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AQUEOUS SOLUTION STUDY OF COPPER(I) FORMATION CONSTANTS WITH ACETONITRILE AND OLEFINS AND COPPER(II) CATALYZED OXIDATION OF CATECHOL

BY

PATRICK MUNDIA KAMAU ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Department of Chemistry

Edmonton, Alberta
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled Aqueous Solution Study of Copper(I) Formation Constants with Acetonitrile and Olefins and Copper(II) Catalyzed Oxidation of Catechol submitted by Patrick Mundia Kamau in partial fulfillment of the requirements for the Doctor of Philosophy.

Professor Robert B. Jordan

Professor Josef Takats

Professor Arthur Mar

Professor Frederick Cantwell

Professor William Page

Professor James K. Hurst
(External Examiner)

June 20. 2001

Dedication

To my family and parents

Abstract

Formation constants for the complexation of copper(I) by acetonitrile and several olefins have been determined by analyzing the rates of reduction of cobalt(III) by copper(I) in varying ligand concentrations. These studies have been carried out at ambient temperatures and 0.032 and 0.108 M $HClO_4$, with the ionic strength maintained at 0.14 M by addition of $NaClO_4$.

For the acetonitrile concentration range of 0.0237 - 2.04 M, the overall formation constants for the mono, bis and tris copper(I)-acetonitrile complexes have been determined to be $(4.30 \pm 0.54) \times 10^2$ M^{-1}, $(1.03 \pm 0.14) \times 10^4$ M^{-2} and $(2.12 \pm 0.29) \times 10^4$ M^{-3}, respectively.

The overall formation constants with copper(I) for the mono complexes of fumaric acid and dimethyl fumarate are $(7.34 \pm 0.15) \times 10^3$ and $(6.08 \pm 0.10) \times 10^3$ M^{-1}, respectively. The lower limit for the formation constants with copper(I) of the bis complexes of these ligands are 3.7×10^4 and 1.2×10^5 M^{-2}, respectively. With fumaronitrile as the ligand, the formation constants with copper(I) for the mono and bis complexes are $(8.53 \pm 0.19) \times 10^2$ M^{-1} and $(2.00 \pm 0.39) \times 10^3$ M^{-2}, respectively. Maleic acid studies yielded $(2.68 \pm 0.43) \times 10^3$ and $(1.69 \pm 0.12\ ) \times 10^4$ M^{-1} values for the complexation of copper(I) by maleic acid and hydrogen maleate ligands, respectively.

No complexation of copper(I) by benzene systems has been detected, with upper limits of 2×10^2 and 0.8 M^{-1} estimated for the formation constants for benzoic acid and p-toluene sulfonate ion, respectively.

The determination of the rate constant and mechanism for the anaerobic oxidation of catechol by aqueous copper(II) also have been investigated. These studies were done as a function of pH (6.4 - 7.4), copper(II) ($(0.144 - 1.44) \times 10^{-3}$ M) and catechol ($(0.8 - 14.4) \times 10^{-3}$ M). The reactive species in solution was ascertained to be the mono copper(II)-catecholate complex. A first-order rate constant of $(4.7 \pm 1.1) \times 10^{-5}\ s^{-1}$ was calculated for the rate determining step, which is proposed to be intramolecular electron transfer. Several rate constants for the proposed reaction schemes also were estimated and found to be at the diffusion limit for reactions involving the radicals.

Acknowledgments

I wish to express my sincere thanks to my supervisor, Professor R. B. Jordan, for his guidance, encouragement and thoughtfulness during the course of this study. Thanks for the invaluable help he gave me in the preparation of this thesis. His wise counsel on computer programming and expertise in glassblowing also are highly appreciated.

To my wife, Mumbi, daughter, Wanjiku and son, Kamau thanks for bearing with me throughout my many years pursuing this study. To my parents Wanjiku Kamau and Kamau Ndiang'ui and mother-in-law Wanjiku Mbiyu, my heartfelt gratitude for the support you have given me over the years. Your question of "when will I ever be through with my schooling" is finally answerable.

