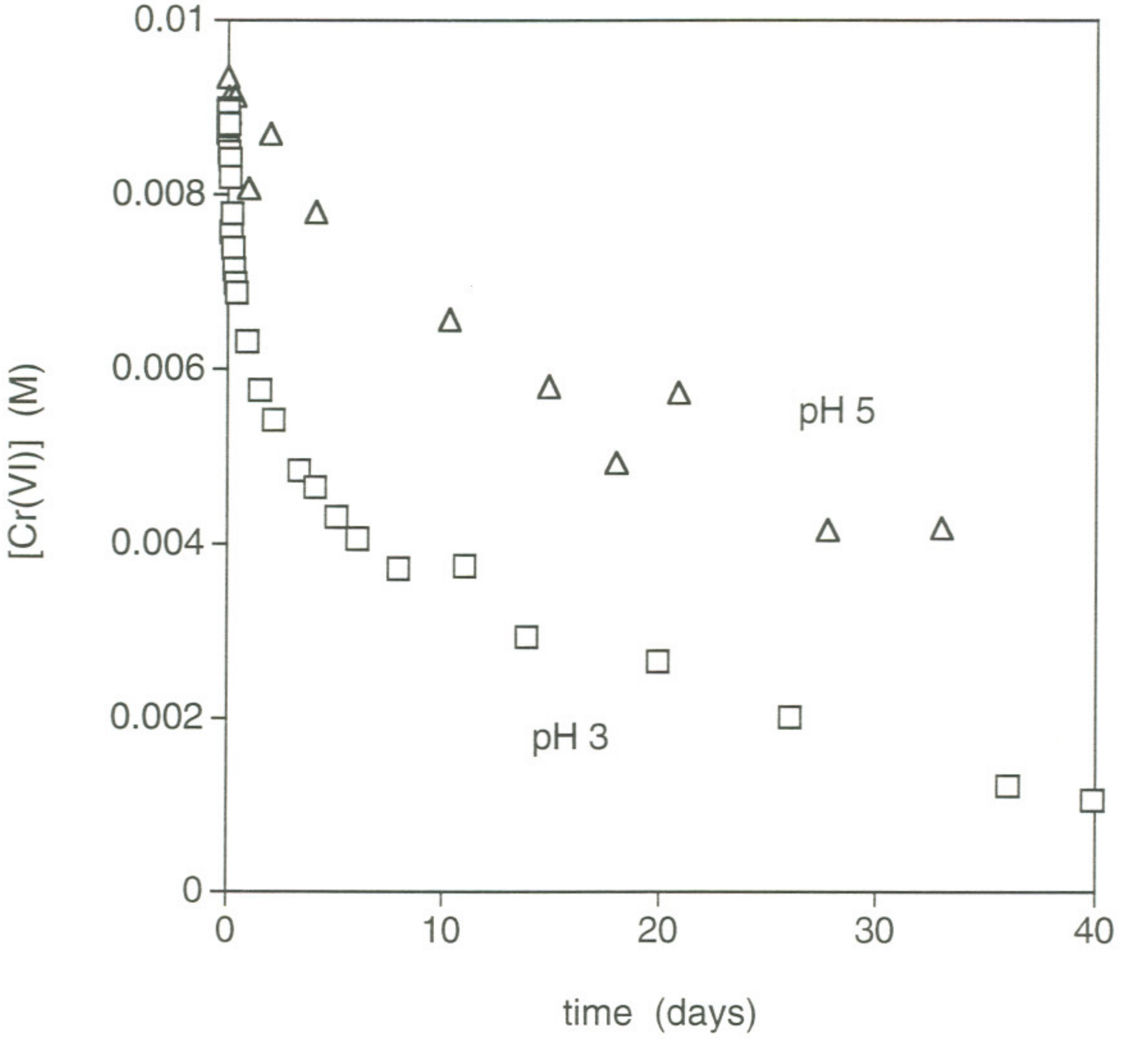


Figure 3.7. Reduction of Cr(VI) by 4MP at pH 3.0 and pH 5.0. Cr(VI) versus time. [4MP] = 0.19 M; $[Cr(VI)]_o$ = 10.0 mM; t = 25 °C. Reactions at pH 1 not shown.

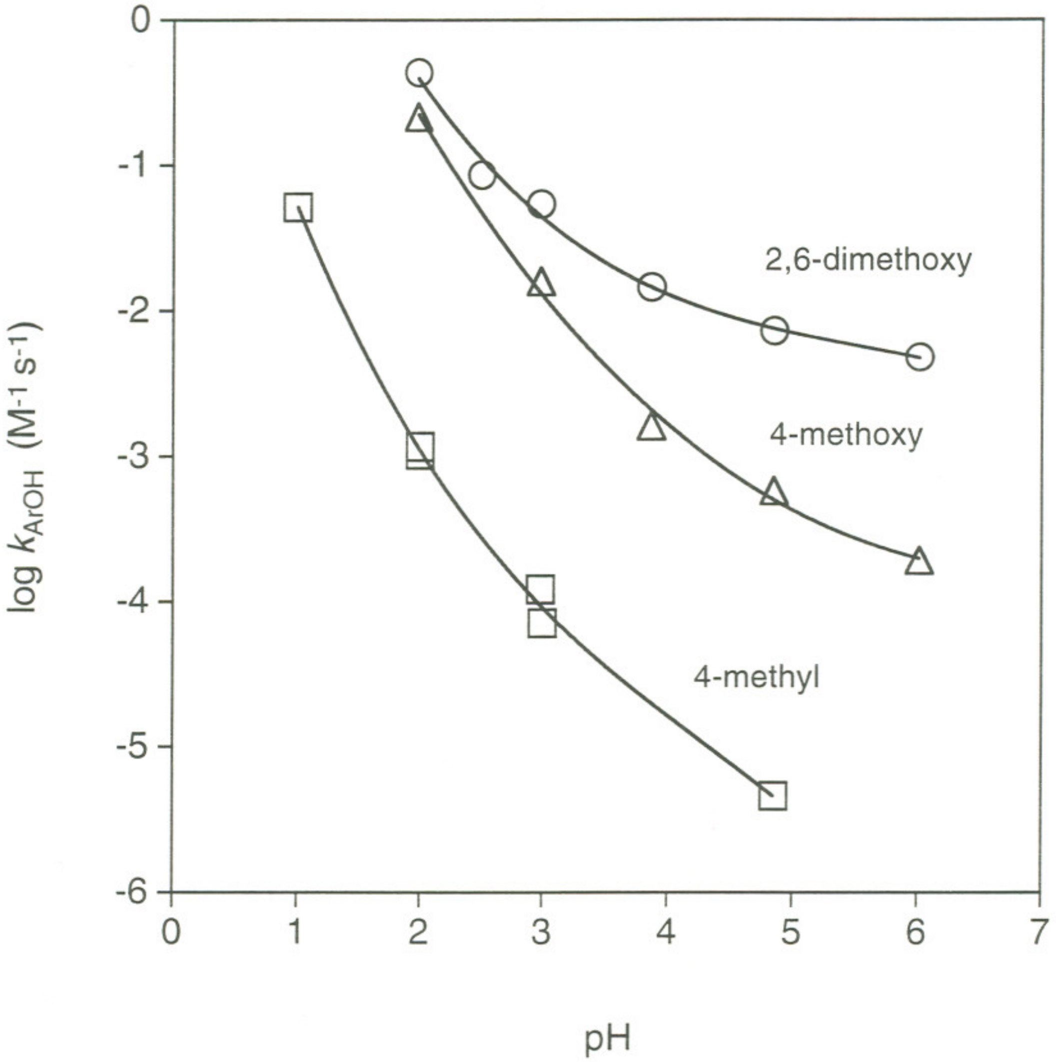


Figure 3.8. Plots of log k_{ArOH} versus pH for the reduction of Cr(VI) by excess 4-methyl-, 4-methoxy-, and 2,6-dimethoxyphenol. Slopes of the fitted curves indicate the empirical reaction order with respect to $[H^+]$. $t = 25\ ^\circ C$; $I = 0.1$ M.

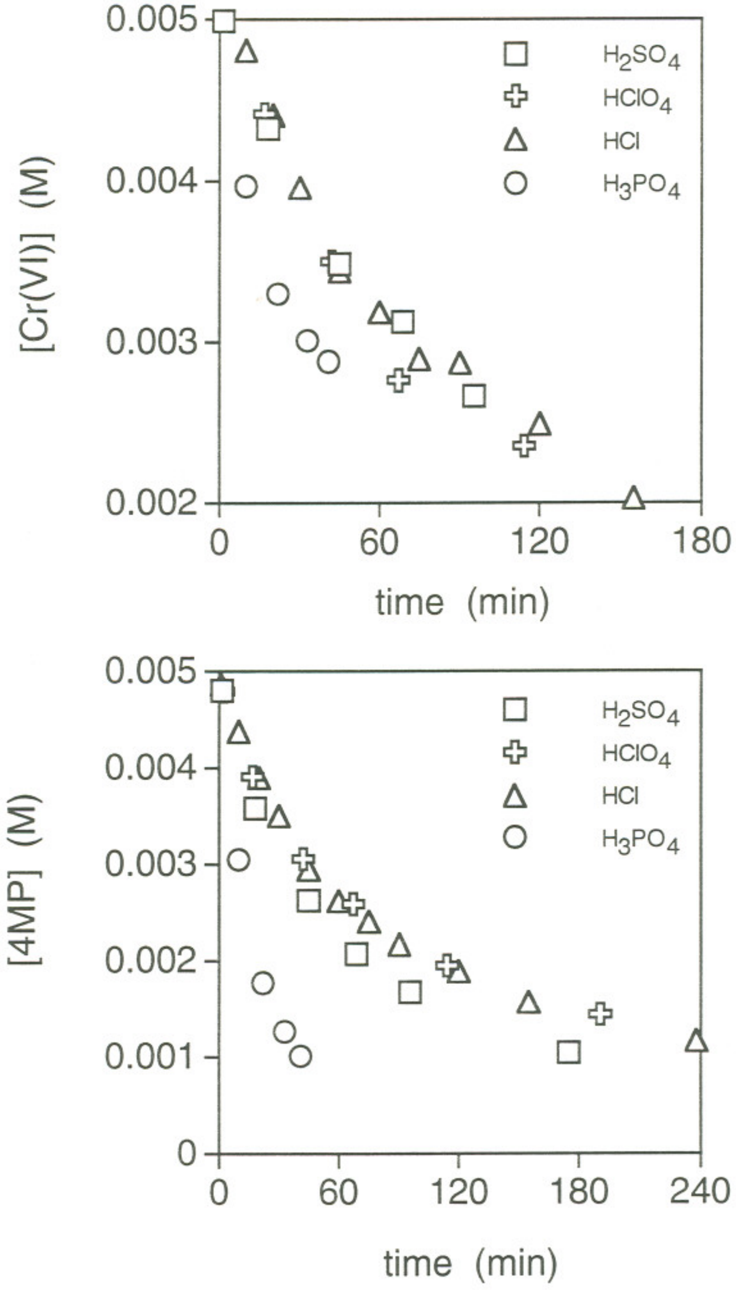


Figure 3.9. Plots of concentration versus time for the equilmolar reaction of 4-methylphenol and Cr(VI) in pH 1.0 solutions of various mineral acids. (A) [Cr(VI)] vs. time. (B) [4MP] vs. time. Initial concentrations of 4MP and Cr(VI) were 5.0 mM. Total concentrations of the acids were approximately: $[HClO_4] = 0.13$ M; $[HCl] = 0.13$ M; $[H_2SO_4] = 0.23$ M; $[H_3PO_4] = 1.4$ M.

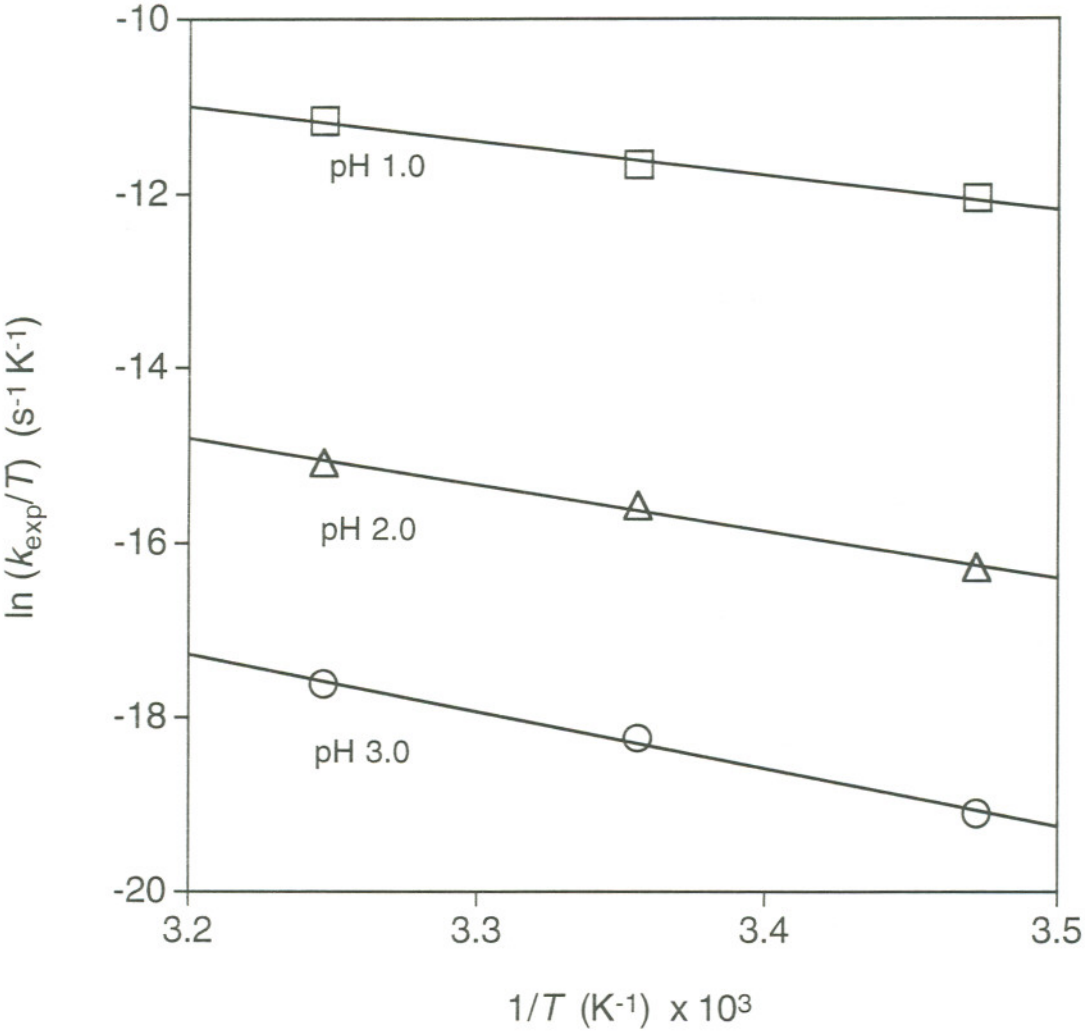


Figure 3.10. Influence of reaction temperature on the observed first-order rate constants for Cr(VI) reduction by 4MP. Plots of log (k_{exp}/T) against $1/T$ for 15, 25, and 35 °C and pH 1, 2, and 3. Curves fitted by a weighted least-squares linear regresssion. Heats ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) of activation calculated from the slopes and intercepts. [4MP] = 0.05 M; $[\mathrm{Cr(VI)}]_o = 0.5$ mM; $I = 0.1$ M.

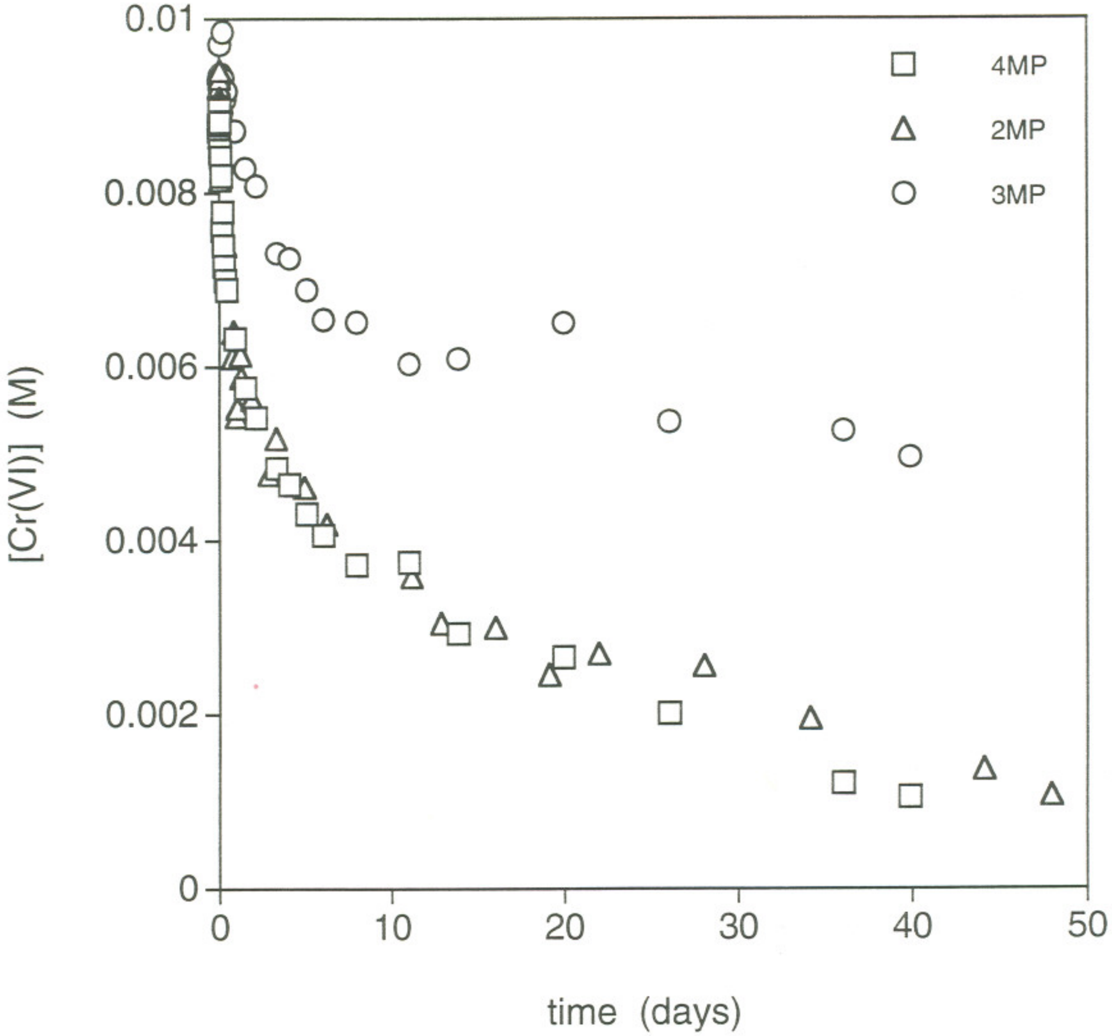


Figure 3.11. Comparison of the reduction of 10.0 mM Cr(VI) by the three methylphenol isomers at pH 3.0 and 25 °C. $[Cr(VI)]_0$ = 10.0 mM; [ArOH] = 0.19 M.

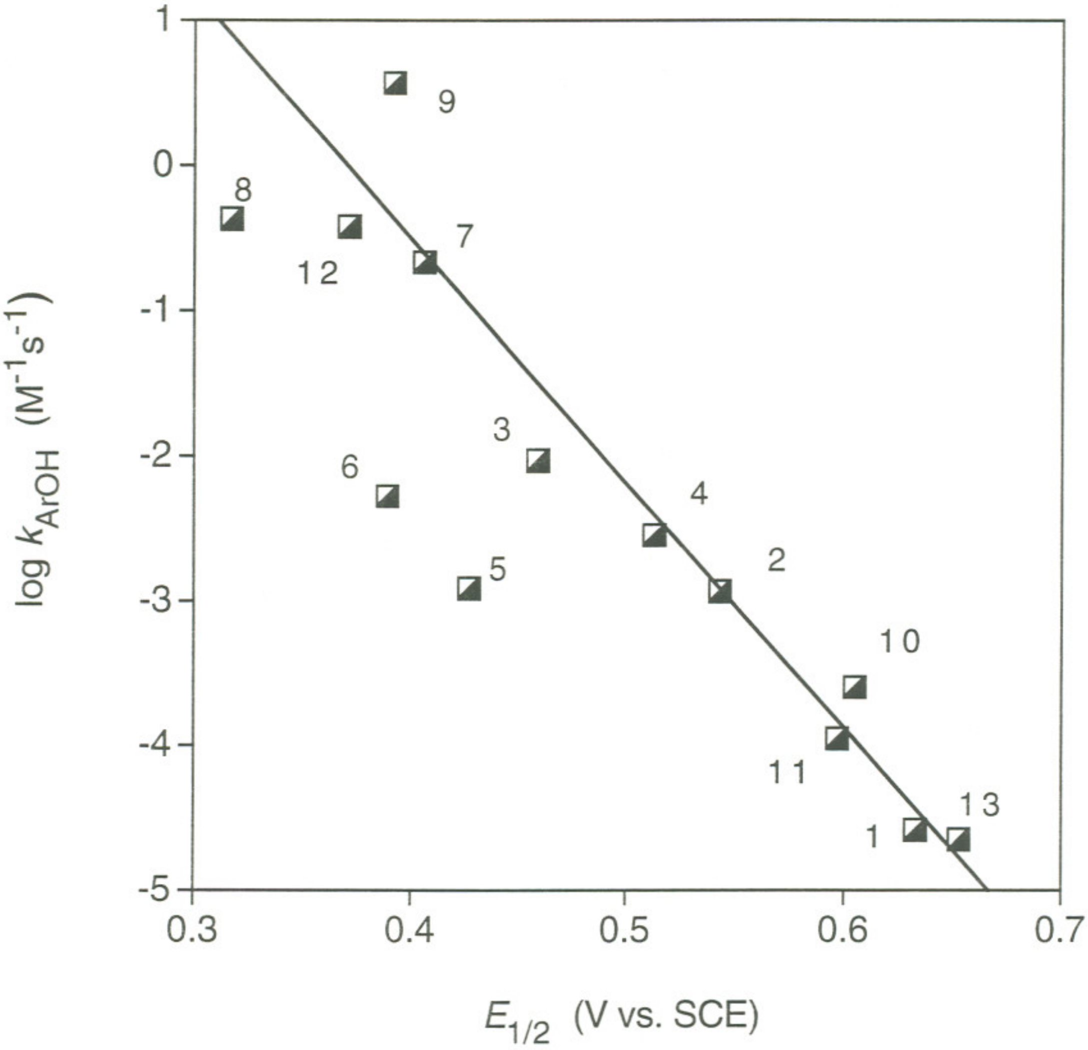


Figure 3.12. Correlation plot of log k_{ArOH} versus $E_{1/2}$ (V vs. SCE) for the reduction of Cr(VI) by various substituted phenols at pH 2.0 and 25 °C. The numbers identify the compound and the corresponding data are shown in Table 3.5. A least-squares linear regression analysis for all compounds excluding 2,6-dimethylphenol (5), 2,4,6-trimethylphenol (6), 2,6-dimethoxyphenol (8), and 4-nitrophenol (not shown) gave a correlation coefficient (r^2) of 0.948. $E_{1/2}$ values taken from ref 54.

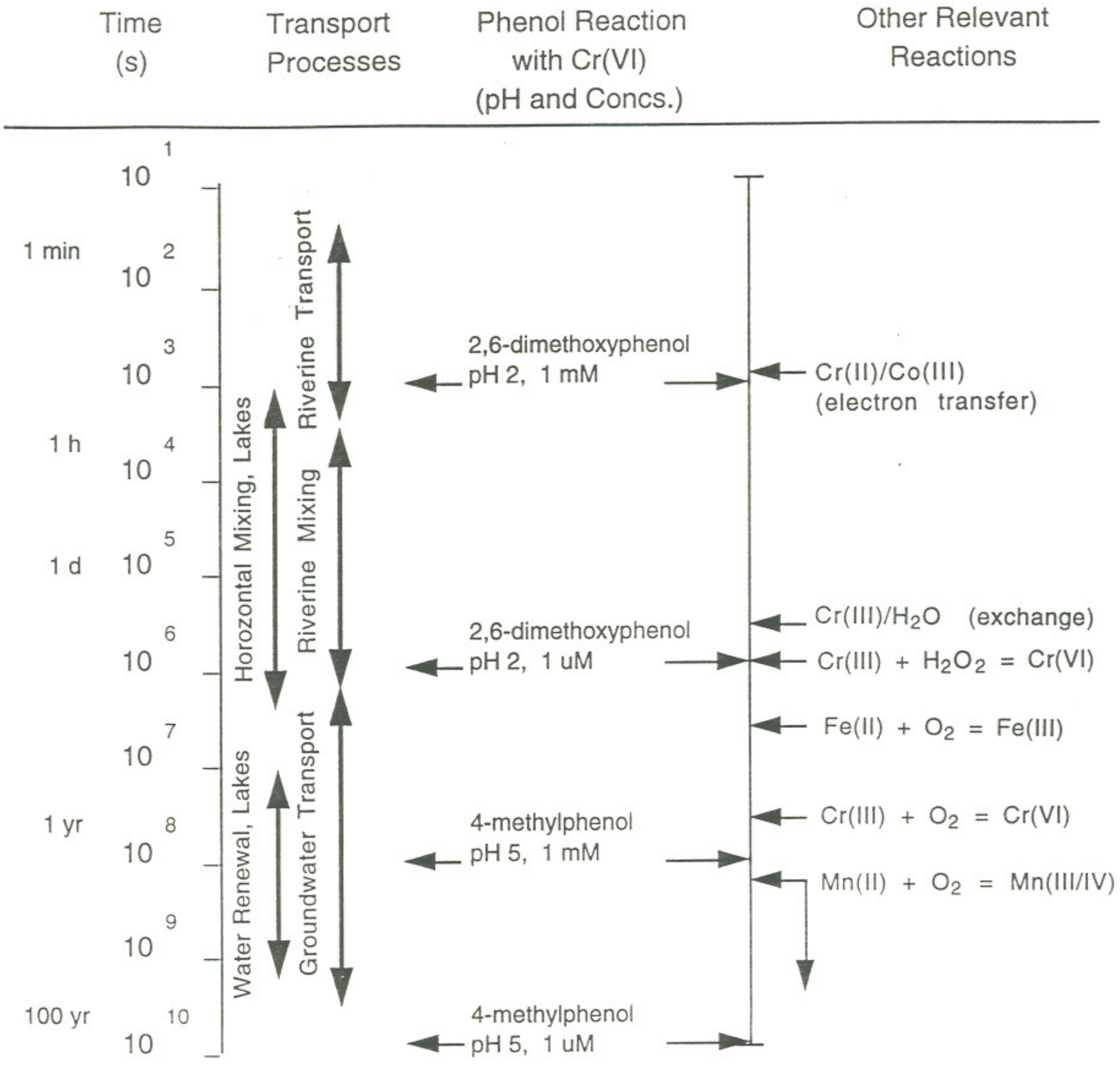


Figure 3.13. Schematic diagram for characteristic time scales of chromium reduction by substituted phenols, major environmental transport processes, and related environmental reactions. Figure adapted from ref 47.

CHAPTER 4

Redox Interactions of Cr(VI) and Substituted Phenols: Products and Mechanism

Abstract

The mechanisms of oxidation-reduction interactions between Cr(VI) and substituted phenols in aqueous solution were characterized by a combination of kinetic analysis and measurements of reaction products and transient intermediates. We have developed a model of the mechanism that successfully predicts reaction rates over a wide range of solution conditions and which is consistent with the observed reaction products. The redox interaction proceeds via a rapid, pre-oxidative equilibrium formation of chromate-ester between $HCrO_4^-$ and undissociated ArOH. Formation of ester intermediates was observed under reaction conditions for which Cr(VI) reduction was negligible. The subsequent rate-limiting decomposition of the ester complex is proton dependent and proceeds via an inner-sphere electron transfer. The overall rate dependence on $[H^+]$ can be explained by three parallel redox pathways involving zero, one, and two protons. The principal pathway at low pH (≤ 2) involves two protons. At $2 < pH < 4$, the single-proton pathway dominates, and at $pH \geq 5$ the proton independent pathway governs the system. The rate law thus derived

$$\text{Rate} = \{k_0 + k_1[H^+] + k_2[H^+]^2\}[\text{ester}] \qquad \text{(i)}$$

$$= \{k_0 + k_1[H^+] + k_2[H^+]^2\}K_e[HCrO_4^-][ArOH] \qquad \text{(ii)}$$

was fitted to rate data for 4-methyl-, 4-methoxy-, 2,6-dimethoxy-, and 3,4-

dimethoxyphenol in the pH range 1 to 6. The resulting model parameters are internally consistent over a wide range of reaction conditions. The model predicts a sharp decline in reaction rates at pH ≥ 6, which is beyond the range of the original calibration. When reactions were conducted at pH 7, the observed rates agreed well with the rates calculated *a priori*. Such evidence suggests that the proposed mechanistic formulation is a robust and accurate description of the system.

Rate constants derived from the model were shown to correlate with Hammett-type substituent parameters. Unstable Cr intermediates (Cr(IV) and Cr(V)) were not observed at measurable concentrations and suppression of either species using scavengers had no effect on overall reaction rates. A survey of significant oxidation products of reactions at pH 2 indicated that both one- and two-electron pathways were operative with the latter being predominant.

Introduction

Millions of tons of hexavalent chromium contaminate the environment at dozens of sites in the U.S *(1)*. Risk assessment for this contamination must account for chromium's ability to undergo redox transformations between two environmentally stable oxidation states, Cr(VI) and Cr(III), that exhibit very different toxicities and mobilities in the environment. Numerous inorganic and organic compounds can reduce Cr(VI) to Cr(III). In particular, hydroxylated organics have been shown to be highly reactive with Cr(VI) in aqueous systems. Because phenols are a prevalent constituent of natural organic matter as well as a common component of industrial waste streams, their interaction with Cr(VI) constitutes an important environmental redox reaction whose dynamics are not well understood.

In the previous chapter, we reported on kinetic investigations of the redox interactions between Cr(VI) and substituted phenols. We found that within the concentration and pH range examined, Cr(VI) reduction occurred on time scales ranging from minutes to months. The reaction was first-order with respect to concentrations of both

Cr(VI) and the phenol reductant and the rate increased with increasing solution acidity. We developed an empirical rate expression, $-\mathrm{d}[\mathrm{Cr(VI)}]/\mathrm{d}t = k_{\mathrm{ArOH}}[\mathrm{Cr(VI)}]_{\mathrm{m}}[\mathrm{ArOH}]$, where k_{ArOH} is a function of the hydrogen ion concentration. An empirical rate law is an important tool for estimating the characteristic time scales for Cr(VI) reduction. Its simplicity allows it to be readily incorporated into contaminant transport models, enabling redox transformations to be coupled with transport processes.

Although an empirical rate law is practical for many applications, its validity is restricted to the conditions from which it was derived. Empirical laws may not be valid for other concentration ranges or more complex systems of waste mixtures. Knowledge of the redox mechanisms and reaction pathways governing the system may improve our ability to extrapolate to these situations. Investigations of Cr(VI) reduction by various organic compounds have revealed many mechanistic details of chromium redox chemistry. Unfortunately, these investigations have not included reactions of Cr(VI) with phenols. However, it is reasonable to assume that certain features of Cr(VI) reduction by compounds such as aliphatic alcohols and thiols also apply to phenols.

The main features of Cr(VI) redox mechanism are depicted in the following reaction scheme.

Scheme I.

$$\mathrm{ROH + HCrO_4^- = ROCrO_3^- + H_2O} \tag{1}$$

$$\mathrm{ROCrO_3^- \rightarrow Cr(IV) + Products} \tag{2}$$

$$\mathrm{2\ Cr(IV) \rightarrow Cr(III) + Cr(V)} \tag{3}$$

$$\mathrm{Cr(IV) + Cr(VI) \rightarrow 2\ Cr(V)} \tag{4}$$

$$\mathrm{2\ (\ Cr(V) + ROH \rightarrow Cr(III) + Products\ )} \tag{5}$$

or

$$\mathrm{Cr(IV) + ROH \rightarrow Cr(III) + R^{\bullet}} \tag{6}$$

$$\mathrm{Cr(VI) + R^{\bullet} \rightarrow Cr(V) + Products} \tag{7}$$

$$\mathrm{Cr(V) + ROH \rightarrow Cr(III) + Products} \tag{8}$$

The first step of the redox reaction between Cr(VI) and alcohols is the formation of a Cr(VI) ester (eq 1). The chromate ester then decomposes with a concomitant transfer of electrons to the Cr(VI) center (eq 2). Cr(VI) is an atypical oxidant because the reduction of

Cr(VI) to Cr(III) involves the transfer of three electrons which, with few exceptions, occurs in several one-electron or two-electron transfer steps. Chromium must therefore pass through intermediate, unstable oxidation states Cr(V) or Cr(IV) before reaching the stable Cr(III) state. The relative importance of one-electron and two-electron transfer pathways, and accordingly the intermediate Cr(IV) and Cr(V) species, is expected to be governed by the properties of the reducing agent and the relative concentrations of the reactants. The organic products of the intermediate steps can be either unstable radicals or stable compounds.

Although reactions between alcohols and Cr(VI) are analogous in some respects to reactions involving phenols, the latter reactions are apt to be strongly influenced by the high electron density associated with the aromatic ring. While there is extensive information on phenol oxidation for synthetic-organic chemistry applications, much less information is available on phenol oxidation in environmental systems. Rate data and an empirical rate expression alone cannot reveal a reaction mechanism, but comparing rates for a variety of changing reaction conditions can furnish important mechanistic details. We studied Cr(VI) reduction rates for 14 mono-, di-, and tri-substituted phenols to ascertain the effect of phenol structure on the kinetics. Possible reaction intermediates were investigated by direct and indirect determinations. Finally, we analyzed oxidation reaction products, which proved useful for two reasons. First, products frequently suggest the mechanisms that produce them, and conversely, a proposed mechanism must be consistent with the observed products. Secondly, product identification indicates the new organic compounds that can be expected to appear in waste mixtures of Cr(VI) and phenols.

Experimental

Kinetic Procedures. Materials and methods for all kinetic investigations were identical to those described previously (Chapter 3 of this thesis) unless otherwise noted. Linear regression analysis was performed with Abacus Concepts, StatView (Abacus Concepts, Inc., Berkeley, CA, 1992), and non-linear curve fitting with DeltaGraph Professional (DeltaPoint, Inc., Monterey, CA, 1991). Several experiments were performed with additions of iodide (I^-) or manganous ion (Mn(II)) to act as scavengers of chromium species of intermediate oxidation states (i.e., Cr(IV) and Cr(V) respectively). Additions I^- or Mn(II) ion to selected Cr(VI)/phenol reaction mixtures were made from 1.0 M stock solutions of NaI (Mallinckrodt) or $MnSO_4$ (Mallinckrodt). Initial concentrations of I^- and Mn(II) were in excess of initial [Cr(VI)]. Reactions were compared to control experiments consisting of Cr(VI) and phenol solutions without added I^- or Mn(II).

Product Analysis. Reaction products of Cr(VI) oxidation of phenols were identified by GC-MS. To obtain products for analysis, reactions were conducted with an excess of phenol at pH 2 and 25 °C. Products were extracted and derivatized in two different ways. The reaction solution was acidified to pH 1 with $HClO_4$, and immediately extracted three times with ethyl acetate. The combined ethyl acetate extracts were dried over anhydrous sodium sulfate, filtered, evaporated to dryness by gentle N_2 blowdown, and then dissolved in methylene chloride. Hydroxylated compounds were acyl-derivatized with 2:1 acetic anhydride/anhydrous pyridine. Alternatively, the reaction mixture was brought to pH 3 with NaOH and the quinone products reduced to hydroquinone with sodium dithionite. Products were extracted and acetylated in the same manner.

GC-mass spectrometry was performed on a Hewlett-Packard 5790 GC operating in the splitless mode with a 30 m x 0.32 mm i.d. DB-5 fused silica column (0.25 μm film thickness). The oven was programmed for 2 min at 50 °C and 50-320 °C at 10 °C/min. The GC was interfaced with a VG 7070E HF mass spectrometer operated in the electron impact mode at 70 eV. Reaction products were analyzed semi-quantitatively by gas chromatography with flame ionization detection. Relative concentrations were computed from internal standards. Significant total-ion chromatogram peaks were identified by mass spectral interpretation and comparison of the mass ion distributions with data-system library matches and those reported in compendia of mass spectra.

Chromate esters were investigated by UV-visible spectrophotometry (Perkin-Elmer Lambda-6 double-beam spectrophotometer) focusing on the 300-500 nm region in which these esters show characteristic absorption bands. The instrument was zeroed to an arrangement of the reference and sample beams passing through matched cuvettes both containing Cr(VI) added to H_2O buffer. The solution in the sample cell was replaced with a reaction solution containing Cr(VI) and phenol in the identical buffer. Differences arising from the internal spectral subtraction are due to the presence of the phenol ($\lambda \leq 300$ nm) or the formation of a Cr(VI)/phenol complex.

X-band EPR spectra of aqueous reaction solutions of Cr(VI) and 4-methylphenol were measured at room temperature on a Varian E-109 EPR spectrometer using a flat quartz cell.

Results

Reaction Intermediates. Reaction intermediates were characterized in several experiments. In particular, we probed the Cr(VI)/substituted phenol system for 1) formation of a chromate/phenol ester, and 2) intermediate chromium species, Cr(IV) and Cr(V). Both direct and indirect methods were used to identify these intermediates.

Chromate/Phenol Ester Formation. UV-visible spectra of mixtures of Cr(VI) and 4-methylphenol (4MP) or 4-chlorophenol exhibited absorption bands in the 350 - 450 nm wavelength range (Figure 4.1) which are consistent with those ascribed to Cr(VI)-oxy esters in the literature *(2-8)*. Reactions of Cr(VI) and 4-methylphenol were performed at pH 2 and 5 to test the hypothesis that either ester formation or decomposition is pH dependent or acid catalyzed. An excess of 4MP was used to maximize ester formation while minimizing successive oxidation steps. At pH 5 the redox reaction proceeded very slowly with negligible reduction of Cr(VI) within the first hour. Spectrophotometric scans completed within 1 minute after mixing revealed a very distinct absorbance band in the region of 380 - 550 nm and a decreased absorbance in the 350 - 380 nm region (Figure 4.1). Continued scanning for 30 minutes showed no further change in the spectrum. Cr(VI) measurements confirmed that essentially no Cr(VI) reduction had occurred within this time. The 380 - 550 nm band is asymmetrical and suggests a combination of an increased absorbance band at 400 nm associated with an ester and decreased absorbance around 350 nm, the λ_{max} of $HCrO_4^-$. In the absence of any Cr(VI) reduction, Cr(VI) and its complexes are the only species that absorb in this spectral region. It thus follows that the spectral shifts observed are due to a rapid formation of a Cr(VI) complex.

At pH 2, succesive spectrophotometric scans showed development of a strong absorbance band in the region 410-450 nm with a concurrent absorbance increase in the 280-340 nm region. These absorbance bands continued to grow as Cr(VI) was consumed, although more slowly as the reaction approached completion. The noticeable formation of colloidal precipatates, presumably phenolic polymerizaion products, over the course of the reaction were most likely responsible for the gradually developing absorbance bands. Overall, it was impossible at pH 2 to distinguish between the spectral absorbance of ester intermediates and that of oxidation products. Therefore, under conditions where the redox reaction is relatively fast, rapid formation of oxidation products interferes with observations of the initial ester formation.

Because oxidation products interfere with ester identification, the slowly oxidized 4-chlorophenol was examined spectrophotometrically at pH 2 and pH 5. The reduction of Cr(VI) by 4-chlorophenol is very slow at pH 2 and negligible at pH 5. Scans performed within minutes after mixing the reactants showed small, but discernable absorbance changes for both pH 2 (Figure 4.2) and pH 5 reactions. Small absorbance bands (approx. 0.05 AU) were found in the 397 nm region as with the 4-methylphenol systems.

Varying the excess concentration of 4-methylphenol at pH 5 and 4-chlorophenol at pH 2 demonstrated that the absorbance increased in proportion to the phenol concentration, [ArOH] (Figures 4.1 and 4.2). Because 4-chloro- and 4-methyphenol do not absorb in the 320-400 nm region, we can interpret the increased absorbance as a result of a shift toward the ester in the esterification equilibrium (eq 1).

Intermediate Cr(V) and Cr(IV) Species. EPR procedures and competitive reactions with iodide were used to explore the role of Cr(V) species. The scavenging effect of I^- towards Cr(V) has been demonstrated for reductions of Cr(VI) by metal centers *(2,3,9-11)*. In moderately acidic solution Cr(VI) (and presumably Cr(IV)) oxidize I^- to I_2 (I_3^-) very slowly. In contrast, Cr(V) reacts with iodide ion orders of magnitude faster *(12,13)*. Addition of I^- to reactions of Cr(VI) and excess 4-methylphenol showed indirect evidence of induced oxidation of I^- by the Cr(V) intermediate. Spectral detection of triiodide (I_3^-) formation in the 350 nm region, the main absorbance band for I_3^-, was masked by the strong absorbance of $HCrO_4^-$ at the same wavelength. However, comparison of the organic reaction products from reactions with and without addition of I^- showed a marked difference in the product distributions. In particular, reactions with iodide present gave 4-hydroxybenzaldehyde as a major product and only traces of Pummerer's ketone and trimeric coupled product(s) (see products section below). In contrast, for reactions conducted in the absence of I^-, Pummerer's ketone was the major reaction product and only trace amounts of 4-hydroxybenzaldehyde product were detected. There was no substantial reduction of Cr(VI) in solutions of Cr(VI) and I^- alone, nor was there any reaction between I^- and 4MP in solutions without Cr(VI). Although we did not determine whether the hydroxybenzaldehyde product resulted from a reaction with Cr(IV) (from reduced Cr(V)) or a reaction with I_2 (from oxidized I^-), it is clear that the differences in the product distribution are due to the presence of iodide and its scavenging of Cr(V). The apparent scavenging of Cr(V) by I^-, however, failed to alter measurably the rate of Cr(VI) reduction by excess 4MP, 4-methoxyphenol, or 2,6-dimethoxyphenol. If we assume Cr(V), if formed, is scavenged by I^-, and I^- additions have no effect on the rate of Cr(VI) reduction, we can conclude that any step involving Cr(V) as a reactant must occur after the rate-limiting step.

The Cr(VI)/4MP system also was studied by EPR spectroscopy to further examine the role of Cr(V). Cr(V) produces a strong X-band EPR signal and EPR techniques have detected Cr(V) formation during chromate reduction by aliphatic alcohols *(14)* hydroxy acids *(12,13,15)* and thiols *(16-24)*. Reactions with 4MP were conducted in pH 2 solutions of $HClO_4$ and the molar ratio of Cr(VI) to 4MP was varied from 2:1 to 1:20. In all cases, the reactions of Cr(VI) and 4MP were EPR-silent. For comparison, a reaction of Cr(VI) and glutathione with a molar ratio 2.5:1 yielded a strong Cr(V) EPR signal. A supplementary experiment utilizing dissolved humic acid as the reducing agent displayed a short-lived, but distinct EPR signal with a similar spectral bands as the glutathione system. Evidently, both glutathione and humic acid are able to stabilize Cr(V) through chelation or ligand exchange *(17-23)*. The failure to detect a Cr(V) signal in the EPR of 4-methylphenol reactions supports the theory that if Cr(V) is produced it does not accumulate which is consistent with its involvement after a rate limiting reaction step.

Cr(IV) Scavenging with Mn(II). Selected reactions were conducted with additions of Mn(II) to scavenge possible Cr(IV) intermediates. For all such experiments, initial concentrations of Mn(II) were in excess of $[Cr(VI)]_o$ to favor a Cr(IV)-Mn(II) reaction. Under conditions of excess 4MP, addition of Mn(II) had no effect on reaction rates. Reactions performed at initial near-stoichiometric molar ratios allowed us to observe changes in the rate of depletion of both reactants as well as variations in the apparent reaction stoichiomety due to the presence of Mn(II). For reaction conditions ranging from a five-fold excess of Cr(VI) to a five-fold excess of 4MP rates of 4MP and Cr(VI) consumption were unaffected by the addition of Mn(II) and the apparent reaction stoichiometry ($\Delta[Cr(VI)]/\Delta[4MP]$) was consistently 2/3. Reactions of Cr(VI) and 2,6-dimethoxyphenol (26DMX; 1:4 mM Cr(VI):26DMX) also failed to show any change in the apparent reaction stoichiometry or rates of Cr(VI) or 26DMX depletion. As was noted in the studies with Cr(V), the absence of a Mn(II)-rate effect does not necessarily exclude Cr(IV) involvement in the reaction sequence, but it does suggest that if produced it is consumed in a step succeeding the initial Cr(VI) reduction step.

Product Analysis. Oxidation of phenolic compounds is notoriously complex in that the phenol substrate can be oxidized to a phenoxy radical or cation, which can undergo coupling reactions to numerous end-products including polymers *(25-28)*. Phenol oxidations have been implicated as principal pathways to natural polymer formation *(25-27,32)*. The reaction schemes and principal aqueous products of Cr(VI) oxidations of several phenols are shown in Figures 4.3a and 4.3b.