I would also like to thank Dr. M. Sisley, G. Wangila and J. Irangu for their friendship and helpful discussions. A special mention to Dr. A Jordan for providing me with dispensers that made the experiments in the second part of this study so much easier to do, thank you. To Dr. Norman Gee, thank you for allowing me to work as a supervisory teaching assistant for introductory chemistry over the years.

The splendid work of the personnel at the MicroAnalytical Laboratory, Chemistry Department, University of Alberta and that of Dr. R. McDonald, X-Ray Crystallography Laboratory, Chemistry Department, University of Alberta is gratefully acknowledged.

Kudos to the supervisory committee, for their enlightening discussions and suggestions during my candidacy examination.

To the Kenyan community here in Edmonton - Ashanteni Sana and as a mwananchi from the slopes I say - Nî Biû - Atî Atîa. Thai Thathaiya Ngai Thai.

Financial assistance from the University of Alberta is gratefully acknowledged.

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List of Terms and Symbols

k_n	specific rate constant
k_{obsd}	overall reaction rate constant
k_f	rate of complex formation
k_r	rate of complex dissociation
k_{ip}	specific rate constant for an ion-pair complex
t	time
K_n	stepwise formation constant
β_n	overall formation constant
K_a	acid dissociation constant
K_{ip}	ion-pair formation constant
μ	ionic strength
L	ligand
I_0	initial absorbance
I_∞	final absorbance
ε	molar absorptivity
l	optical path length
λ	wavelength
E^0	standard electrode potential
$E_{1/2}$	reduction potential
υ	wavenumber
σ	Hammett sigma value
Δ	change
Σ	sum

Chapter 1. Introduction

This study is concerned generally with determination of formation constants of copper(I) with π-acids in aqueous solutions in Chapters 2 and 3 and the oxidation of catechol by copper(II) in aqueous solutions in Chapter 4. In particular this study is geared towards development of kinetic methods using pentaamminecobalt(III) complexes as probes for aqueous copper(I) chemistry.

Copper Chemistry

Copper is the first metal of the coinage triad, followed by silver and gold. The electronic configuration for elemental copper is $[Ar]3d^{10}4s^1$. The most common oxidation state of copper is copper(II) (d^9) especially in aqueous solutions, but copper(I) (d^{10}) compounds are also well known. Copper(III) (d^8) compounds are very uncommon.

Many organic processes of biological, synthetic and industrial interest which are catalyzed by copper(II) complexes involve copper(I) complexes as key intermediates, where they act as the active species in these catalytic processes.[1] On the biological front among others, interest in the reactivity[2] of copper(I) complexes towards organic free radicals has increased due to the role of copper ions in deleterious biological processes initiated by free radicals. In the synthetic and industrial fields[3] a lot has been accomplished on the use and importance of copper(I) compounds both as catalysts and as the end products. Copper[4] is the third most abundant transition metal element in the human body, following iron and zinc, and it is important in all other forms of life as well.

Copper(I). The copper(I) ion prefers 4-coordination in the solid state,[5] but its d^{10} configuration and relatively low effective nuclear charge lead to ligand-dependent variations in structures, reactivities and reaction mechanisms.[6] The wide range of geometries of copper(I) stems from the fact that their crystal field stabilization energy (CFSE) is 0. This means that there is no electronically preferred spatial orientation of the ligands complexing with copper(I). For example, 2-coordinate linear,[7] 3-coordinate triangular,[8] and 4-coordinate tetrahedral[5] structures have been observed in single crystals with monodentate ligands. Funahashi et al.[9] suggested that the 4-coordinate structure is the most stable one for copper(I) ion in pyridine, 4-methylpyridine, and acetonitrile on the basis of ab initio molecular orbital methods.[10] Furthermore, in the case of multidentate ligands[11] some copper(I) complexes are 5-coordinate and such complexes also have been observed as reaction intermediates.[12]