Oxidation of 4-methylphenol (**I**) with Cr(VI) in aqueous solution, carried essentially to completion, yielded a final reaction mixture of soluble products and a reddish-brown resinous precipitate. The amorphous, probably polymeric precipitate was insoluble in ethyl acetate, methylene chloride, and hexane. Shorter reaction times yielded considerably less polymer. We therefore restricted product analyses to moderate reaction times and focused on the initial, low molecular weight products. Gas chromatography of reaction products revealed three main classes of compounds corresponding to momomeric, dimeric and trimeric products. The dimeric ketone (**1,** Pummerer's ketone) was the most abundant product, followed by dimeric (**2**) and trimeric (**3**) coupled phenol species. Trace amounts of coupled phenol tetramer also were observed. Coupled products are presumably *ortho*-linked phenols *(26)*. Oxidized monomeric products, expected to elute prior to the dimer in the GC, included trace amounts of the aldehyde (**5**) and the carboxylic acid (**6**) and are evidence of a two-electron transfer. Formation of coupled products are generally believed to occur via a one-electron production of a phenoxy radical (**X1**) and subsequent radical-radical coupling *(25,26,31)*. Alternatively, coupling could proceed with a phenoxy cation/phenol interaction given a strong oxidant like Cr(VI) and a low pH *(25,27)*. The formation of the dimeric ketone and coupled phenols for 4-methylphenol oxidation by numerous oxidizing agents *(26)* including Cr(VI) *(29)* is well-known. The formation of oxidized monomers with Cr(VI), however, has not been reported previously.

Cr(VI) oxidation of mono-substituted 4-methoxyphenol (**II**) and 4-chlorophenol (**III**) also produced *ortho*-linked dimers and traces of higher polymers. The methoxy analog of Pummerer's ketone (**1**) was detected only in trace amounts, and no definitive identification of ketone was detected in the oxidation of 4-chlorophenol. In constrast to 4-methylphenol, however, the major product of the oxidation of 4-methoxyphenol and 4-chlorophenol was unsubstituted *p*-benzoquinone (**7**) formed from hydrolysis and elimination of the chloro and methoxy substituent at the *para* position of the phenoxy cation (**X2**). Methoxy- and chloro-substituted quinones were also detected (**9**). In general, these products are signature compounds for two electron oxidations.

The reaction products of a few poly-substituted phenols were also identified. 2,6-dimethoxy-phenol was oxidized to the dibenzoquinone (**10**) almost exclusively in short reaction times. The formation of the dibenzoquinone was accompanied by a strong absorbance in the visible spectrum (λ_{max} = 472 nm) which has been reported previously for Mn(III) oxidation *(33)*. Product analysis from the oxidaton of 2,6-dimethylphenol also showed predominantly *para-para* coupling. Dibenzoquinone **10** was the major identifiable product, however there were also significant quantities of yet unidentified products, potentially monomers, that eluted after the dimer in the GC. The preferred mechanism for the formation of dibenzoquinone is a radical-radical coupling mechanism *(33)* although heterolytic coupling of a phenoxy cation has also been proposed *(31)*.

The oxidation of 2,4,6-trimethylphenol was unique among the phenols we studied in that the *para* and both *ortho* positions, the preferred coupling positions, were substituted with a relatively poor leaving group. Identfication of major products **13**, **14**, and **15** suggest an initial two-electron oxidation of **VI** to a quinone methide species (**X3**) with subsequent hydrolysis at the methyl carbon to form stable compound **13**. Compounds **14** and **15** result from facile oxidation of the newly formed alcohol group. The principal reaction products from oxidation of 2,4-dimethylphenol **VII** were a mixture of potentially one-electron products, the dimethyl analogs of Pummerer's ketone (**17**) and dimer **18**, and and an oxidized monomer, the 2,4-dimethyl-*o*-quinone **16**.

Discussion

General Characteristics of the Reaction. The general features of the kinetics of Cr(VI) reduction by substituted phenols closely resemble those of alcohols, aldehydes, and thiols despite a disparity in the characteristic time scales of these reactions and the obvious dissimilarity in reductants' molecular structures. It is resonable to anticipate that the parallels among these reaction kinetics are related to the general nature of Cr(VI)/organic reaction mechanisms and, in particular, to the initial reaction steps prior to and including the rate limiting step. It is well established that these initial steps involve formation of a Cr(VI) ester intermediate, often in a pre-oxidation equilibrium step, followed by electron transfer with ester decomposition. By analogy, the mechanism of Cr(VI) reduction by phenols is likely to follow this same general reaction pathway. The results presented here confirm this hypothesis and extend the general Cr(VI)/organic reaction scheme to include phenolic compounds as well.

Development of an overall reaction mechanism wherein Cr(VI) is reduced by phenols must account for the results reported here and in the previous chapter. The important points with respect to the initial reaction steps are:

1). Cr(VI)/phenol ester formation precedes the first electron transfer step and reaches a rapid equilibrium concentration.

2). The overall reaction is first-order with respect to the concentration of phenol and one or more monomeric Cr(VI) species.

3). The apparent reaction order with respect to $[H^+]$ approaches 2 at low pH, approaches 0 at pH 6, and varies depending on the phenol reductant.

4). Reaction products indicate both one-electron and two-electron pathways.

Chromate Ester Formation. Formation of a chromate ester has been well established in the Cr(VI) oxidation of alcohols *(34-39)* and aldehydes*(40-43)*. Analogous Cr(VI)-thiol esters have been observed in Cr(VI) oxidations of compounds with sulfhydryl moieties *(44-49)*. The initial step of Cr(VI) oxidations of these compounds is the formation of a Cr–O–C or Cr–S–C ester/thioester linkage. Decomposition of the chromate ester intermediate proceeds in conjunction with inner-sphere electron transfer. These investigations typically use stopped-flow or temperature-jump methods to study the rapid kinetics of ester formation. Using these techniques, values of the stability constant for ester formation, K_e, were determined to be *ca.* 10^3 M^{-1} for thiol esters *(46-49)* but only on the order of 1-10 M^{-1} for most Cr(VI)-oxy esters *(50-54)*. The small absorbance changes observed here for the Cr(VI)/phenol esters are consistent with the reports of relatively weak stabilities of Cr(VI)-oxy esters.

In this study, at pH 5 ester formation was essentially instantaneous and therefore not rate-limiting. Because we could not directly observe ester formation at low pH for most of our phenols, we must consider the possibility that at low pH electron transfer becomes so rapid that ester formation becomes rate-limiting. This could be a consequence of the redox step having a higher order dependence on $[H^+]$. With 4-chlorophenol at pH 2 and pH 5 and with 4-methylphenol at pH 5, the ester reached steady-state concentrations within the time it took to initiate the reaction and perform a spectrophotometric scan (typically < 60 s), which is substantially less than the half-life of all redox reactions examined, with the exception of 3,4-dimethoxyphenol at pH 2 ($t_{1/2}$ = 44 s). The actual time scale of ester formation is likely to be shorter than the conservative estimate of 60 s because reaction half-lives reported for Cr(VI)-alcohol and Cr(VI)-thiol esterification are in the range of 10^{-2} - 10^{1} s *(47-50)*. While there is no consistent agreement in the literature on the exact pH dependence of the esterification equilibrium, there is evidence for acid catalysis *(52,53,55)*, and therefore, at low pH we expect the half-life of esterification to be substantially shorter than the 60 s approximation. Hence, it is reasonable to assume that for our system, in the pH range examined, ester formation was always fast relative to the electron transfer ester decomposition.

At a fixed pH, a general reaction scheme that accounts for the first and second points outlined above is of the form

$$\mathrm{HCrO_4^-} + \mathrm{ArOH} \underset{k_r}{\overset{k_f}{=}} [\mathrm{HCrO_4^-} \bullet \mathrm{ArOH}] \qquad K_e = k_f/k_r \tag{9}$$

$$[\mathrm{HCrO_4^-} \bullet \mathrm{ArOH}] \xrightarrow{k_d} \text{products} \tag{10}$$

where [$\mathrm{HCrO_4^-}$ • ArOH] is the ester complex. Given the evidence for rapid formation of the ester (eq 9) and that equilibrium is strongly shifted to the left (i.e., K_e is small; $k_f[\mathrm{HCrO_4^-}][\mathrm{ArOH}] < k_r[\mathrm{ester}]$), the redox step (eq 10) is rate-limiting ($k_d[\mathrm{ester}] \ll k_f[\mathrm{HCrO_4^-}][\mathrm{ArOH}] - k_r[\mathrm{ester}]$) and the rate equation can be written as

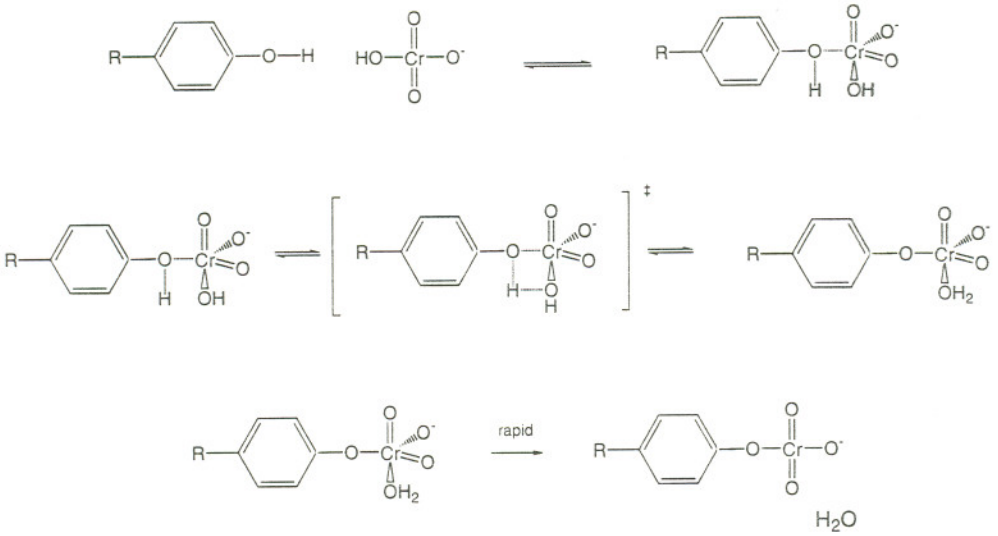
$$\mathrm{Rate} = k_d[\mathrm{ester}] \tag{11}$$

$$= k_d K_e [\mathrm{HCrO_4^-}][\mathrm{ArOH}] \tag{12}$$

Under these conditions, the reaction demonstrates first-order kinetics with respect to the concentrations of both Cr(VI) and phenol. This scheme has been used to describe Cr(VI) reduction by alcohols *(14,36,56,58)*, aldehydes *(40,43)*, and more recently several thiols *(45,48,49)*.

A detailed mechanism proposed for Cr(VI) ester formation with alcohols and thiols is the same as that proposed for ligand exchange reactions on the Cr(VI) center with dihydrogen phosphate, thiosulfate, and thiocyanate *(52)*.

Scheme II.



(13a)

(13b)

(13c)

Ester formation follows from an associative ligand substitution on $HCrO_4^-$ with the rate limiting step involving an internal proton shift from the hydroxy group on the phenol to a Cr(VI) hydroxy ligand (eq 13b). Although the rate limiting step is thought to be acid catalyzed, catalysis has no effect on the ester equilibria. Consequently, the value of K_e is independent of the proton concentration and does not depend on whether the reaction proceeds through an internal proton transfer or through an acid-catalyzed pathway. For eqs 11 and 12 to obtain, it is necessary only that equilibration be rapid and shifted predominantly towards the reactants.

Most literature evidence supports the ligand exchange/esterfication mechanism (in the range pH 1 to pH 7) as a reaction between $HCrO_4^-$ and an undissociated hydroxy or thiol group on the reductant. The analogous association of $HCrO_4^-$ and undissociated phenol (ArOH) in this system is realistic since ArOH typically comprises greater than 99% of the total phenol concentration in all experiments, and $HCrO_4^-$ typically greater than 85% in experiments excess in phenol.

Rate Determining Redox Steps. The rate-limiting redox reaction can be interpreted as the decomposition of the ester species (eq 10). Because ester equilibrium is independent of [H+], the redox steps must account for the pH dependence of the overall reaction. The overall plot of log k_{ArOH} versus pH for a particular compound can be explained as a composite of three straight-line plots of slope 2, 1, and 0 corresponding to three parallel reaction paths involving two, one and zero protons respectively. The three parallel reaction pathways define a rate expression in which k_{d} in eq 10 is composed of three kinetic terms. The combined rate law is

$$\mathrm{Rate} = \{k_2[\mathrm{H}^+]^2 + k_1[\mathrm{H}^+] + k_0\}[\mathrm{ester}] \tag{14}$$

$$= \{k_2[\mathrm{H}^+]^2 + k_1[\mathrm{H}^+] + k_0\}K_e[\mathrm{HCrO}_4^-][\mathrm{ArOH}] \tag{15}$$

For reactions with excess phenol ([ArOH]»[Cr(VI)]) within the pH range studied, the concentration of ArOH is

$$[\mathrm{ArOH}] = [\mathrm{ArOH}]_{\mathrm{tot}} - [\mathrm{ArO}^-] - [\mathrm{ester}] \tag{16}$$

$$\approx [\mathrm{ArOH}]_{\mathrm{tot}} \tag{17}$$

and, for the relatively dilute concentrations of Cr(VI), dimerization is negligible and the concentration of HCrO_4^- is

$$[\mathrm{HCrO}_4^-] = [\mathrm{Cr(VI)}]_{\mathrm{tot}} - ([\mathrm{CrO}_4^{2-}] + [\mathrm{H}_2\mathrm{CrO}_4] + [\mathrm{ester}]) \tag{18}$$

$$\approx [\mathrm{Cr(VI)}]_{\mathrm{tot}} - [\mathrm{CrO}_4^{2-}] \tag{19}$$

$$= [\mathrm{Cr(VI)}]_{\mathrm{tot}}/(1 + (1/K_2[\mathrm{H}^+])) \tag{20}$$

where K_2 is the stability constant for protonation of the chromate dianion.

$$\mathrm{H}^+ + \mathrm{CrO}_4^{2-} = \mathrm{HCrO}_4^- \qquad K_2 = 1.33 \times 10^6 \ (25\ ^\circ\mathrm{C}, I = 0) \tag{21}$$

Substitution of eqs 17 and 20 into eq 15 yields

$$-d[\mathrm{Cr(VI)}]/dt = \frac{\{k_2[\mathrm{H}^+]^2 + k_1[\mathrm{H}^+] + k_0\}K_e[\mathrm{Cr(VI)}]_{\mathrm{tot}}[\mathrm{ArOH}]_{\mathrm{tot}}}{(1 + (1/K_2[\mathrm{H}^+]))} \tag{22}$$

$$= k_{\mathrm{H}}K_e[\mathrm{Cr(VI)}]_{\mathrm{tot}}[\mathrm{ArOH}]_{\mathrm{tot}} \tag{23}$$

where k_{H} is a composite value of the kinetic rate terms and the denominator term. The product $k_{\mathrm{H}}K_{\mathrm{e}}$ can be equated to the empirical second-order rate constant k_{ArOH}

$$-d[\mathrm{Cr(VI)}]/dt = k_{\mathrm{ArOH}}[\mathrm{Cr(VI)}]_{\mathrm{tot}}[\mathrm{ArOH}]_{\mathrm{tot}} \tag{24}$$

Rearrangement of the empirical second-order rate constant (k_{ArOH}) in eqs 22 and 24 gives

$$k_{\mathrm{ArOH}} = \frac{\{k_2[\mathrm{H}^+]^2 + k_1[\mathrm{H}^+] + k_0\}K_e}{(1 + (1/K_2[\mathrm{H}^+]))} \tag{25}$$

A weighted least-squares fit of eq 25 was used to determine the products k_0K_e, k_1K_e, and k_2K_e for reactions involving 4-methylphenol, 4-methoxyphenol, 2,6-dimethoxyphenol, and 3,4-dimethoxyphenol (Table 4.2). Activity corrections for the value of K_2 at $I = 0.1$ were accounted for by using the Davies equation *(59)*. The resulting constants gave a close fit of the experimental data and accurately represented the changing relative contributions of the three reaction pathways (Figure 4.4).

One interesting feature of the rate law is that at pH values greater than approximately 6, the predicted reaction rate drops sharply with decreasing [H+] whereas the trend in the experimental rate data for pH ≤ 6 suggests a leveling-out of the reaction rate at higher pH. The curves fitted to plots of k_{ArOH} vs. $[\mathrm{H}^+]$ for data at pH ≤ 6 (Figure 4.4) demonstrate an inflection point at $[\mathrm{H}^+] \approx 10^{-6}$ and predict a rate decrease of unit slope for lower acidities due to the fact that at pH values greater than the $\mathrm{p}K_a$ of $\mathrm{HCrO_4^-}$ ($\mathrm{p}K_a$ = 6.52, eq 21), $\mathrm{HCrO_4^-}$ decreases in proportion to $[\mathrm{H}^+]$. Because eq 25 was fitted only to rate data for pH ≤ 6, the distinct decline in rates predicted for higher pH presented an excellent opportunity to test the validity of the rate law at conditions beyond which it was calibrated. For 3,4- and 2,6-dimethoxyphenol, at pH = 7 ($I = 0.1$) the model predicts k_{ArOH} values of 6.7×10^{-4} ($\mathrm{M^{-1}s^{-1}}$) and 1.1×10^{-3} ($\mathrm{M^{-1}s^{-1}}$), respectively. Apparent second-order rate constants measured at pH 7.0 for the reduction of Cr(VI) by excess 3,4- and 2,6-dimethoxyphenol were 7.5×10^{-4} and 7.2×10^{-4} ($\mathrm{M^{-1}s^{-1}}$). These measured values are in good agreement with the predicted values, but more importantly, they explicitly reflect the predicted downward turn in the rate plots at pH ≥ 6. Not only does this lend strong support to the reaction model, but it also validates use of the rate constants and the rate law for extrapolating to conditions of pH > 6.

The evaluation of the rate law as defined by Table 4.1 was carried out under reaction conditions of excess phenol. Rate data for excess Cr(VI) reactions were used to re-evaluate the rate law and thereby test its predictave cabability for a full range of conditions. The rate of oxidation of 4MP was measured at four pH values in the range pH 1 to 2. Under these conditions, the rate law is of the form

$$-d[\mathrm{ArOH}]/dt = \{k_2[\mathrm{H}^+]^2 + k_1[\mathrm{H}^+] + k_0\}K_e[\mathrm{HCrO_4^-}][\mathrm{ArOH}] \quad (26)$$

which is analogous to eq 15. The experimental second-order rate constant, k_{ArOH}, can be expressed by eqs 27 - 28,

$$k_{\mathrm{ArOH}} = \{k_2[\mathrm{H}^+]^2 + k_1[\mathrm{H}^+] + k_0\}K_e \quad (27)$$

$$= k_{\mathrm{exp}}/[\mathrm{HCrO_4^-}] \quad (28)$$

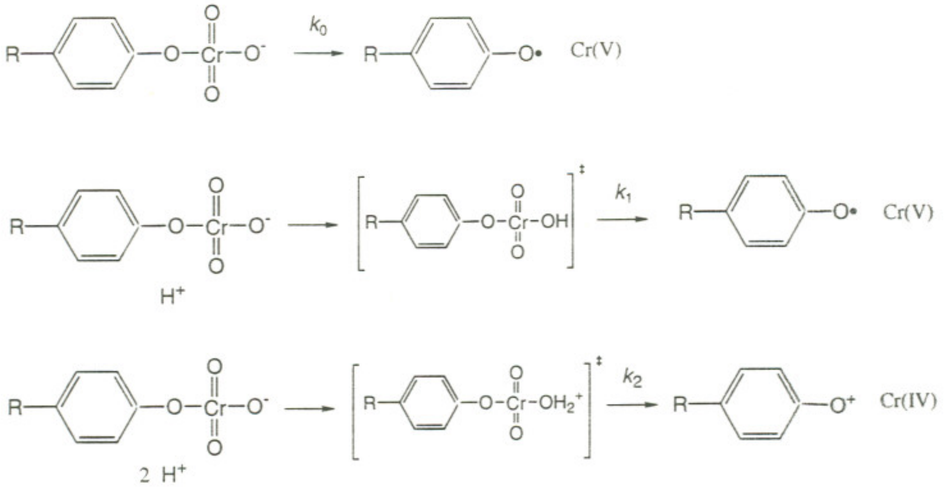
in which case eq 29 obtains:

$$k_{\mathrm{exp}}/[\mathrm{HCrO_4^-}] = \{k_2[\mathrm{H}^+]^2 + k_1[\mathrm{H}^+] + k_0\}K_e \quad (29)$$

Within the pH range examined (pH 1 - 2) the proton-independent pathway is not expected to contribute significantly to the net reaction and therefore the k_0 rate component in eq 29 is difficult to fit accurately to the rate data. In order to get a more realistic fit of eq 29, we used a value of $k_0K_e = 3.39 \times 10^{-6}$ determined previously from the excess 4-methylphenol experiments. The products k_1K_e and k_2K_e were determined from the plot of $k_{\mathrm{exp}}/[\mathrm{HCrO_4^-}]$ vs. $[\mathrm{H}^+]$ (Figure 4.5, Table 4.1). Comparison of the rate constants obtained from the two data sets are within 7 % for the two-proton pathway and within a factor of 2 for the single-proton pathway. The apparent reaction order with respect to $[\mathrm{H}^+]$ for 4MP in this pH range is 1.7 thus indicating the predominance of the two-proton pathway. The excellent agreement between the values of the two rate constants for the two-proton pathway (k_2K_e) lends support to the proposed mechanism.

A tentative mechanism scheme for the electron transfer decomposition of the ester involving three parallel reaction pathways is depicted in Scheme III.

Scheme III.



(29)

(30)

(31)

The proton independent pathway (eq 29) is a unimolecular decomposition of the ester, possibly via a homolytic cleavage of the Cr–O bond, leading to Cr(V) and phenoxy radical products. This pathway would tend to dominate at less acidic conditions (> pH 5). The proton dependent pathways (eqs 30 and 31) are rapid, successive protonations of a Cr(VI) hydroxy ligand with subsequent electron transfer and Cr–O bond cleavage. Each succesive proton addition would make the chromium center a better electron acceptor. A single-proton pathway exhibits a first-order rate dependence on $[H^+]$ and would dominate at moderately acidic conditions (e.g.; pH 2 - 5) potentially yielding Cr(V) and a phenoxy radical as before. Similarly, the two-proton pathway shows second-order rate dependence and dominates at low pH (pH < 2). Depending on the phenol reactant, heterolytic cleavage of the Cr–O bond with a two-electron transfer might be expected.

The assignment of homolytic or heterolytic cleavage of the the Cr–O ester bond depicted above is conjectural, but is, nonetheless, plausible based on 1) our product studies, 2) our investigations of Cr(V) and Cr(IV) intermediates and 3) behavior of similar reaction systems reported in the literature. For our system, the organic products from reactions at pH 1 and 2 are predominantly two-electron products although there is evidence suggesting limited contribution from one-equivalent processes as well. Whether these products stem from the initial reduction of Cr(VI) or a subsequent reaction with an intermediate chromium species is uncertain, but the formation of oxidized monomers is good evidence of a two-electron pathway. Likewise, coupled products suggest phenoxy radical polymerization resulting from one-electron processes. In acidic solutions, aliphatic alcohols have been shown to react predominantly via a two-equivalent pathway with Cr(VI) reduced directly to Cr(IV) *(2,3,14,36,60)*. On the other hand, thiols in the range of pH 2 - 7 tend toward an initial one-electron transfer: a homolytic ester cleavage producing Cr(V) and a sulfhydryl radical *(45-49)*.

Role of Cr(V) and Cr(IV) Intermediates. The results of the Cr(V) and Cr(IV) investigations provide additional insight into the initial redox step. At pH 1 and 2, there was no evidence for Cr(V) as a reaction intermediate, suggesting that if Cr(V) is produced it is consumed so rapidly such that a measurable concentration does not develop. The ability of manganous ion to scavenge Cr(IV) has been demonstated previously *(3,36,58,61)* for Cr(VI) reductions by alcohols where the elimination of Cr(IV) from the reaction sequence results in a halving of the Cr(VI) reduction rate. The lack of a Mn(II) scavenging effect on the rates or stoichiometries of reactions with an excess of 4MP or 2,6-dimethoxyphenol suggests that Cr(IV), if produced, does not react with a second Cr(VI) molecule as suggested previously *(14,39)*, but instead disproportionates to Cr(V) and Cr(III) (eq 3). Altenatively, Cr(IV) may react with a second molecule of 4MP (eq 6) when the reductant is in great excess. Reactions monitored as $d[\mathrm{ArOH}]/dt$ (excess Cr(VI) or Cr(VI) and ArOH at stoichiometric ratios) are difficult to interpret when Mn(II) is added because Mn(III) can oxidize phenol *(29,62)*. In the absence of Mn(II), Cr(IV) may disproportionate or react with Cr(VI), which is in relative abundance. In either case, the removal of one oxidizing equvalent in the form of Cr(IV) is replaced by one oxidizing equivalent in the form of Mn(III), and hence, no change in the phenol oxidation rate is observed.

The absence of an effect of Mn(II) on reaction rates in our Cr(VI)/phenol studies is in agreement with a previous study of Cr(VI) oxidations of 4-methylphenol and creosol *(29)*. Despite the apparent scavenging of Cr(IV) (based on substantial increases in dimeric products yields), Tanaka and co-workers found that Mn(II) had no effect on rates of Cr(VI) reduction.

General Trends in Reactivity. In the context of the proposed two-step reaction mechanism, the overall reactivity of the Cr(VI)/phenol system is dependent on both the prerequisite formation of a Cr(VI) ester complex and the subsequent electron transfer step. An examination of eqs 9 and 10 and the proposed rate law (eq 12) indicates that the reaction rate should depend on the stability of the Cr(VI) ester (i.e., K_e), and on the sum of the rates of the electron transfer reactions as reflected by k_d in eq 12. We anticipate that substitution of the phenol structure affects these reaction processes through resonance, field, and steric effects, but it is likely that these substituent effects influence esterification and electron transfer to differing extents.

The extent of ester formation is governed by a rapidly achieved equilibrium between the undissociated phenol and the chromate ester. Thus the effect of a substituent R on esterification can be inferred from its effect on the relative thermodynamic stabilities of the reactant phenol and the product ester. The phenol stability is governed by the strength of the RArO–H bond, the ester stability by the strength of the RArO–CrO_3^- bond. In both cases bond stability should be enhanced by electron-donating substituents (methyl, methoxy), that increase π-electron density and electron density on the phenyl oxy/hydroxyl group. Conversely, bond stabilities should be relatvely diminished by electron-withdrawing substituents (e.g., nitro, chloro, and aldehyde). However, because the ArO–H bond of the phenol is significantly stronger than the ArO–CrO_3^- bond of the ester, substituent effects will influence phenol stability more than ester stability. Therefore, the overall substituent effects of ester formation will be dominated by the substituent effects on the phenol stabilty. Overall we expect phenols with electron-withdrawing substituents (with positive Hammett σ constants) to promote higher equilibrium concentrations of chromate esters than electron-donating substituents (with negative σ constants). In terms of our nomenclature, K_e should increase with increasing values of the Hammett constants (line a, Figure 4.6). This predicted trend for phenol complexation is opposite of the trend reported for Fe^{3+} complexation with phenolate anions (at high pHs where dissociated phenol is the dominant form) in which case substituents affect the Fe^{+3} linkage more than the unpaired electrons on the hydroxyl group *(63,64)*.

The rate of electron transfer from the organic to the chromate is also strongly influenced by phenol substituents. Electron donating substituents that increase π-electron density make electron transfer more favorable. Electron-withdrawing groups weaken the reducing power of the phenol. These trends are a reflection of thermodynamic differences and have been confirmed by electrochemical measurements of redox potentials *(65,66)*. In our terms, k_d should decline with increasing values of the Hammett constants (line b, Figure 4.6). The slopes of lines a and b in Figure 4.6 depend on the magnitude of the substituent effects (but are drawn arbitrarily) and a overall Hammett plot of the empirical second-order rate constants ($k_{ArOH} = k_H K_e$) therefore has a slope and intercept that reflect the relative contributions of the esterification and the electron-transfer steps and the magnitude of the respective substituent effects on each of these steps.

Plots of log k_{ArOH} vs. various σ scales (σ, σ^o, σ^-, and σ^+) for the reduction of Cr(VI) by 13 phenols demonstrated the best linearity with Brown's substituent constants (σ^+) *(67)* (Figure 4.7) and indicates a dominance of the electron donating effects, and hence, a strong overall dependence on the electron transfer step. This was to be expected since we attained a very linear relationship with $E_{1/2}$ values (see Chapter 3) and the colinearity between $E_{1/2}$ values and σ^+ values is well established *(65,69)*. Because Hammett-type σ scales are not well defined for substituents in the ortho position, we used para σ^+ values for ortho substituents, but restricted our correlation analysis to para and meta substituted phenols. Reaction rates for the seven para and meta substituted phenols demonstrated a good correlation with Brown's σ^+ scale (eq 32, Figure 4.7).

$$\log k_{ArOH} = (-5.14 \pm 0.38)\sigma^+ - (4.50 \pm 0.19) \qquad (32)$$

$$(r^2 = 0.973;\ s = 0.351;\ n = 7)$$

The reasonably good correlation with the σ^+ scale, which provides for additional resonance effects due to π-electron donor substituents such as *para*-methyl and *para*-methoxy groups, may indicate the importance of enhanced resonance stabilization within the ester charge transfer complex or stabilization of the electron deficient phenoxy radical or cation resulting from electron transfer. In Figure 4.7, the points representing the subset of all ortho-substituted phenols (with the exception of vanillin) all had k_{ArOH} values below the correlation line defined by the para and meta reactivity. The anomalously low reactivities of the ortho-substituted phenols suggest the influence of steric effects. In order to better predict the reactivities of ortho-substituted compounds with the correlation analysis, we took the approach of Tratnyek and Hoigné *(68)* and adopted the method of Fujita and Nishioka *(70)* which accounts for the "ortho effect" with a two term extension of the Hammett equation. The two additional terms, $\sum F$ and $\sum E_{s,}$ represent polar and steric proximity effects associated with the ortho-substituent. This treatment of the "ortho effect" inproved the correlation between predicted and measured values of k_{ArOH} for all substituent positions (Figure 4.8). For all 13 phenols, comparing the output of a linear regession of log k_{ArOH} versus $\sum\sigma^+$ (eq 33, Figure 4.8a) to a multiple linear regression of log k_{ArOH} versus $\sum\sigma^+$, $\sum F$, and $\sum E_s$ (eq 34, Figure 4.8b) shows a better correlation with the Fujita and Nishioka model

$$k_{\mathrm{ArOH}} = -4.09 \pm 0.85 \ - \ 3.07 \pm 0.51\sum\sigma^+ \qquad (33)$$

$$(r^2 = 0.768;\ s = 0.849;\ n = 13\ )$$

$$k_{\mathrm{ArOH}} = -3.53 \pm 0.62 \ - \ 3.98 \pm 0.47\sum\sigma^+ \ - \ 2.3 \pm 1.23 \sum F$$

$$+ \ 0.66 \pm 0.21\sum E_s \qquad (34)$$

$$(r^2 = 0.907;\ s = 0.594;\ n = 13)$$

The $\sum\sigma^+$, $\sum E_s$, and intercept terms in eq 34 were all significant to the 99% confidence interval, and the polar proximity term $\sum F$ was significant to the 90% confidence interval. However, the linear fit ($r^2 = 0.907$) was not exemplary, and thus as a QSAR for predicting rate constants for other phenols it is not as precise or as as the correlation based on phenol half-wave potentials ($E_{1/2}$) developed in the previous chapter. Nevertheless, the fact that we obtained statistically significant coefficients for the ortho proximity terms $\sum F$ and $\sum E_s$ is a strong indication of the presence of steric effects for reaction with ortho-substituted phenols.

With respect to the proposed reaction mechanism, steric factors might affect formation of the Cr(VI) ester complex, or alternatively, they might affect the ester decomposition step associated with the electron transfer step. Verification of steric hindrance could have interesting application to Cr(VI) interactions with other highly sterically hindered phenols (e.g.; 2,6-di-tert-butyl-phenols)*(71)* as well as for more complex natural reductants such as humic and fulvic acids. The best direction for future research on this topic would involve direct measurement of ester stability constants and a QSAR analysis of substituent positioning and ester stability. If, for instance, the stability constants for ortho-substituted compounds were found to be consistently lower than their para and meta analogs a strong argument could be made for esterification being sterically hindered.

Conclusions

From kinetic investigations of the redox interactions between Cr(VI) and subsituted phenols we have developed a reaction model that accounts for the reaction rate over a wide range of $HCrO_4^-$, phenol, and H^+ concentrations. The rate law derived from the reaction mechanism accurately predicts reaction rates for conditions not necesssarily included in the model calibration. A rate law based on a chemical mechanism, as opposed to an empirical rate expression, is advantageous for two reasons. First, it allows us to extrapolate to reaction conditions more accurately than with an empirical rate expression. Secondly, it allows us to better extrapolate to Cr(VI) interactions with other reductant systems. From the outset, we expected certain features of Cr(VI)/phenol interactions to be similar to Cr(VI) redox reactions with other organic compounds, such as alcohols, aldehydes and thiols, that also contain heteroatoms. By analogy to these sytems, Cr(VI)/phenol reactions proceed via a precusor ester complex followed by a rate-limiting electron transfer step. The establishment of these two separate reaction steps has allowed us to consider the effects of phenol structure on the overall reactivity with Cr(VI). Phenols with electron-donating ring substituents are clearly more reactive than unsubstituted phenol or phenols with electron-withdrawing substituents. Correlation of reaction rates and σ^+ constants suggests that groups with an enhanced ability to delocalize positive charge increase reactivity. Correlation analysis also suggests that the reactivity of phenols substituted in the ortho position is decreased due to steric hindrance, possibly during the initial nucleophilic association of the phenolic hydroxyl group and the Cr(VI) center. While this conclusion is preliminary, its ramifications on Cr(VI) interactions with complex natural reductants, such as humic materials, is noteworthy.

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Table 4.1. Composite Rate Constants Corresponding to Zero-, One-, and Two-Proton Dependent Pathways for Reaction between Cr(VI) and Substituted Phenols in Aqueous Solution at 25 °C and I = 0.1 M.

Compound	k_0K_e (M^{-1} s^{-1})	k_1K_e (M^{-2} s^{-1})	k_2K_e (M^{-3} s^{-1})
<u>excess phenol</u>			
4-methylphenol	3.39×10^{-6}	7.56×10^{-2}	2.05
4-methoxyphenol	3.65×10^{-4}	1.08×10^{1}	3.39×10^{2}
2,6-dimethoxyphenol	8.09×10^{-3}	2.68×10^{1}	2.03×10^{2}
3,4-dimethoxyphenol	4.84×10^{-3}	1.01×10^{1}	1.28×10^{4}
<u>excess Cr(VI)</u>			
4-methylphenol	[a] 3.39×10^{-6}	1.36×10^{-1}	1.92

[a] This value was used as a fitting parameter in eq 29 and corresponds to k_0K_e for excess phenol.

Table 4.2. Second Order Rate Constants and QSAR Parameters for Cr(VI) Reductions by Substituted Phenols.

compound	phenol derivative	k_{ArOH} ± s.d. (M^{-1} s^{-1})	$\sum\sigma^{+}$ [a]	$\sum E_s$ [b]	$\sum F$ [b]
1	phenol	2.63 ± 0.06 x 10^{-5}	0.00	0	0
2	4-methyl	1.17 ± 0.01 x 10^{-3}	-0.31	0	0
3	2,4-dimethyl	9.37 ± 0.08 x 10^{-3}	-0.62	-1.24	-0.04
4	3,4-dimethyl	2.84 ± 0.05 x 10^{-3}	-0.38	0	0
5	2,6-dimethyl	1.23 ± 0.01 x 10^{-3}	-0.62	-2.48	-0.08
6	2,4,6-trimethyl	5.30 ± 0.04 x 10^{-3}	-0.93	-2.48	-0.08
7	4-methoxy	2.18 ± 0.04 x 10^{-1}	-0.78	0	0
8	2,6-dimethoxy	4.35 ± 0.18 x 10^{-1}	-1.56	-1.10	0.52
9	3,4-dimethoxy	3.75 ± 0.055	-0.92 [c]	0	0
10	3,5-dimethoxy	2.54 ± 0.02 x 10^{-4}	-0.28 [c]	0	0
11	2-methoxy-4-aldehyde	1.12 ± 0.01 x 10^{-4}	-0.05	-0.55	0.26
12	2-methoxy-4-methyl	3.84 ± 0.02 x 10^{-1}	-0.22	-0.55	0.26
13	4-chloro	2.26 ± 0.03 x 10^{-5}	0.11	0	0
14	4-nitro	unreactive < 10^{-7}	0.79	0	0

[a] values from ref 67 unless otherwise noted. [b] values from ref 70. [c] Values from ref 65.

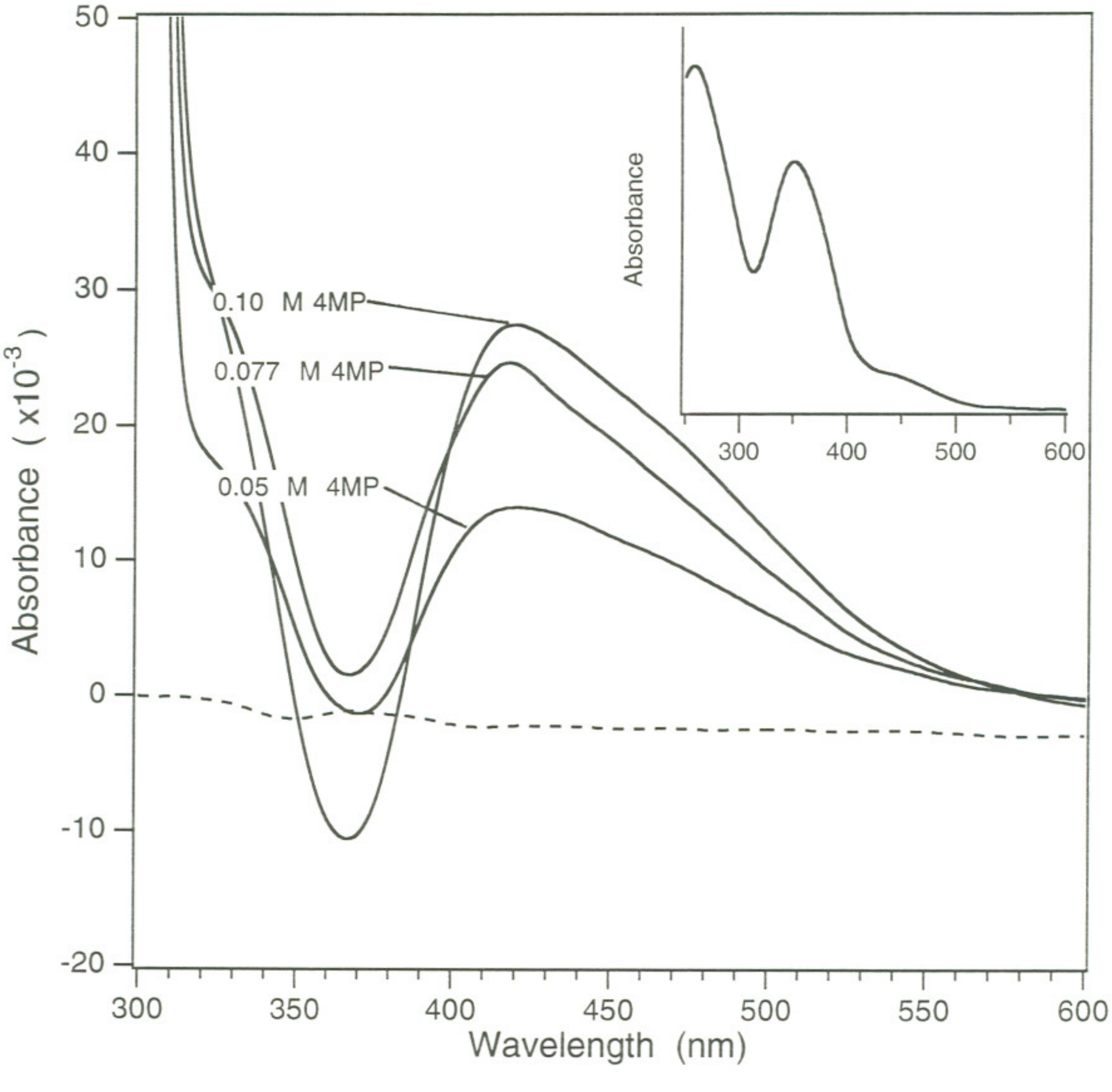


Figure 4.1. UV/Vis absorbance spectra of solutions containing 0.5 mM Cr(VI) and 0.1, 0.077, and 0.05 M 4-methylphenol at pH 5.0. Cell pathlength l = 1.0 cm, 25 °C, *I* = 0.1 M. Inset: spectra of Cr(VI) at pH 5. Spectra taken after 1 min.

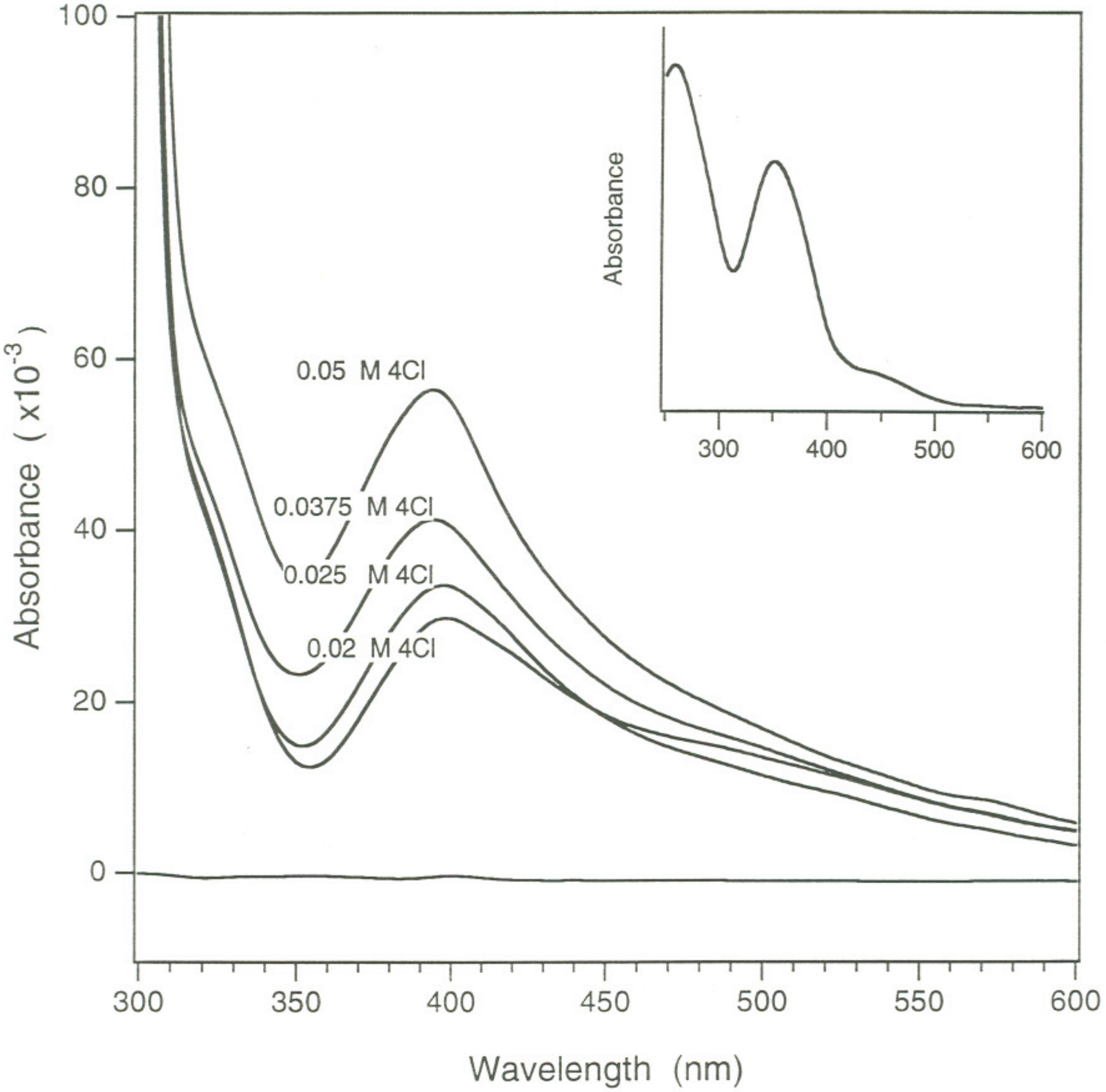


Figure 4.2. UV/Vis spectra of Cr(VI) and 4-chlorophenol at pH 2 showing the increasing absorbance band at 397 nm for increasing concentrations of 4-chlorophenol: 0.05, 0.0375, 0.025, and 0.02 M. [Cr(VI)] = 5.0 mM, cell pathlength l = 0.2 cm, 25 °C, I = 0.1 M. Inset: Cr(VI) at pH 2. Spectra taken after 1 min.