Much can be learned about the stabilities of copper complexes by considering electrode potential data. Standard electrode potentials[13] for the oxidation and reduction of copper(I) are given in eqs. 1.1 and 1.2.

$$\mathrm{Cu^{+}_{(aq)}} \longrightarrow \mathrm{Cu^{2+}_{(aq)}} + \mathrm{e^{-}} \qquad E^{0}_{\mathrm{ox}} = -0.153\,\mathrm{V} \tag{1.1}$$

$$\mathrm{Cu^{+}_{(aq)}} + \mathrm{e^{-}} \longrightarrow \mathrm{Cu_{(s)}} \qquad E^{0}_{\mathrm{red}} = +0.521\,\mathrm{V} \tag{1.2}$$

The resultant sum of eqs 1.1 and 1.2, eq. 1.3, indicates that aqueous copper(I) spontaneously disproportionates under standard-state conditions.

$$2\mathrm{Cu^{+}_{(aq)}} \longrightarrow \mathrm{Cu^{2+}_{(aq)}} + \mathrm{Cu_{(s)}} \qquad E^{0}_{\mathrm{cell}} = +0.368\,\mathrm{V} \tag{1.3}$$

However, metastable aqueous solutions of copper(I) compounds are possible, and stabilization by complexation also is possible, as will be discussed shortly.

Copper(II). In aqueous solutions, copper(II) occurs as the pale blue aquo ion or as other complex ions. The latter are usually 4-coordinate, square planar, as in $\mathrm{Cu(NH_3)_4^{2+}}$ or 6-coordinate, distorted octahedral, as in $\mathrm{Cu(EDTA)^{2-}}$ and $\mathrm{Cu(H_2O)_6^{2+}}$. The two trans bonds required to convert the square planar structure into the octahedral structure are weaker and longer than the coordinate bonds of the square planar structure, a direct consequence of the Jahn-Teller effect.[14] The effect states that for a non-linear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy and lower the energy. For octahedral complexes the only configurations having non-degenerate ground states are d^3, high spin d^5, low spin d^6, d^8 and d^{10}. All other configurations i.e. d^1, d^2, d^4, low spin d^5, high spin d^6, d^7 and d^9 are expected to spontaneously undergo Jahn-Teller distortions. This phenomenon is presented in Figure 1.1 for copper(II) under various ligand fields.

Formation Constants

Eq. 1.3 can be written as an equilibrium as shown in eq. 1.4. Species that complex more strongly to copper(I) than copper(II), however displace the disproportionation equilibrium in favor of copper(I) in eq. 1.4.

$$2Cu^{+}_{(aq)} \overset{\longrightarrow}{\longleftarrow} Cu^{2+}_{(aq)} + Cu_{(s)} \qquad (1.4)$$

Water containing nitriles and gases like CO and C_2H_2 are known[15,16] to stabilize copper(I). Organic nitriles bond to copper(I) using the non-bonding pair on the nitrogen and π-back-bonding from the filled metal d-orbital to the π^* anti-bonding orbital of the nitrile.[15] Analogous π-back-bonding is thought to stabilize the complexes with CO, C_2H_2 and other unsaturated organic species.[16]

Copper(I) complexes with acetonitrile have been known since the first preparation of tetrakis(acetonitrile)copper(I) nitrate by Morgan in 1923.[17] Later other groups[18] have prepared these complexes and crystal structures have been determined for the perchlorate,[19] hexafluorophosphate[20] and tetrafluoroborate[21] salts.