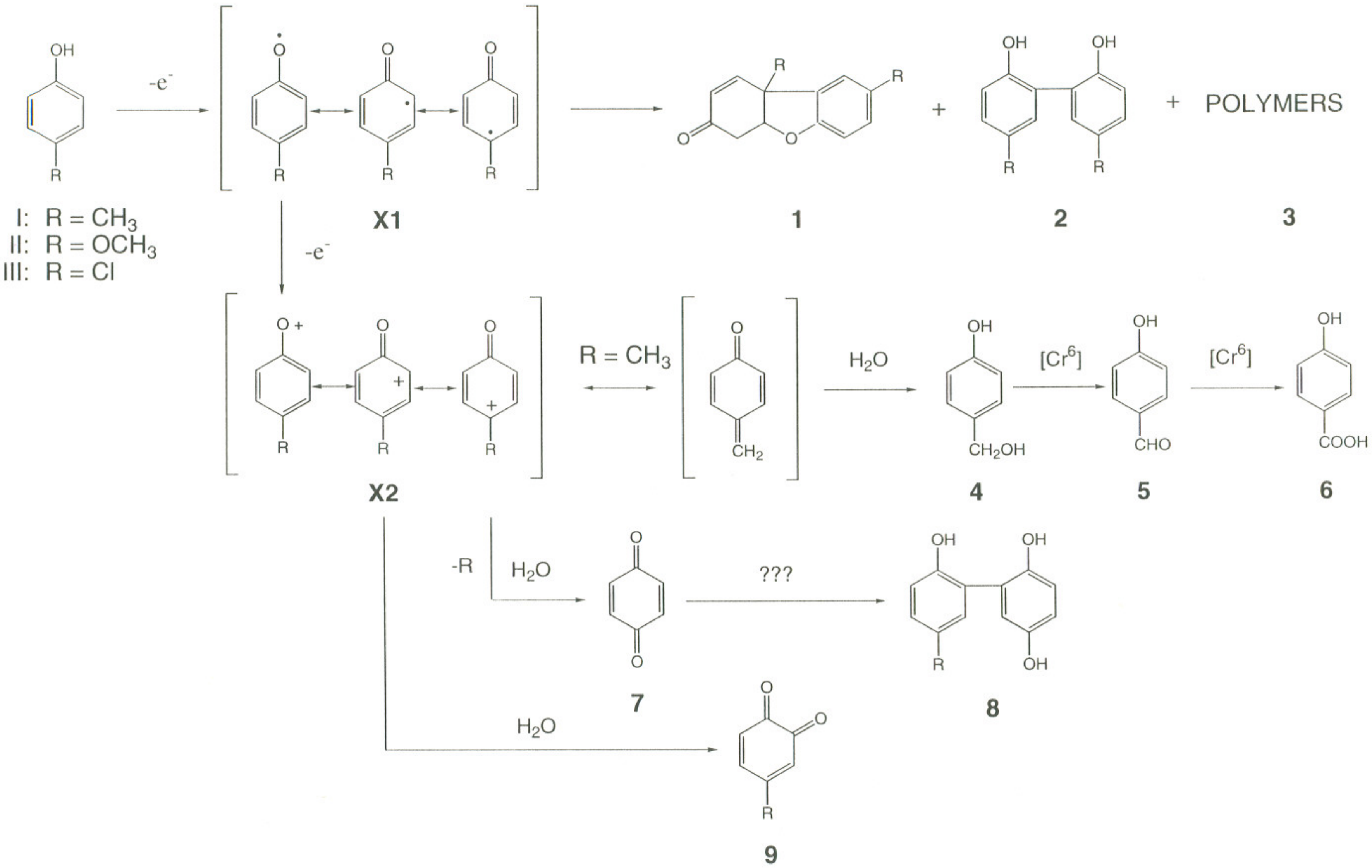


Figure 4.3a. Reaction products and partial mechanisms for the oxidation of 4-methyl, 4-methoxy, and 4-chlorophenol by Cr(VI).

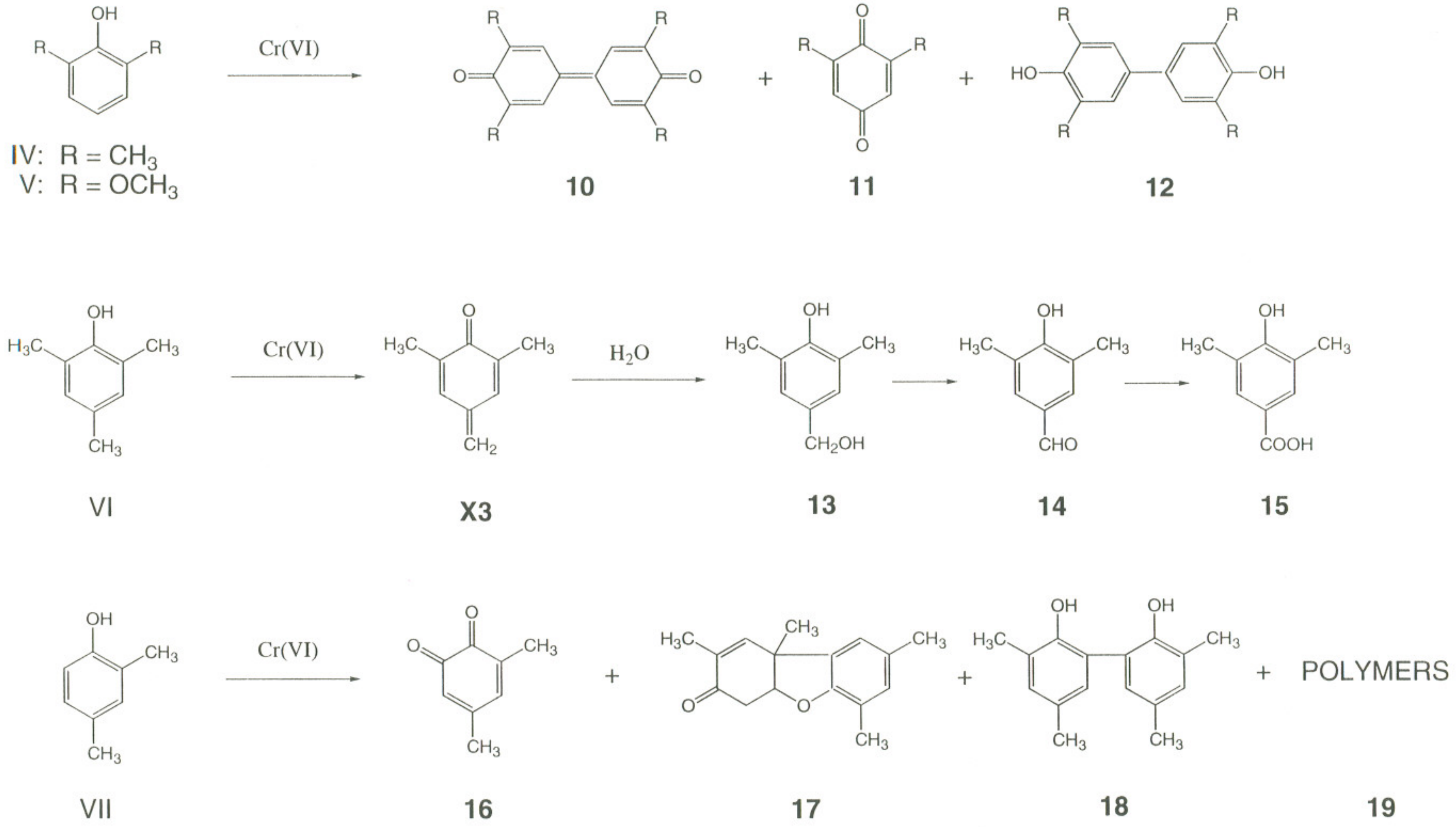


Figure 4.3b. Reaction products and partial mechanisms for the oxidation of various multi-substituted methyl and methoxy phenols byCr(VI).

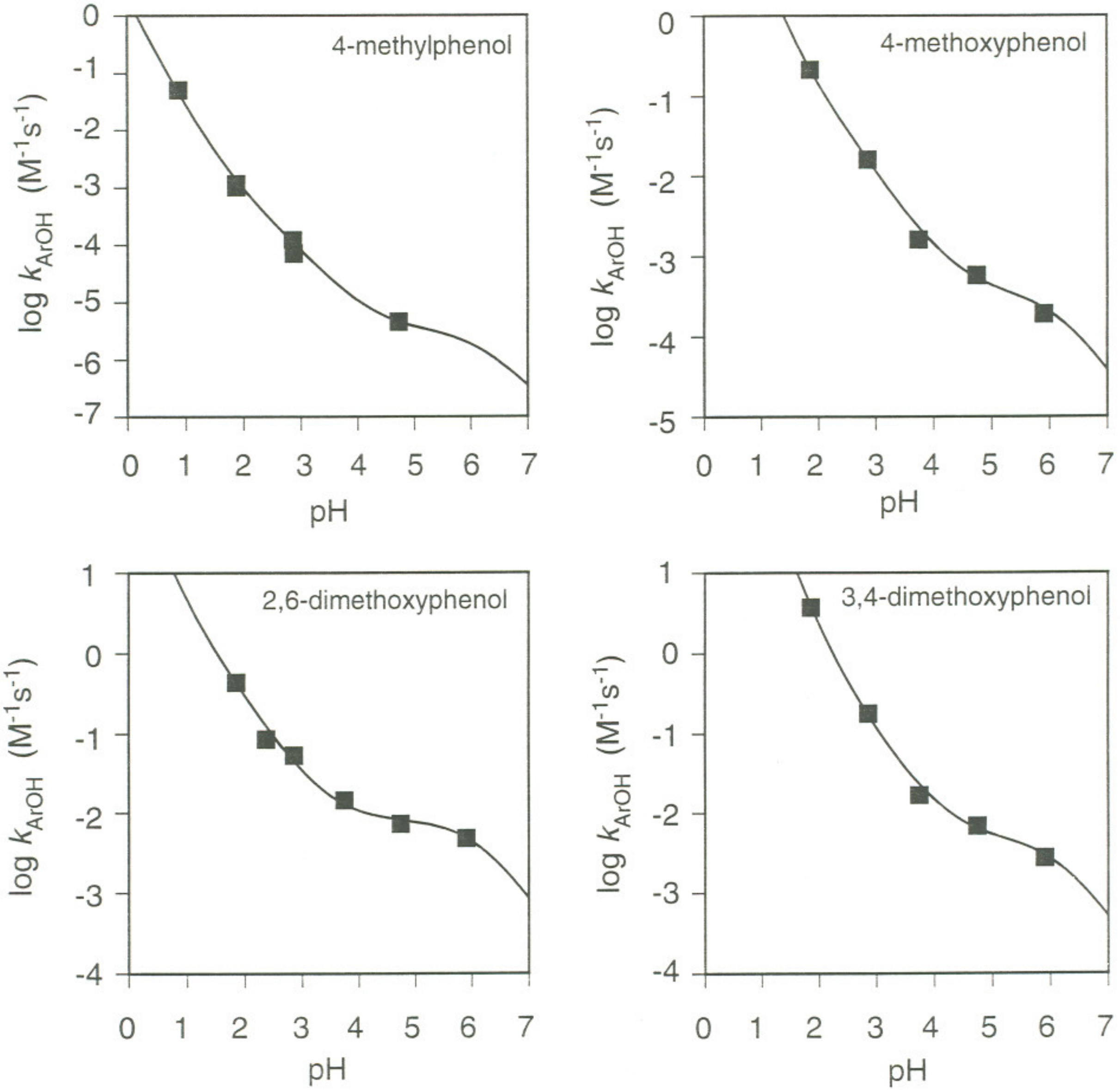


Figure 4.4. Plots of log of the apparent second-order rate constants, k_{ArOH}, vs. pH for reduction of Cr(VI) by 4-methyl-, 4-methoxy-, 2,6-dimethoxy-, and 3,4-dimethoxyphenol in H_2O at 25 °C and $I = 0.1$ M. Curves represent the least-squares fit of eq 25.

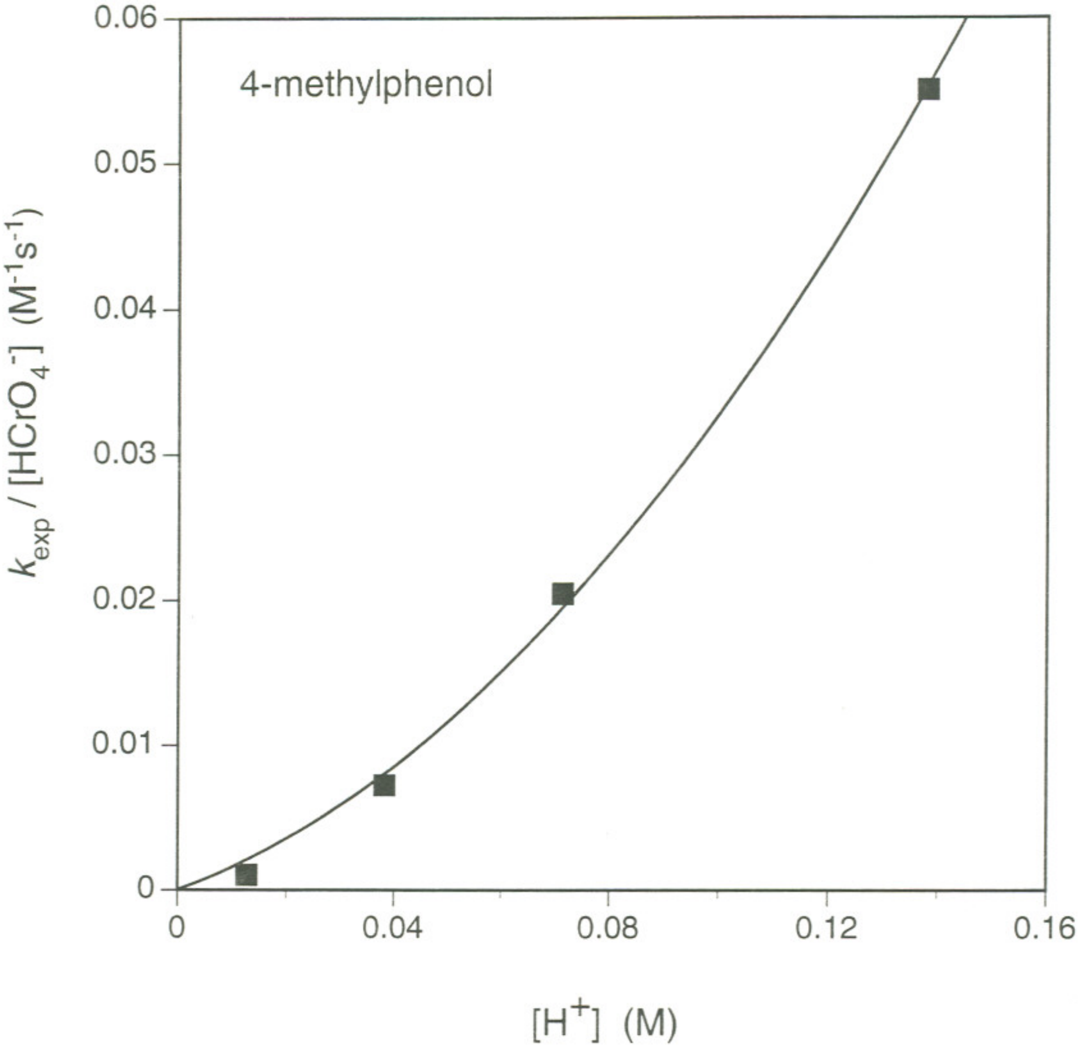


Figure 4.5. Plot of k_{exp}/[$HCrO_4^-$] vs. [H^+] for the oxidation of 4-methylphenol by excess Cr(VI) at pH 1.0 and 25 °C.

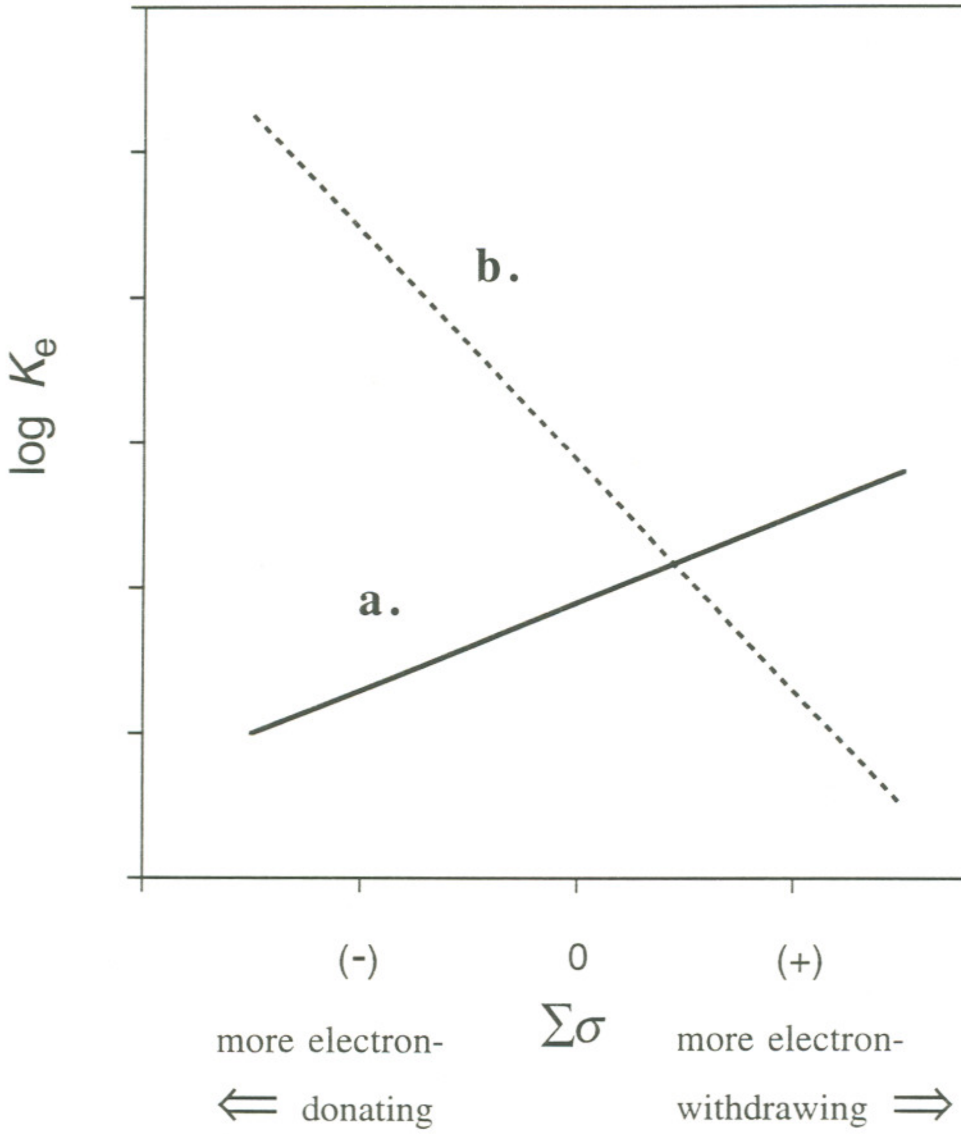


Figure 4.6. Theoretical Hammett plots for showing the expected trends in K_e (line a) and k_H (line b) with changing substituent effects as reflected by Hammett σ constants.

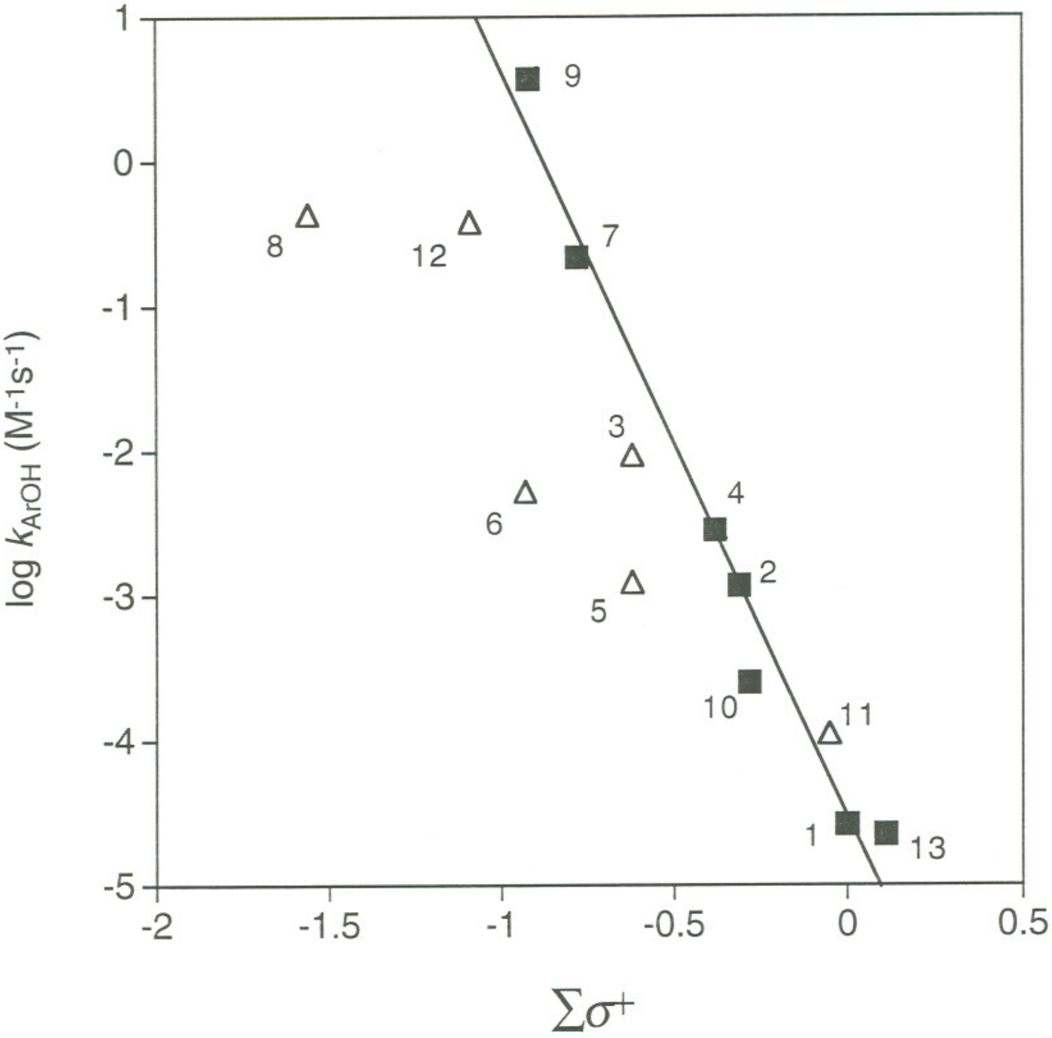


Figure 4.7. Hammett plot of log k_{ArOH} of Cr(VI) reduction by various phenols at pH 2 vs. σ^+ values. Least-squares regression (eq 32) includes the data corresponding to para and meta substituted phenols represented by the filled squares. The open triangles correspond to phenols substituted in the ortho position. The numbers correspond to the compounds in Table 4.2. Brown σ^+ values from ref 67.

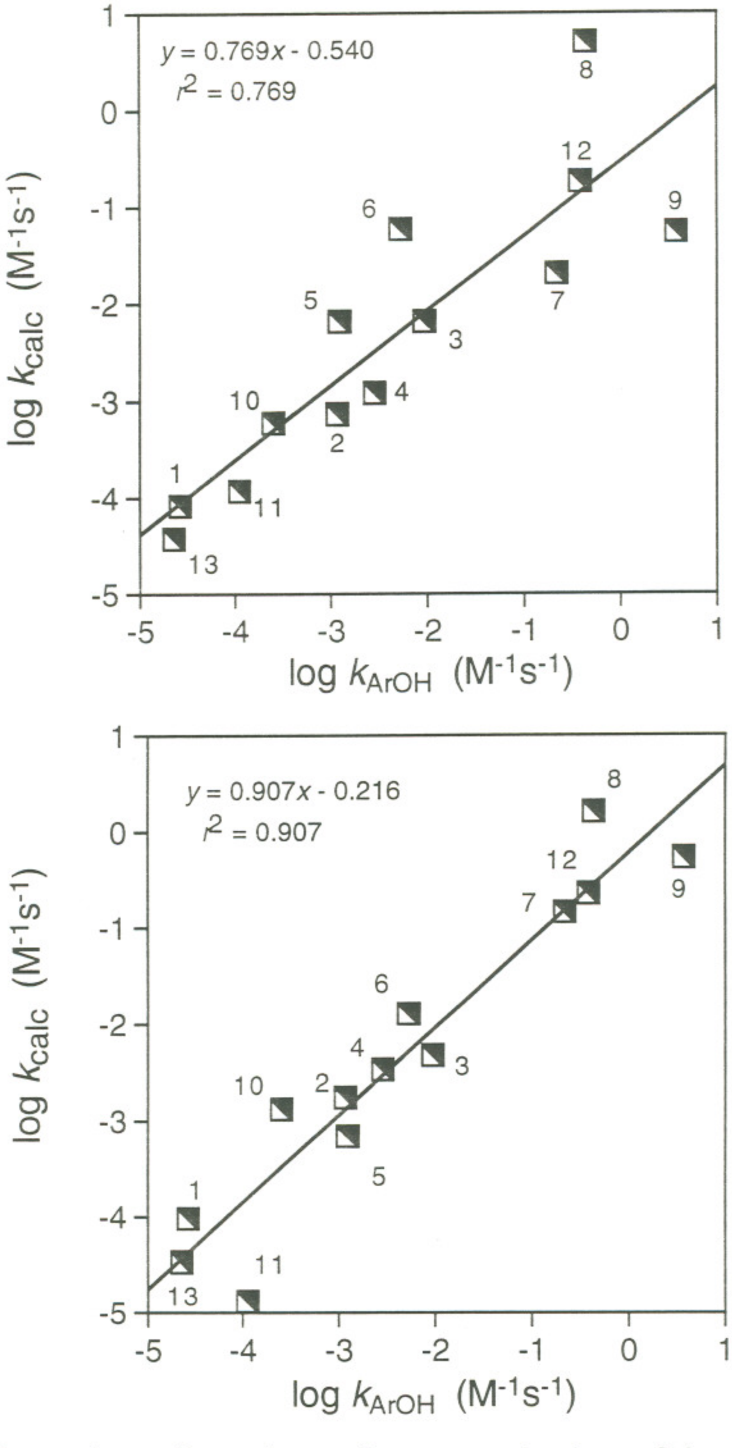


Figure 4.8. Comparison of experimentally measured values of the apparent second-order rate constants (k_{ArOH}) and values derived from eq 32 (top) and eq 33 (bottom). A line of unit slope and 0 intercept would signify a perfect fit to the model. The numbers correspond to the compounds in Table 4.2.

CHAPTER 5

Summary and Conclusions

The results presented in this thesis provide a comprehensive investigation of aqueous phase oxidation-reduction reactions between Cr(VI) and substituted phenols under conditions typical of waste mixtures at contaminated sites. The reactions of Cr(VI) and phenols are largely unexplored in the chemical literature and completely undefined in an environmental context. This research has addressed the need for redox reaction data for these two components under environmentally significant conditions. The results enable a coherent understanding of Cr(VI)/phenol interactions and allow subsequent field-site investigations and modeling efforts to take redox transformation processes of these compounds into account.

Chapters 3 and 4 detail a systematic investigation of the redox interactions between Cr(VI) and phenols. The overall research strategy was divided into two stages: a kinetic investigation, and an investigation and analysis of the "course of reaction." In the kinetic studies, Cr(VI) was reacted with 14 different phenolic compounds in single-phase aqueous solution and the redox reaction rates were measured. Several system parameters (Cr(VI) concentration, phenol concentration, pH, ionic strength, temperature, and phenol structure) were varied systematically to determine their effects on reaction rates. The results comprise a novel experimental data set that encompasses wide range of conditions. Additionally, identification of particular system parameters that strongly affect the reaction kinetics provided a framework for mechanistic analysis. The second research agenda focussed on identifying suspected reaction intermediates and products in order to elucidate individual reaction steps. Taken together, the information gained from these two stages, and with supporting literature concerning Cr(VI) interactions with other organic and inorganic compounds, and oxidations of phenols by other oxidizing agents, we have deduced a reaction scheme and a rate law that has been successfully calibrated over a wide range of reactant concentrations and pH values.

For the most part, the research described above in the previous chapters was an exercise in applied physical organic chemistry. We started with a reaction, worked our way from the empirical level down to the molecular level, and ended with a reasonable reaction mechanism and rate law that accounts for the experimental evidence. This stratagem is typical of the deductive process involved in determining a reaction mechanism. Characterizing the redox processes on both a macroscopic, empirical level as well as a molecular or mechanistic level is not only useful from a fundamental chemistry perspective, but it is also an important step in understanding the environmental relevance of these particular interactions.

The overall goal of this research project was to gain an understanding of the propensity for Cr(VI)/phenol redox transformations in the environment and their potential effects on contaminant characteristics. Given that Cr(VI) and phenols are both reactive materials found in the environment, our primary questions of environmental relevance were: 1), do they react in such a way as to fundamentally alter their transport and toxicity characteristics, 2), what are the timescales of these reactions and are they environmentally relevant , and 3), what are the environmental conditions that affect the rates and can we characterize these effects? Rather than devoting this chapter to a step-by-step recapitulation of each experimental result, we will examine these questions in the context of our research goals.

Redox Transformations

One of the most vexing problems in assessing the fate of environmental contaminants is the potential for chemical transformations to alter their toxicity and transport properties. The redox transformations of Cr(VI) and phenolic co-contaminants are a particuarly illustrative example of this phenomenon. As we have already discussed in the Chapter 1 and Chapter 2 of this thesis, Cr(VI) and Cr(III) exhibit acutely different toxicities and mobilities. Reduction of Cr(VI) to Cr(III) changes it from a soluble, weakly sorbing, and toxic anion to a relatively insoluble, non-toxic cation.

Our finding of Cr(VI) reduction was rather intuitive in comparison to the observed oxidative transformations of phenols. The oxidation of phenols in water involve free-radical mechanisms that can lead to a multiplicity of products resulting from primary and secondary reactions. The main goal of the product analysis was to identify and characterize the new organic compounds that can be expected to appear in waste mixtures of Cr(VI) and phenols. Our analysis focussed on the oxidized monomers and low molecular weight "polymers" (mostly dimers) that are believed to be the initial oxidation products. Overall, these reactions led to the formation of phenols with oxidized substituents, oxygen additions, and usually an assortment of coupled products and aromatic polymers. These products are consistent with mechanisms involving the initial formation of phenoxy radicals or cations followed by secondary hydrolysis or ring-coupling reactions.

Longer reaction times tended to produce a higher yield of insoluble polymers. Although Cr(VI) is considered to be a strong oxidant, it did not demonstrate the ability to completely mineralize phenols under the conditions we studied. The formation of insoluble polymers from relatively soluble reactants is a striking example of a way in which the mobility of a waste constituent can change dramatically as a result of reactivity in a waste mixture. In addition, depending on the phenol, the toxicity of the transformed phenol may be of even greater concern than that of the parent compound. The major reaction products reported in Chapter 4 do not to our knowledge represent a significant health concern. However, these compounds are congeners of benzofurans and dibenzo-*p*-dioxins, which are a major environmental concern. We stress that we did not detect formation of benzofurans or dibenzo-*p*-dioxins in any of our experiments, and suggest only the possibility of their formation. These highly toxic, high molecular weight condensation products may be produced in these reactions at lower concentrations than our experimental detection limits . A complete analysis of all reaction products was not the objective of this research project, but in light of the typical oxidation products identified, research devoted to identifying and quantifying the reaction products of Cr(VI) oxidation of phenols would improve our knowledge of potentially hazardous phenol oxidation products.

Reaction Timescales

From the results of our kinetic investigations we found that phenols readily reduce Cr(VI) to Cr(III) on timescales comparable to environmental transport timescales. The data show that the velocities at which theses components react vary by many orders of magnitude depending on reactants and solution conditions. Reaction rates are most strongly affected by pH, and phenol structure. The log k_{ArOH}-pH profiles shown in Figure 4.4 (chapter 4), indicate that rates can vary up to six orders of magnitude over the pH range 1 - 7 depending on the phenolic compound. Comparison of the pH profiles for the four compounds shown reveal that the pH dependency for Cr(VI) reduction is specific for each phenol. Rates spanned 4 orders of magnitude for 4-methoxyphenol but only 3 orders for 2,6-dimethoxyphenol over the same pH range, indicating that rates depend heavily on phenol structure. At pH 2, for example, rates for Cr(VI) reduction by 14 phenols spanned 6 orders of magnitude (Table 3.5, chapter 3). In general, electron-donating substituents (methyl, methoxy) increased reactivity, and electron-withdrawing groups (chloro, nitro, aldehyde) decreased reactivity relative to unsubstituted phenol.

Figure 3.13 (in Chapter 3) illustrates the broad range of reaction timescales and shows their relationship to characteristic timescales of transport processes in both surface and subsurface waters. This schematic representation shows that these reactions are fast enough to be environmentally significant, and also slow enough that we can not assume instantaneous reactions or chemical equilibrium. Accurate prediction of the transport and fate of these components and their redox transforms therefore requires explicit treatment of the time dependent changes in the concentrations of both the parent compounds and the reaction products.

Rate Effects: An Explicit Analysis

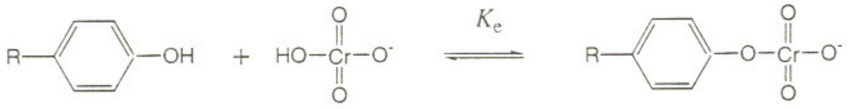
In order to adequately predict the environmental impact of these redox transformations we must be able to model the kinetics in sufficient detail such that the principal factors affecting the reaction rate are included in the rate expression. In general, the simpler the kinetic model, the more easily it can be incorporated into transport models such that migration and transformations can be described both temporally and spatially. At constant pH the reaction kinetics can be modeled successfully by a second-order rate expression

$$\text{rate} = k_{\text{ArOH}}[\text{HCrO}_4^-][\text{ArOH}] \qquad (1)$$

in which the overall rate is proportional to $HCrO_4^-$ and phenol concentrations. A simple empirical rate expression of this nature is computationally appealing. We also found it quite useful for determining characteristic reaction timescales and predicting reaction rates given appropriate data. However, the general applicability of this rate expression is limited by an inability to find a simple mathematical expression that fits k_{ArOH} as a function of pH. Relatively complex equations (e.g., third-order polynomials) can be used to fit the data, but this negates the computational efficiency of the second-order rate formulation.

An alternative to rate equations based on empirical observations is a fully developed rate law based on a proposed reaction mechanism. A rate law based on a mechanism gives us a much more rigorous basis for prediction of reaction rates. Variables such as reactant speciation, pH, and ionic strength effects can be dealt with in a much more precise manner. In addition, knowledge of the molecularity of the reaction provides insights into Cr(VI) or phenol interactions in systems yet unexamined.

From interpretation of experimental and literature evidence, we proposed that the redox interaction of Cr(VI) and substituted phenols proceeds via a rapid pre-oxidative equilibrium formation of chromate-ester between $HCrO_4^-$ and undissociated ArOH. The subsequent rate-limiting decomposition of the ester complex is proton dependent and proceeds via an inner-sphere electron transfer. The overall rate dependence on $[H^+]$ was explained by three parallel redox pathways involving zero, one, and two protons. The mechanism of these reaction steps are summarized in the following scheme.



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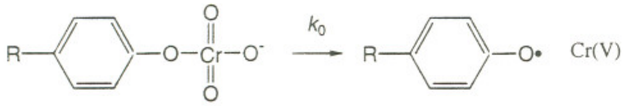

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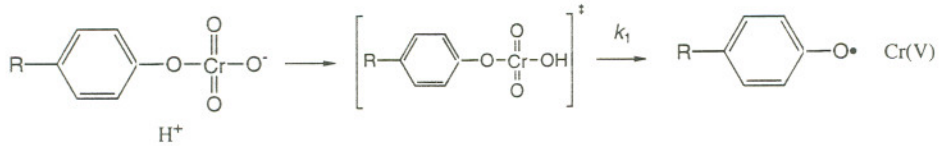

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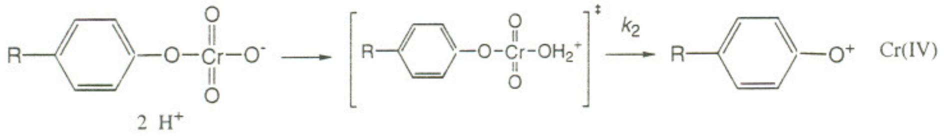


(5)

The rate data and rate law thus derived follow a three-term rate expression,

$$\text{Rate} = \{k_0 + k_1[\text{H}^+] + k_2[\text{H}^+]^2\}[\text{ester}] \tag{6}$$

$$= \{k_0 + k_1[\text{H}^+] + k_2[\text{H}^+]^2\}K_e[\text{HCrO}_4^-][\text{ArOH}] \tag{7}$$

Fitting the kinetic model to rate data collected as a function of $[H^+]$, $[HCrO_4^-]$, and [ArOH] resulted in the pH profiles shown in Figures 4.4 and 4.5. The general features of the curves reflect the factors controlling the reaction rate. In the pH range 1 - 6, Cr(VI) speciation is nearly constant, and the reaction rate is most sensitve to changes in pH. At approximately pH 6, the model predicts a sharp decline reaction rates as Cr(VI) speciation makes a shift from $HCrO_4^-$ dominance to CrO_4^{2-} dominance. The three electron transfer pathways (eqs 3 - 5) are dominated by the proton-independent pathway (eq 5) and thus the electron transfer step is relatively insensitive to $[H^+]$. In this region and the $HCrO_4^-$ concentration becomes a determinant factor in reaction rates.

Rate data for Cr(VI) reduction by 4-methyl-, 4-methoxy-, 2,6-dimethoxy-, and 3,4-dimethoxyphenol in the pH range 1 to 6 were fitted to the rate law above. The rate parameters derived from the model fit were very different for each phenol thus reflecting their overall differences in reactivity with Cr(VI). Using the rate parameters derived from pH 1 - 6 data, we calculated the apparent second-order rate constant for 2,6- and 3,4-dimethoxyphenol at pH 7. The *a priori* model predictions of a sharp drop in rate (i.e., from pH 6 to pH 7) agreed very well with rates measured at pH 7. Such evidence suggested that the proposed mechanistic formulation was a robust and accurate description of the system.

Elucidation of a reaction mechanism and the corresponding rate law revealed several fundamental features of the reaction that were impossible to infer fom empirical investigations alone. Two of the most prominent features of the Cr(VI)/phenol system are the kinetic dependence on the concentration of the $HCrO_4^-$ species as opposed to dependence on total Cr(VI) concentration, and the strong rate dependence on the proton concentration. These two phenomena are partially linked, and, in effect, there are two separate pH effects that influence the reaction. The first pH effect can be attributed to rapid acid-base equilibria involving the aqueous speciation of Cr(VI). In the general pH range 1-14, the only important acid-base equilibrium involving Cr(VI) is the dissociation of $HCrO_4^-$

$$HCrO_4^- = CrO_4^{2-} + H^+ \qquad pK_a = 6.52 \qquad (8)$$

In essence, this rapid equilibrium which precedes the rate-determining step causes a change in the concentration of the reactive $HCrO_4^-$ species. Thus, at pH values greater than the pK_a of $HCrO_4^-$, the reaction rate drops sharply in response to the dominant Cr(VI) species passing from $HCrO_4^-$ to CrO_4^{2-}.

The second effect we can ascribe to the participation of protons in the rate-determining reaction steps (eqs 3 - 5). The relative contributions of each of the three parallel reaction pathways are specific for each phenol, but the general features are the same. Rate data generated for Cr(VI) reduction as a function of $[H^+]$ in the pH range 1 - 6 indicated that rates were strongly dependent on the proton concentration at low pH, but less so at near-neutral pH values. Rates increased sharply for increasing $[H^+]$ showing a near second-order dependence *ca.* pH 1 - 2. At moderate acidities (pH 2 - 4) the rate showed an approximate first-order proton dependence, and at lower acidities (pH 4 - 6) the reaction rate appeared to approach a region of pH-independence. This last region of lowest acidity is perhaps the most environmentally relevant, and unfortunately, as discussed below, Cr(VI) redox investigations are rarely conducted at these pHs.

The critical dependence of reaction rates on Cr(VI) speciation and proton concentration raises several points. First, calculations of Cr(VI) reduction rates must take careful consideration of Cr(VI) speciation. This is perhaps an intuitive point, but frequently $HCrO_4^-$ and Cr(VI) are used interchangeably, and Cr(VI) concentrations in field samples are usually logged as *total* [Cr(VI)]. For dilute solutions of Cr(VI) and in the pH range 1 to 6, $HCrO_4^-$ is the dominant species and there is minimal error in using total Cr(VI) for $HCrO_4^-$. However, at pH values greater than the pK_a of the $HCrO_4^-/CrO_4^{2-}$ equilibria (eq 8), CrO_4^{2-} becomes the dominant species. Also, at pH < 6 and concentrations of Cr(VI) greater than approximately 0.05 M, dimerization

$$2\ HCrO_4^- = Cr_2O_7^{2-} + H_2O \qquad K_d \approx 35.5 \qquad (9)$$

becomes important and dichromate $Cr_2O_7^{2-}$ and its protonated forms become the dominant Cr(VI) species. For these two situations in particular, failure to make the distinction between $HCrO_4^-$ and Cr(VI) can lead to large overestimates of Cr(VI) reduction rates.

Second, as we cautioned earlier, it is dubious to extrapolate from lab studies conducted at extremely high acidities and reactant concentrations to relatively dilute, mildly acidic conditions found in the environment. Our Cr(VI)/phenol results illustrate this point very well. In the lower pH region, the $HCrO_4^-$ and pH dependencies for Cr(VI) and phenol are consistent with the $HCrO_4^-$ dependence and the first- and second-order proton dependencies determined for reduction of Cr(VI) by various reducing agents including Fe(II), alcohols, aldehydes, and thiols. However, the vast majority of these other studies have been restricted to the pH range 0 - 3. If we had, for instance, restricted our studies to a pH region 0 - 3, we would have undoubtedly concluded that the reaction follows a second-order rate dependence with respect to $[H^+]$. A rate expression with a second-order proton dependence would greatly underestimate reaction rates at higher pH values 4 - 8.

Application and Extensions into Other Environmental Systems

These conclusions can be of fundamental importance with respect to remediation strategies involving Cr(VI) contamination. A case in point involves the strategy of passive remediation of contaminated aquifers. Active remediation techniques such as excavation and pump-and-treat are effective at remediating highly contaminated plume areas, but often their inability to remove the last residual "traces" of contaminant make these techniques both time and cost prohibitory. The passive, or "natural attenuation," approach may be an appropriate option if the aquifer system shows both a *chemical* and *kinetic* potential to reduce the residual amounts of Cr(VI). Various tests are used to determine a system's Cr(VI)-reduction capacity. However, these tests provide little information on the timescales over which these transformations will occur in the environment. Consideration of reduction kinetics can be important if, for example, transport processes are much faster than the actual reaction rates in which case the plume may migrate significant distances before Cr(VI) reduction can occur. Given a relatively simple rate expression and appropriate rate data, transport models can be modified to include kinetic transformations so that an estimate not only of the reduction potential but also of the reaction timescales can be made.

These conclusions concerning Cr(VI)/phenol interactions can also have important implications towards understanding Cr(VI) or phenol redox interactions in other environmentally relevant systems. For example, field and lab studies have shown that Cr(VI) is reduced to Cr(III) in the presence of naturally occuring reducing agents such natural organic matter (NOM). In particular, humic and fulvic acids have been implicated as a principal Cr(VI) reducing agents in surface waters and upper soil horizons. A significant fraction of humic and fulvic acids are believed to be composed of phenolic moieties, and such materials almost certainly contain phenol moieties substituted with methyl, methoxy and aldehyde groups. Our findings of the importance of phenol substituent identity and position may be a useful starting point for a detailed investigation of the active Cr(VI) reductant-moieties in natural organic matter.

APPENDIX A

SELECTED EXPERIMENTAL DATA

1. EXCESS PHENOL EXPERIMENTS

The majority of the kinetic experiments were performed under reaction conditions excess in concentration of the phenol reductant. Reactions were initiated by mixing a small amount of concentrated Cr(VI) stock solution into aqueous solutions of phenol. Reaction progress was monitored as a change (decrease) in the Cr(VI) concentration as determined by the diphenylcarbazide (DPC) colorimetric procedure. Experiments were conducted where one reaction parameter was varied in order to elucidate its kinetic dependence. The data listed in Tables A.1.a.-A.1.e. correspond to excess phenol experiments discussed in Chapter 3 and Chapter 4.