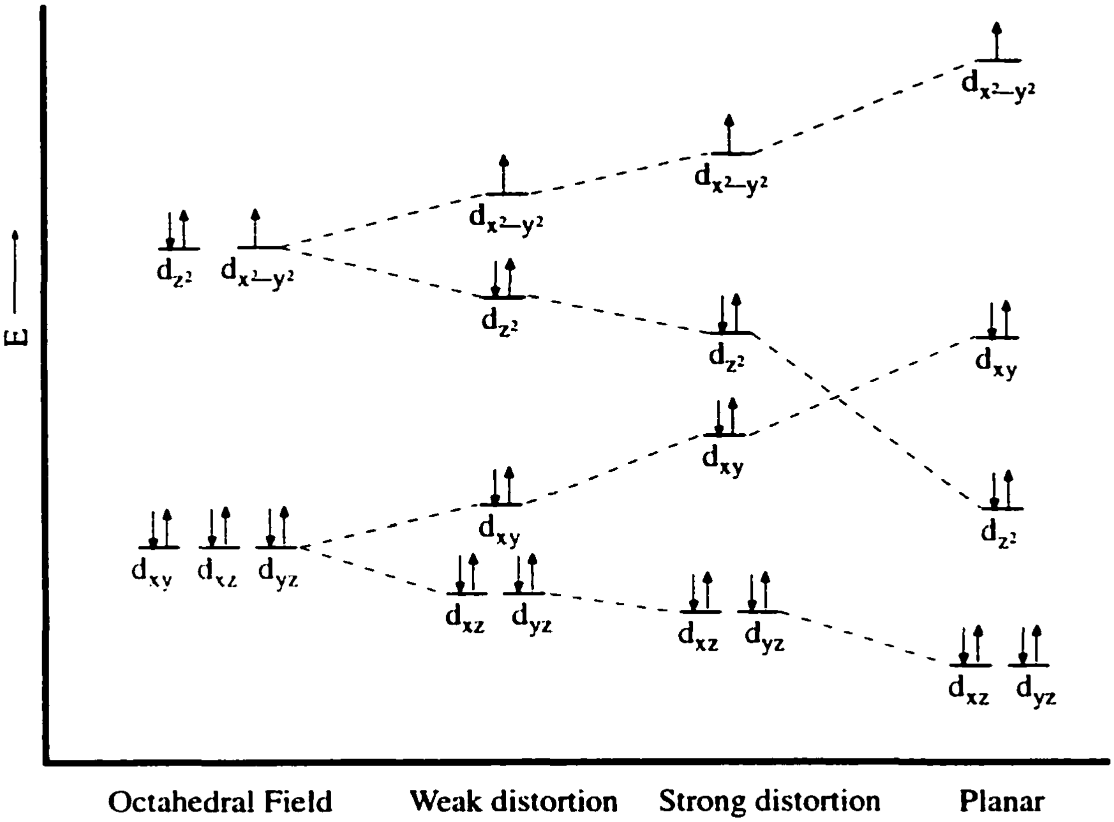


Figure 1.1. Increasing Jahn-Teller effect on an octahedral copper(II) complex.

Although it has been known for many years that acetonitrile is able to stabilize copper(I), a literature review reveals only a handful of studies undertaken to determine formation constants for copper(I) with acetonitrile in aqueous solutions. Hemmerich and Sigwart[18a] first determined the formation constant value, β_2, for bis(acetonitrile)copper(I) from polarographic studies. Later, also using polarography, Manahan and Iwamoto[22] reported β_2 and β_3 values for bis(acetonitrile)copper(I) and tris(acetonitrile)copper(I) complexes, respectively. Using the β_2 value of Hemmerich and Sigwart[18a], Zuberbuhler and Gunter[23] reported a β_1 for the mono(acetonitrile)copper(I) complex from polarographic studies. Later β_3 values were determined from polarographic data by Zuberbuhler[24] and from kinetic studies by Zuberbuhler and Mi.[25] In the later study, it was also shown that β_3 was independent of pH. The details of these studies will be described later when comparisons are made to our results in Chapter 2.

A need to redetermine copper(I)-acetonitrile formation constants arose since the literature values are inconsistent. This was also coupled with the desire to develop a kinetic method requiring only standard laboratory equipment that was simple and accurate.