2. EXCESS Cr(VI) EXPERIMENTS

Several experiments were performed under conditions of excess Cr(VI). 4-methylphenol was used as the reductant in the majority of these experiments, but several other reactions were performed utilizing other phenols as the reducing agent . "Dilute" solutions of the chosen phenol were made up in pH buffer solution. The reactions were initiated by addition of a small volume of concentrated Cr(VI) stock solution made up as $K_2Cr_2O_7$ dissolved in QH_2O. Reaction progress was followed by withdrawing a small aliquots of the reaction solution and analyzing for phenol concentration by HPLC with UV/vis detection. As discussed in Chapter 3, during these experiments phenol speciation was essentially constant, and $[ArOH] \approx [ArOH]_{tot}$. At these high concentrations of Cr(VI), however, Cr(VI) speciation becomes dependent on the Cr(VI) dimerization eq 3. Cr(VI) speciation was calculated using the following equilibria:

$$H_2CrO_4 \;=\; H^+ + HCrO_4^- \qquad K_1 = 1.21\ \text{M} \tag{1}$$

$$HCrO_4^- \;=\; H^+ + CrO_4^{2-} \qquad K_2 = 3.0 \times 10^{-7}\ \text{M} \tag{2}$$

$$2\ HCrO_4^- \;=\; Cr_2O_7^{2-} + H_2O \qquad K_d = 35.5 \tag{3}$$

$$HCr_2O_7^- \;=\; H^+ + Cr_2O_7^{2-} \qquad K'_2 = 0.85\ \text{M} \tag{4}$$

These equilibria constants were taken from Wiberg [1965] (see references at the back of Chapter 2) and refer to aqueous solution in the absence of other ions, $[Cr(VI)]_{tot} = 0.1$ mM, and $t = 25$ °C. The value given in eq 4 is not well established. Cr(VI) speciation was calculated both with and without inclusion of this equilibrium. The calculated speciation was not affected significantly by inclusion of the acid-dichromate species $HCr_2O_7^-$.

For the excess *phenol* experiments, ionic strength was set to $I = 0.1$ eq/L by addition of $KClO_4$ to the initial pH buffer solutions. The values of the ionic strength of the excess *Cr(VI)* experiments were in excess of 0.1 eq/L due to the addition of Cr(VI) to the system. The final ionic strength was determined using an iterative process to determine the Cr(VI) speciation and the ionic strength. Ionic strength was calculated by eq 5, and the activity coefficients for activity corrections of equilibria constants were determined using the Davies equation (eq 6). Selected data for the experiments conducted in the presence of excess Cr(VI) are given in Tables A.2.a - A.2.e.

$$I \;=\; 0.5\{2\text{x}[KClO_4]_{salt} + [H^+] + [ClO_4^-]_{acid} + [K^+]_{Cr(VI)} + [HCrO_4^-] + 2\text{x}[CrO_4^{2-}] + 2\text{x}[Cr_2O_7^{2-}] + [HCr_2O_7^-]\} \tag{5}$$

$[KClO_4]_{salt}$ ≡ $KClO_4$ added to the buffer to set $I = 0.1$ eq/L
$[ClO_4^-]_{acid}$ ≡ ClO_4^- from perchloric acid ($HClO_4$) added to the buffer to attain desired pH
$[K^+]_{Cr(VI)}$ ≡ K^+ from Cr(VI)-$K_2Cr_2O_7$ added to reaction solution

Davies equation: $$\log \gamma_i \;=\; -0.5 z_i^2(\sqrt{I}/(1+\sqrt{I}) - 0.21I) \tag{6}$$

Table A.1.a. Pseudo-first-order rate constants for the reduction of Cr(VI) by excess 4-methylphenol as a function of the reaction temperature and pH. $[\mathrm{Cr(VI)}]_o = 5.0 \times 10^{-4}$ M; $I = 0.1$ M; $[\mathrm{PO_4}] = 0.05$ M.

pH	**$[H^+]$ (M)**	t **°C**	**[4MP] (M)**	k_{exp} **(s^{-1})**
1.0	1.332×10^{-1}	15	0.05	$1.69 \pm 0.07 \times 10^{-3}$
1.0	1.332×10^{-1}	25	0.05	$2.57 \pm 0.03 \times 10^{-3}$
1.0	1.332×10^{-1}	35	0.05	$4.41 \pm 0.11 \times 10^{-3}$
2.0	1.295×10^{-2}	15	0.05	$2.46 \pm 0.06 \times 10^{-5}$
2.0	1.295×10^{-2}	25	0.05	$5.16 \pm 0.10 \times 10^{-5}$
2.0	1.295×10^{-2}	35	0.05	$8.74 \pm 0.16 \times 10^{-5}$
3.0	1.295×10^{-3}	15	0.05	$1.45 \pm 0.05 \times 10^{-6}$
3.0	1.295×10^{-3}	25	0.05	$3.57 \pm 0.13 \times 10^{-6}$
3.0	1.295×10^{-3}	35	0.05	$6.90 \pm 0.21 \times 10^{-6}$

Table A.1.b. Pseudo-first-order rate constants for the reduction of Cr(VI) by excess 4–methylphenol as a function of varying concentrations of reductant. $[Cr(VI)]_o$ = 0.5 mM, pH = 2.0, I = 0.1 M, t = 25 °C.

[4-methylphenol] (M)	k_{exp} (s^{-1})
0.02506	$2.93 \pm 0.02 \times 10^{-5}$
0.03754	$4.45 \pm 0.02 \times 10^{-5}$
0.05002	$5.16 \pm 0.10 \times 10^{-5}$
0.06255	$7.25 \pm 0.02 \times 10^{-5}$
0.07503	$8.75 \pm 0.07 \times 10^{-5}$

Table A.1.c. Pseudo-first-order rate constants for the reduction of Cr(VI) by 4-methylphenol and 4-methoxyphenol as a function of pH.

4-methylphenol

pH	**$[H^+]$ (M)**	**[ArOH] (M)**	**k_{exp} (s^{-1})**
1.0	1.33×10^{-1}	0.05	$2.57 \pm 0.03 \times 10^{-3}$
2.0	1.33×10^{-2}	0.05	$5.50 \pm 0.10 \times 10^{-5}$
2.984	1.38×10^{-3}	0.10	$1.21 \pm 0.01 \times 10^{-5}$
3.0	1.33×10^{-3}	0.05	$3.57 \pm 0.12 \times 10^{-6}$
4.853	1.87×10^{-5}	0.10	$4.57 \pm 0.04 \times 10^{-7}$

4-methoxyphenol

pH	**$[H^+]$ (M)**	**[ArOH] (M)**	**k_{exp} (s^{-1})**
1.98	1.39×10^{-2}	0.02	$4.31 \pm 0.06 \times 10^{-3}$
2.984	1.38×10^{-3}	0.02	$3.19 \pm 0.01 \times 10^{-4}$
3.871	1.79×10^{-4}	0.02	$3.23 \pm 0.10 \times 10^{-5}$
4.853	1.81×10^{-5}	0.02	$1.16 \pm 0.01 \times 10^{-5}$
6.071	1.24×10^{-6}	0.02	$3.82 \pm 0.07 \times 10^{-6}$

Table A.1.d. Pseudo-first-order rate constants for the reduction of Cr(VI) by 2,6–dimethoxyphenol and 3,4-dimethoxyphenol as a function of pH.

2,6-dimethoxyphenol

pH	[H$^+$] (M)	[ArOH] (M)	k_{exp} (s^{-1})
1.98	1.39 x 10^{-2}	0.02	8.70 ± 0.05 x 10^{-3}
2.50	4.21 x 10^{-3}	0.02	1.72 ± 0.02 x 10^{-3}
2.984	1.38 x 10^{-3}	0.02	2.91 ± 0.02 x 10^{-3}
3.871	1.79 x 10^{-4}	0.02	146 ± 0.10 x 10^{-4}
4.853	1.81 x 10^{-5}	0.02	1.16 ± 0.02 x 10^{-4}
6.071	1.24 x 10^{-6}	0.02	9.59 ± 0.12 x 10^{-5}
7.00	1.30 x 10^{-7}	0.02	1.30 ± 0.05 x 10^{-5}

3,4-dimethoxyphenol

pH	[H$^+$] (M)	[ArOH] (M)	k_{exp} (s^{-1})
1.98	1.39 x 10^{-2}	4.00 x 10^{-3}	1.50 ± 0.02 x 10^{-2}
2.984	1.38 x 10^{-3}	0.02	3.55 ± 0.02 x 10^{-3}
3.871	1.79 x 10^{-4}	0.02	3.38 ± 0.07 x 10^{-4}
4.853	1.81 x 10^{-5}	0.02	1.38 ± 0.02 x 10^{-4}
6.071	1.24 x 10^{-6}	0.02	5.49 ± 0.10 x 10^{-5}
7.00	1.30 x 10^{-7}	0.02	1.45 ± 0.05 x 10^{-5}

Table A.1.e. Apparent second-order rate constants for the reduction of Cr(VI) by 4-methyl, 4-methoxy, 2,6-dimethoxy, and 3,4–dimethoxyphenol as a function of [H+]. Values of k_{ArOH} correspond to the data in Table A.1.c. and Table A.1.d.

pH	**[H+] (M)**	**k_{ArOH} ($M^{-1}s^{-1}$)**			
		4-methyl	**4-methoxy**	**2,6-dimethoxy**	**3,4-dimethoxy**
1.00	1.33×10^{-1}	$5.15 \pm 0.06 \times 10^{-2}$			
1.98	1.39×10^{-2}		$2.16 \pm 0.03 \times 10^{-1}$	$4.35 \pm 0.10 \times 10^{-1}$	3.75 ± 0.06
2.00	1.33×10^{-2}	$1.10 \pm 0.02 \times 10^{-3}$			
2.50	4.21×10^{-3}			$8.58 \pm 0.12 \times 10^{-2}$	
2.98	1.38×10^{-3}	$1.21 \pm 0.01 \times 10^{-4}$	$1.59 \pm 0.01 \times 10^{-2}$	$5.40 \pm 0.04 \times 10^{-2}$	$1.77 \pm 0.01 \times 10^{-1}$
3.00	1.33×10^{-3}	$7.14 \pm 0.26 \times 10^{-5}$			
3.87	1.79×10^{-4}		$1.61 \pm 0.05 \times 10^{-3}$	$1.45 \pm 0.01 \times 10^{-2}$	$1.69 \pm 0.04 \times 10^{-2}$
4.85	1.81×10^{-5}	$4.57 \pm 0.04 \times 10^{-6}$	$5.82 \pm 0.05 \times 10^{-4}$	$7.28 \pm 0.08 \times 10^{-3}$	$6.89 \pm 0.08 \times 10^{-3}$
6.01	1.24×10^{-6}		$1.91 \pm 0.03 \times 10^{-4}$	$4.80 \pm 0.06 \times 10^{-3}$	$2.75 \pm 0.05 \times 10^{-3}$
7.00	1.30×10^{-7}			$6.50 \pm 0.25 \times 10^{-4}$	$7.25 \pm 0.25 \times 10^{-4}$

Table A.2.a. Pseudo-first-order rate constants for the oxidation of 4–methylphenol by excess Cr(VI) as a function of Cr(VI) concentration. $[4MP]_o$ = 1.0 mM, pH = 1.0, t = 25 °C. Cr(VI) speciation and ionic strength calculations are shown in Tables A.2.b.-A.2.c.

[Cr(VI)] (M)	k_{exp} (s^{-1})
0.020	$5.19 \pm 0.06 \times 10^{-4}$
0.040	$8.32 \pm 0.19 \times 10^{-4}$
0.060	$1.02 \pm 0.12 \times 10^{-3}$
0.080	$1.23 \pm 0.03 \times 10^{-3}$
0.1765	$2.17 \pm 0.05 \times 10^{-3}$
0.500	$4.10 \pm 0.06 \times 10^{-3}$

Table A.2.b. Ionic strength, [H+], and Cr(VI) speciation calculations for the excess Cr(VI) experiments tabulated in Table A.2.a. Cr(VI) speciation does not include the dichromate/acid-dichromate equilibrium (eq 4).

$[Cr(VI)]_{tot}$ (M)	*I* (M)	[H+] (M)	$[H_2CrO_4]$ (M)	$[HCrO_4^-]$ (M)	$[CrO_4^{2-}]$ (M)	$[Cr_2O_7^{2-}]$ (M)
0.020	0.158	0.1378	5.666×10^{-4}	9.006×10^{-3}	6.426×10^{-8}	5.214×10^{-3}
0.040	0.178	0.1375	8.551×10^{-4}	1.388×10^{-2}	1.032×10^{-7}	1.263×10^{-2}
0.060	0.197	0.1373	1.065×10^{-3}	1.761×10^{-2}	1.355×10^{-7}	2.066×10^{-2}
0.080	0.217	0.1372	1.233×10^{-3}	2.072×10^{-2}	1.645×10^{-7}	2.903×10^{-2}
0.1765	0.313	0.1366	1.785×10^{-3}	3.170×10^{-2}	2.798×10^{-7}	7.151×10^{-2}
0.500	0.635	0.1355	2.900×10^{-3}	5.445×10^{-2}	5.331×10^{-7}	2.213×10^{-1}

Table A.2.c. Ionic strength, [H^+], and Cr(VI) speciation calculations for the excess Cr(VI) experiments tabulated in Table A.2.a. Cr(VI) speciation includes the dichromate/acid-dichromate equilibrium (eq 4).

$[Cr(VI)]_{tot}$ (M)	I (M)	[H+] (M)	$[H_2CrO_4]$ (M)	$[HCrO_4^-]$ (M)	$[CrO_4^{2-}]$ (M)	$[Cr_2O_7^{2-}]$ (M)	$[HCr_2O_7^-]$ (M)
0.020	0.157	0.1376	5.565×10^{-4}	8.859×10^{-3}	6.329×10^{-8}	5.043×10^{-3}	2.491×10^{-4}
0.040	0.177	0.1369	8.371×10^{-4}	1.364×10^{-2}	1.017×10^{-7}	1.218×10^{-2}	5.770×10^{-4}
0.060	0.196	0.1365	1.040×10^{-3}	1.730×10^{-2}	1.338×10^{-7}	1.992×10^{-2}	9.090×10^{-4}
0.080	0.216	0.1360	1.201×10^{-3}	2.035×10^{-2}	1.627×10^{-7}	2.799×10^{-2}	1.236×10^{-3}
0.1765	0.310	0.1340	1.723×10^{-3}	3.117×10^{-2}	2.800×10^{-7}	6.909×10^{-2}	2.714×10^{-3}
0.500	0.628	0.1284	2.704×10^{-3}	5.360×10^{-2}	5.540×10^{-7}	2.145×10^{-1}	7.325×10^{-3}

Table A.2.d. Pseudo-first-order rate constants for the oxidation of 4-methylphenol by excess Cr(VI) at pH 1 - 2. $[Cr(VI)]_o$ = 0.01 M, *t* = 25 ˚C.

pH_o	pH	*I* (M)	$[H^+]$ (M)	k_{exp} (s^{-1})	weighted avg.
1.0	0.987	0.148	1.380×10^{-1}	$3.05 \pm 0.12 \times 10^{-4}$ $3.10 \pm 0.09 \times 10^{-4}$ $2.97 \pm 0.10 \times 10^{-4}$	$3.05 \pm 0.06 \times 10^{-4}$
1.25	1.262	0.120	7.143×10^{-2}	$1.23 \pm 0.06 \times 10^{-4}$ $1.12 \pm 0.05 \times 10^{-4}$	$1.17 \pm 0.04 \times 10^{-4}$
1.5	1.533	0.110	3.827×10^{-2}	$4.08 \pm 0.26 \times 10^{-5}$ $4.27 \pm 0.26 \times 10^{-5}$	$4.17 \pm 0.18 \times 10^{-5}$
2.0	2.012	0.110	1.270×10^{-2}	$5.92 \pm 0.14 \times 10^{-6}$ $6.05 \pm 0.14 \times 10^{-6}$	$5.98 \pm 0.10 \times 10^{-6}$

Table A.2.e. Ionic strength, [H^+], and Cr(VI) speciation calculations for the excess Cr(VI) experiments tabulated in Table A.2.d. Cr(VI) speciation includes the dichromate/acid-dichromate equilibrium (eq 4).

pH_o	**pH**	***I*** (M)	**[H^+]** (M)	**[H_2CrO_4]** (M)	**[$HCrO_4^-$]** (M)	**[CrO_4^{2-}]** (M)	**[$Cr_2O_7^{2-}$]** (M)	**[$HCr_2O_7^-$]** (M)
1.0	0.987	0.148	1.380 x 10^{-1}	3.528 x 10^{-4}	5.543 x 10^{-3}	3.868 x 10^{-8}	1.954 x 10^{-3}	9.881 x 10^{-5}
1.25	1.262	0.120	7.143 x 10^{-2}	1.982 x 10^{-4}	5.724 x 10^{-3}	6.984 x 10^{-8}	1.982 x 10^{-3}	5.732 x 10^{-5}
1.5	1.533	0.110	3.824 x 10^{-2}	1.074 x 10^{-4}	5.785 x 10^{-3}	1.315 x 10^{-7}	2.022 x 10^{-3}	3.140 x 10^{-5}
2.0	2.012	0.110	1.270 x 10^{-2}	3.588 x 10^{-5}	5.830 x 10^{-3}	4.002 x 10^{-7}	2.056 x 10^{-3}	1.057 x 10^{-5}

APPENDIX B

SUMMARY OF REGRESSION ANALYSIS FOR QSAR CORRELATIONS

QSAR correlations discussed in Chapter 3 and Chapter 4 were performed using both simple linear and multiple regression analysis. Regression analysis was performed with a statistical software package Abacus Concepts, StatView (Abacus Concepts, Inc., Berkeley, CA, 1992). The following tables and figures are printouts of the StatViw program.

Figure B.1. corresponds to the linear regression analysis of log k_{ArOH} vs. $E_{1/2}$ QSAR discussed in Chapter 3 and shown in Figure 3.12. The corresponding regression equation is eq. 8 (Chapter 3) and data are presented in Table 3.5. The regression excluded the three compounds that were di-ortho substituted (2,6-dimethyl-, 2,4,6-trimethyl-, and 2,6-dimethoxyphenol).

Figure B.2 - Figure B.6. correspond to the simple and multiple regression analysis discussed in Chapter 4. The multiple regression analysis (Figure B.3. - Figure B.6.) was referred to as the "Fujita" method.

Figure B.2 represents the linear-regression analysis corresponding to eq. 32 (Chapter 4) and Figure 4.7. excluding all ortho-substituted compounds.

Figure B.3. - Figure B.6. relate to the Fujita analysis. Log k_{ArOH} was correlated with $\sum\sigma^+$ (Figure B.3.), $\sum\sigma^+$ and $\sum E_s$ (Figure B.4.), $\sum\sigma^+$ and $\sum F$ (Figure B.5.), and $\sum\sigma^+$, $\sum E_s$, and $\sum F$ (Figure B.6.). The single parameter analysis coincides with Figure 4.8 (top) and eq. 33 (Chapter 4). The three parameter correlation ($\sum\sigma^+$, $\sum E_s$, and $\sum F$) corresponds to Figure4.8 (bottom) and eq. 34 (Chapter 4).

Regression Summary
log k(ArOH) vs. E(1/2)

Count	10
Num. Missing	4
R	.974
R Squared	.948
Adjusted R Squared	.942
RMS Residual	.439

ANOVA Table
log k(ArOH) vs. E(1/2)

	DF	Sum of Squares	Mean Square	F-Value	P-Value
Regression	1	28.279	28.279	1.47E2	<.0001
Residual	8	1.539	.192		
Total	9	29.818			

Regression Coefficients
log k(ArOH) vs. E(1/2)

	Coefficient	Std. Error	Std. Coeff.	t-Value	P-Value
Intercept	6.245	.733	6.245	8.522	<.0001
E(1/2)	-16.866	1.391	-.974	-1.2E1	<.0001

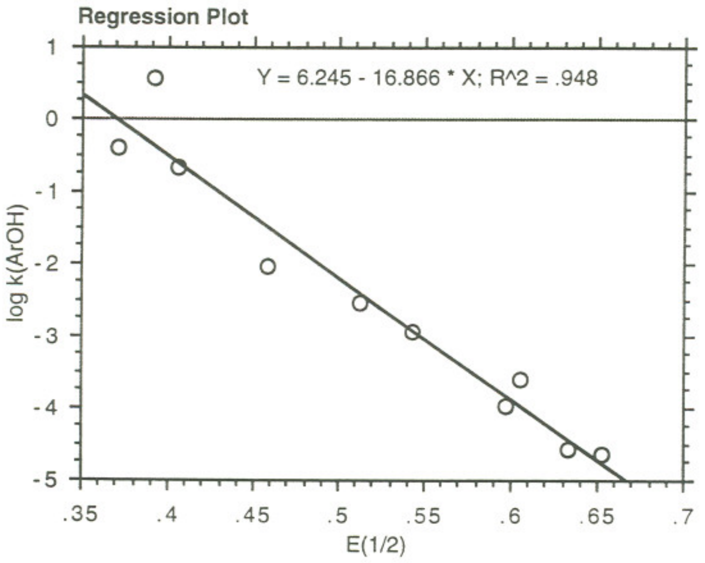


Figure B.1. Regression analysis for log k_{ArOH} vs. $E_{1/2}$ corresponding to eq. 8 (Chapter 3) and Figure 3.12.

Regression Summary
log k vs. s(+)

Count	7
Num. Missing	0
R	.987
R Squared	.973
Adjusted R Squared	.968
RMS Residual	.351

ANOVA Table
log k vs. s(+)

	DF	Sum of Squares	Mean Square	F-Value	P-Value
Regression	1	22.422	22.422	181.937	<.0001
Residual	5	.616	.123		
Total	6	23.039			

Regression Coefficients
log k vs. s(+)

	Coefficient	Std. Error	Std. Coeff.	t-Value	P-Value
Intercept	-4.506	.192	-4.506	-23.422	<.0001
s(+)	-5.137	.381	-.987	-13.488	<.0001

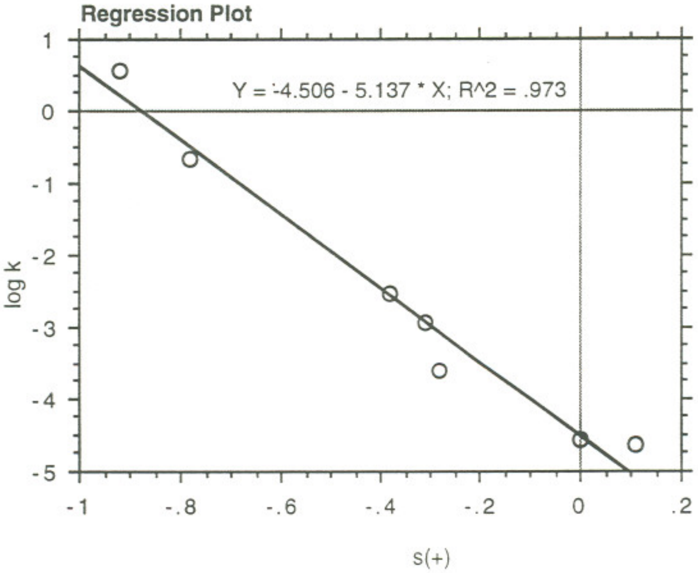


Figure B.2. Regression analysis for log k_{ArOH} vs. $\Sigma\sigma^{+}$ corresponding to eq. 32 (Chapter 4) and Figure 4.7. Analysis includes only para- and meta-substituted compounds.

Regression Summary
log k vs. 1 Independents

Count	13
Num. Missing	0
R	.877
R Squared	.769
Adjusted R Squared	.748
RMS Residual	.849

ANOVA Table
log k vs. 1 Independents

	DF	Sum of Squares	Mean Square	F-Value	P-Value
Regression	1	26.328	26.328	36.551	<.0001
Residual	11	7.923	.720		
Total	12	34.252			

Regression Coefficients
log k vs. 1 Independents

	Coefficient	Std. Error	Std. Coeff.	t-Value	P-Value
Intercept	-4.087	.374	-4.087	-10.941	<.0001
s(+)	-3.068	.507	-.877	-6.046	<.0001

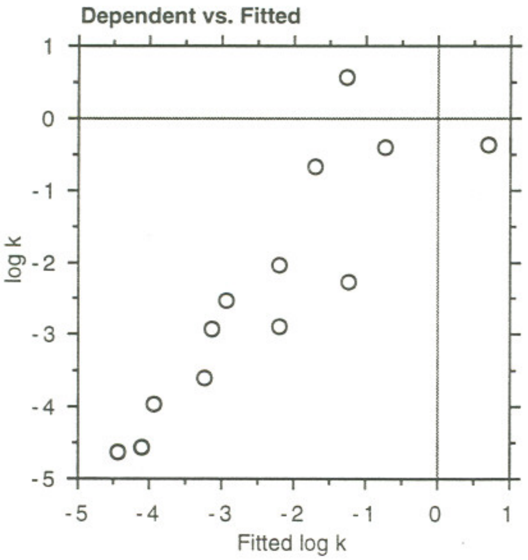
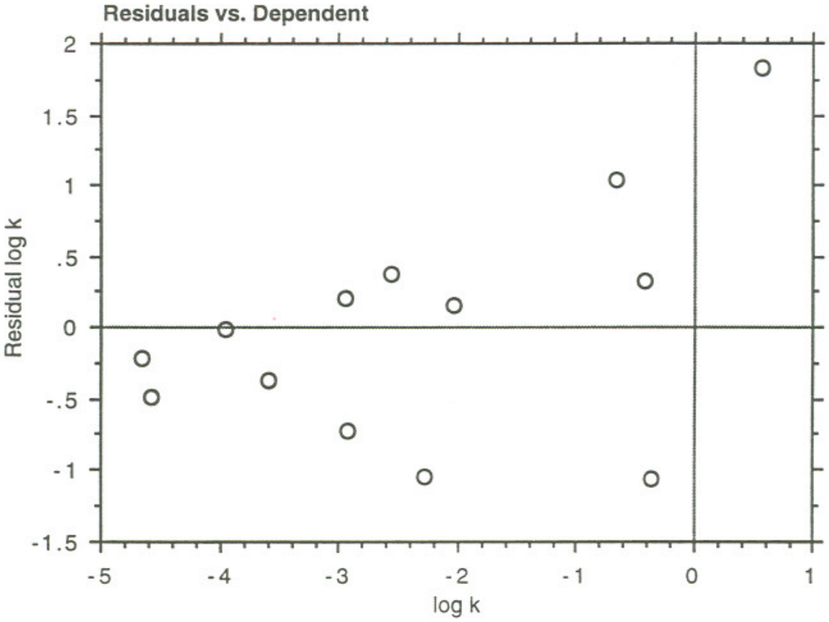
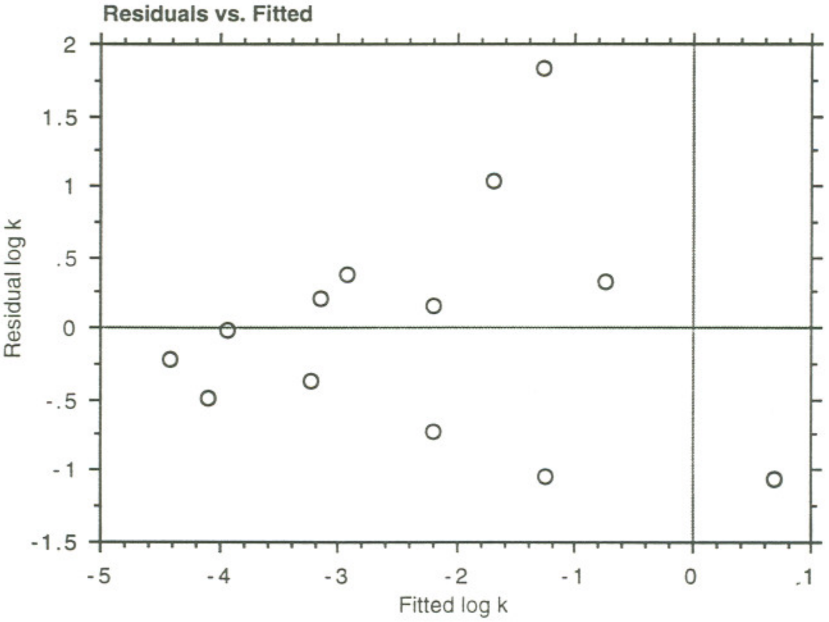


Figure B.3. Single parameter linear-regression analysis for log k_{ArOH} vs. $\Sigma\sigma^+$ corresponding to eq. 33 (Chapter 4) and Figure 4.8 (top). Regression analysis includes all (13) compounds (with the exception of 4-nitrophenol).


Residuals vs. Dependent


Residuals vs. Fitted

Regression Summary
log k vs. 2 Independents

Count	13
Num. Missing	0
R	.928
R Squared	.860
Adjusted R Squared	.833
RMS Residual	.691

ANOVA Table
log k vs. 2 Independents

	DF	Sum of Squares	Mean Square	F-Value	P-Value
Regression	2	29.471	14.735	30.823	<.0001
Residual	10	4.781	.478		
Total	12	34.252			

Regression Coefficients
log k vs. 2 Independents

	Coefficient	Std. Error	Std. Coeff.	t-Value	P-Value
Intercept	-3.962	.308	-3.962	-12.856	<.0001
s(+)	-3.535	.452	-1.010	-7.825	<.0001
E	.606	.236	.331	2.564	.0282

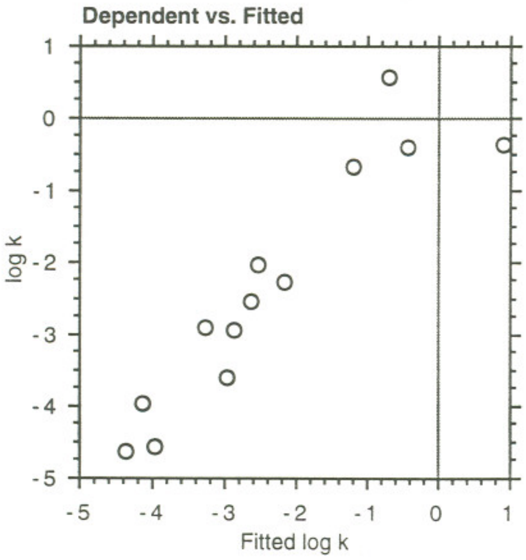
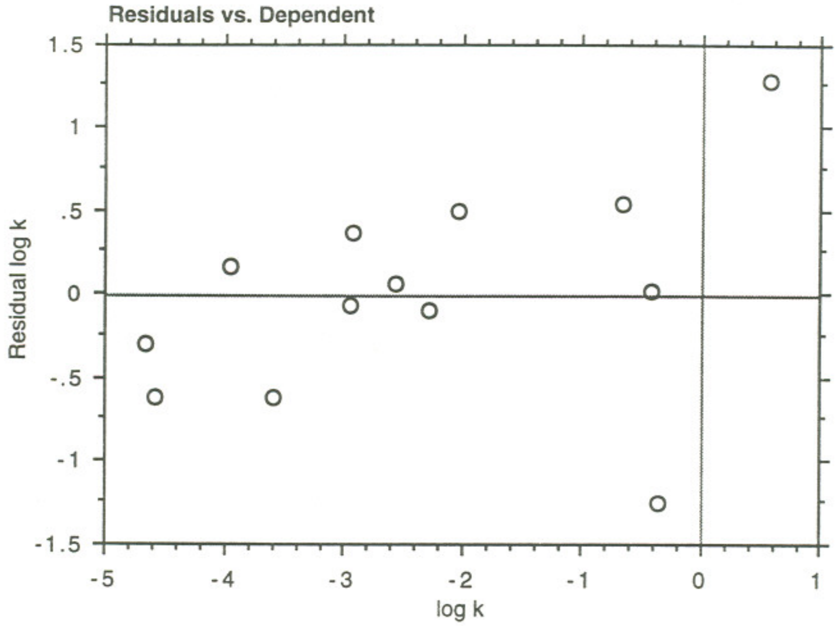
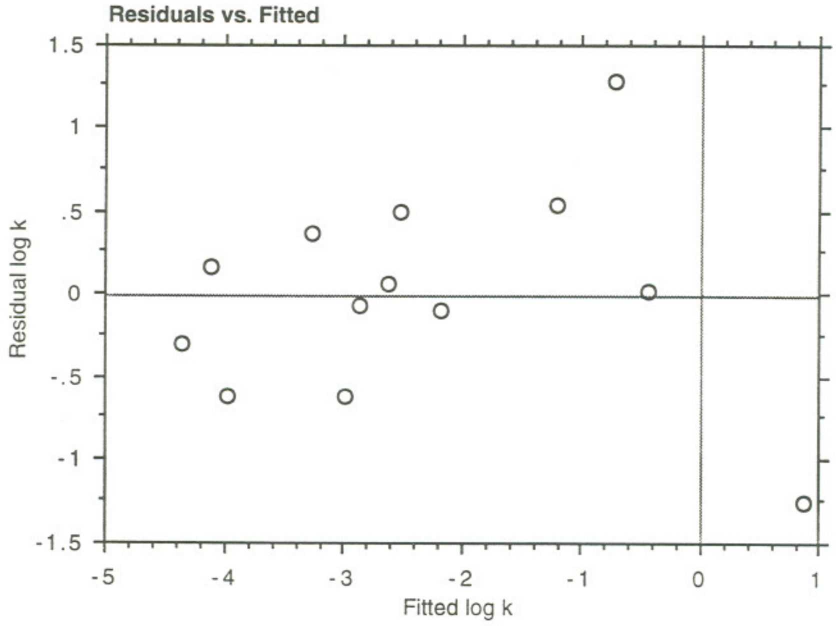


Figure B.4. Two-parameter multiple regression analysis for log k_{ArOH} vs. $\sum\sigma^{+}$ and $\sum E_s$.


Residuals vs. Dependent
1.5
1
.5
0
-.5
-1
-1.5
Residual log k
-5
-4
-3
-2
-1
0
1
log k


Residuals vs. Fitted
1.5
1
.5
0
-.5
-1
-1.5
Residual log k
-5
-4
-3
-2
-1
0
1
Fitted log k

Regression Summary
log k vs. 2 Independents

Count	13
Num. Missing	0
R	.883
R Squared	.780
Adjusted R Squared	.736
RMS Residual	.868

ANOVA Table
log k vs. 2 Independents

	DF	Sum of Squares	Mean Square	F-Value	P-Value
Regression	2	26.726	13.363	17.756	.0005
Residual	10	7.526	.753		
Total	12	34.252			

Regression Coefficients
log k vs. 2 Independents

	Coefficient	Std. Error	Std. Coeff.	t-Value	P-Value
Intercept	-4.126	.386	-4.126	-10.700	<.0001
s(+)	-3.271	.589	-.935	-5.554	.0002
F	-1.184	1.628	-.122	-.727	.4839

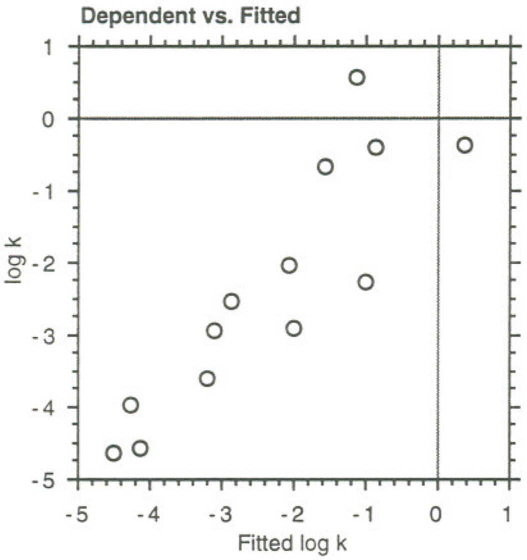
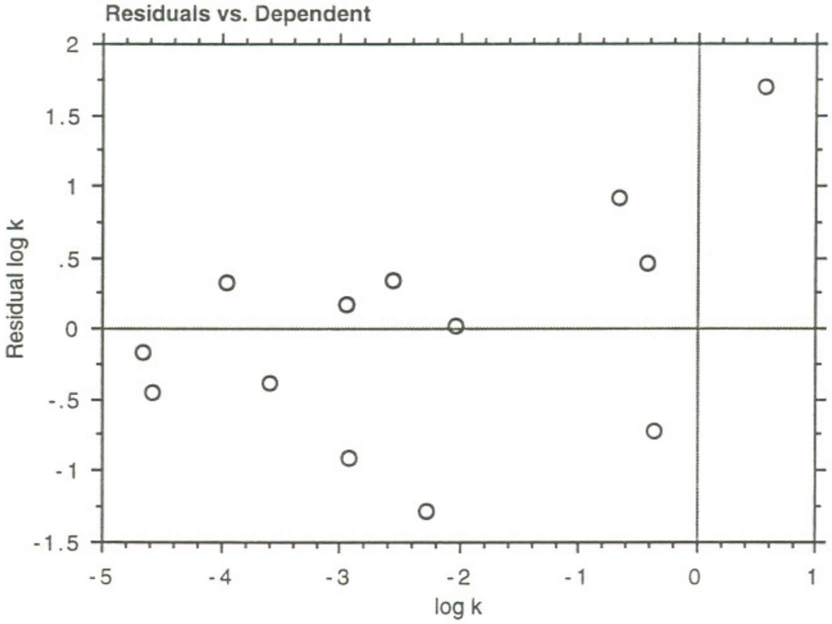
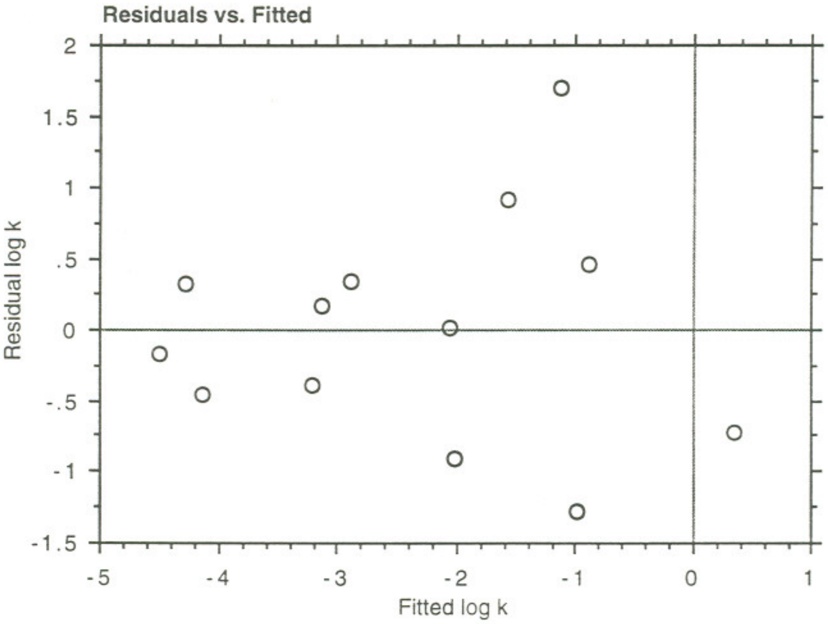


Figure B.5. Two-parameter multiple regression analysis for log k_{ArOH} vs. $\Sigma\sigma^{+}$ and ΣF.


Residuals vs. Dependent


Residuals vs. Fitted

Regression Summary
log k vs. 3 Independents

Count	13
Num. Missing	0
R	.952
R Squared	.907
Adjusted R Squared	.876
RMS Residual	.594

ANOVA Table
log k vs. 3 Independents

	DF	Sum of Squares	Mean Square	F-Value	P-Value
Regression	3	31.074	10.358	29.333	<.0001
Residual	9	3.178	.353		
Total	12	34.252			

Regression Coefficients
log k vs. 3 Independents

	Coefficient	Std. Error	Std. Coeff.	t-Value	P-Value
Intercept	-4.015	.266	-4.015	-15.093	<.0001
s(+)	-4.077	.464	-1.165	-8.783	<.0001
E	.752	.214	.411	3.509	.0066
F	-2.509	1.178	-.259	-2.130	.0620

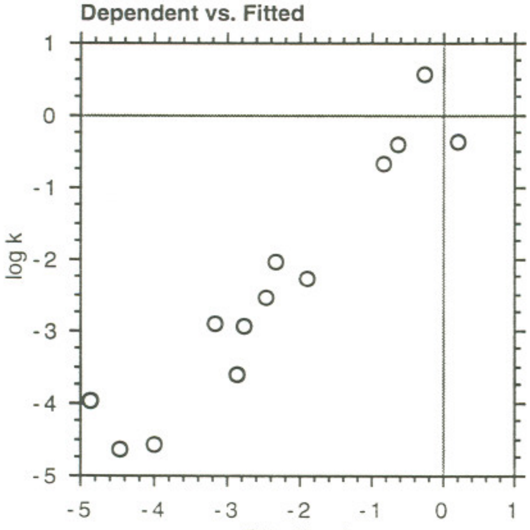
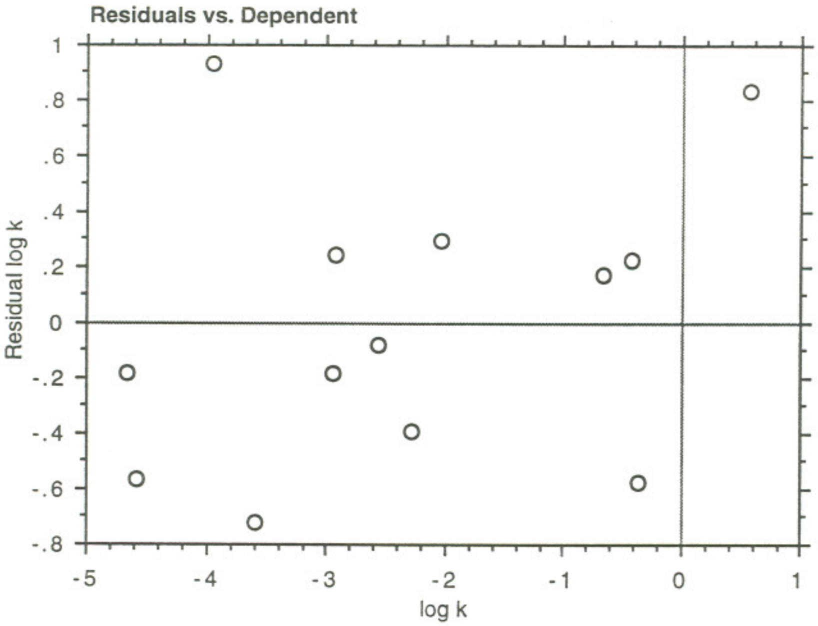
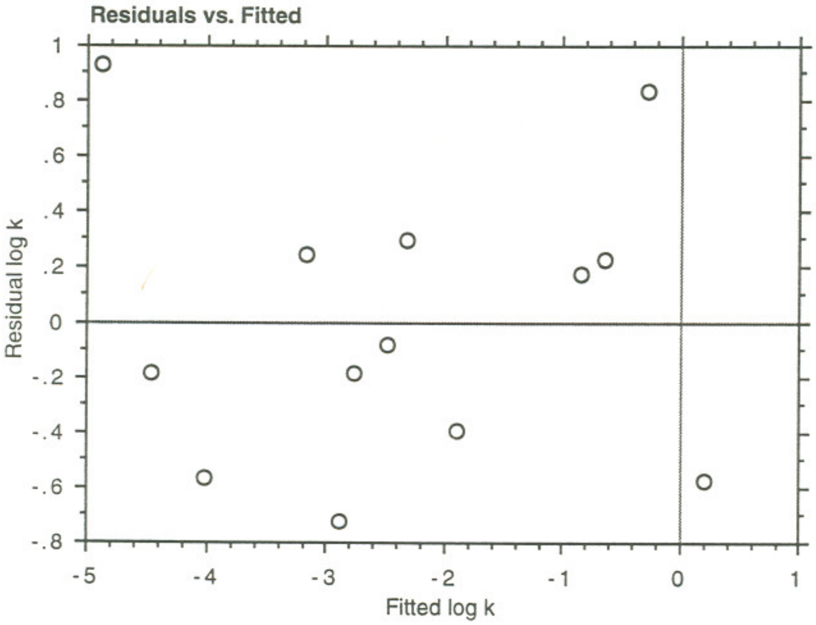


Figure B.6. Three-parameter multiple regression analysis for log k_{ArOH} vs. $\sum\sigma^+$, $\sum E_s$, and $\sum F$. The full Fujita treatment corresponds to eq. 34 (Chapter 4) and Figure 4.8 (bottom).


Residuals vs. Dependent
Residual log k
1
.8
.6
.4
.2
0
-.2
-.4
-.6
-.8
-5
-4
-3
-2
-1
0
1
log k


Residuals vs. Fitted
Residual log k
1
.8
.6
.4
.2
0
-.2
-.4
-.6
-.8
-5
-4
-3
-2
-1
0
1
Fitted log k

VITA

The author was born on April 20, 1965, in New York City. At the age of six, his family moved to Indianapolis, Indiana where he attended Springmill Elementary, Northview Junior High, and graduated from North Central High School in May 1983. The following Fall, he returned to his spawning grounds near the confluence of the East and Harlem Rivers for undergraduate studies at Columbia University, School of Engineering and Applied Science. Four years and countless meals at Tom's Diner later, the author completed his undergraduate studies and graduated in May 1987 with a B.S. in Chemical Engineering and truly an education in life.

In September of 1987, much to the chagrin of almost every chemical engineering professor who felt he was throwing away his education to some soft science (fools!, fools!), and much to the bewilderment of most of his classmates who ended up working for investment banks on Wall Street or Midtown (greedy fools!), the author packed up the covered wagon (it was a Ford Bronco actually) and headed out West to begin his graduate studies in Environmental Science and Engineering at the Oregon Graduate Center. In the summer of 1988 he began work under the auspices of Dr. William Fish on a short research project dealing with the reduction of Cr(VI) by cresol isomers. Many, many months later, the author returned to this research topic for his dissertation work and successfully defended a thesis proposal in December 1989. After countless kinetics experiments, numerous slices of Escape From New York pizza, and several changes in the school's official stationary, the author completed the requirements for the degree of Doctor of Philosophy in April of 1993 (just beating out his 28th birthday).

Realizing no one should enjoy life as much as he had for the previous 5 1/2 years, he left the rivers, mountains, and friends in Oregon to begin an National Research Council Post-Doctoral Fellowship at the EPA Environmental Research Lab in Athens, Georgia.