The binding of unsaturated hydrocarbons to copper(I) has been studied with special interest with regard to the C=C bond distance,[26] the olefinic proton and carbon NMR shifts of the coordinated olefin[27,28] and the formation constants.[29-33] Mostly, the carbon-carbon double bond in these copper(I)-olefin complexes is only slightly longer than that in uncomplexed ligands (1.348 Å).[26] The forming of the bond between copper(I) and the double bond activates the olefin moiety for further reaction.[34] Kochi et al.[27] inferred from ^{13}C and ^{1}H NMR shift data that the relative contributions of σ-bonding and π-back-bonding depend on the olefin involved. The nature of the copper(I)-olefin bonding also has been the subject of numerous theoretical studies[35] which have been equivocal on the relative importance of σ-bonding and π-back-bonding in copper(I)-ethylene.

The first quantitative measurements of formation constants for copper(I) with olefins were presented in a series of papers by Andrews et al.[29] about 50 years ago. Using a method based on the solubility of copper(I) chloride, they reported values for several unsaturated acids and alcohols. Meyerstein et al.[30] determined values for complexation of copper(I) with two unsaturated acids and several benzene systems. The first reported values from Meyerstein using a kinetic method[30a] were for fumaric and maleic acids in acidic media. Later Meyerstein et al.[30b] reported values for the complexation of copper(I) with fumaric and maleic acids (β_1), hydrogen -fumarate and -maleate (β_{12}) and fumarate and maleate (β_{13}) using spectrophotometry and cyclic voltammetry. Using the same methods Meyerstein et al.[30c] have reported values for a series of substituted benzene systems.

Hurst and Lane[31] studied the complexation of copper(I) with $[(NH_3)_5Co(fumarate)]^{2+}$ and $[(NH_3)_5Co(benzoate)]^{2+}$ and reported a β_1 value for the fumarate system, but were unable to detect any complexation of copper(I) with the benzoate ligand and only could suggest an upper limit for the β_1 value. Buxton et al.[32] using spectrophotometry, have determined β_1 values for copper(I) with ethylene, isobutene and acrylamide.

The details of these studies will be described later when comparisons are made to our results in Chapter 3. The disparity of the values of copper(I)-olefin formation constants reported in the literature, and the importance of the system prompted us to undertake this study.

Methods Used to Determine Formation Constants

Since the reliability of a given formation constant value depends to a large extent on the method used for its measurement, a presentation of these values would be incomplete without some discussion of the methods used to get these values. Though the discussion in the following paragraphs targets copper(I), there are many instances where these methods are applicable to other metal centers.[33]

Solubility Method. Formation constants of copper(I)-olefin complexes have been determined by measuring the solubility of copper(I) salts in olefin solutions.[29] The solubility method depends upon the accurate analysis of the total copper(I) in the saturated solution. The solubility product of the metal salt must be independently known as well as the formation constants for other metal complexes that might be in solution. It is essential to ensure that the composition of the solid phase and hence its solubility product remains constant over the concentration ranges being investigated. Since the solubility product is fixed, the ligand concentration cannot be varied independently of the metal ion concentration or vice versa. A potential pitfall is precipitation of the copper(I)-olefin complex which would cause the solution to contain less copper(I) and give an incorrectly small β value. This is hard to detect since the undissolved solid metal salt is always present. This could be overcome by analyzing the solid for olefin but this would add to the complexity of the method.

Spectrophotometry Methods. Changes in the electronic spectrum of a copper(I) complex can be used to determine the formation constant between the metal ion and the ligand.[30,31,32] Basically there are two spectrophotometric methods used to determine formation constants: a direct method from measurements of the absorbance due to a copper(I) complex, or a displacement method where the effect of some ligand on the absorbance of a copper(I) complex is monitored. Both of these methods are suitable if the extinction coefficient of the copper(I) complex being monitored is measurable in some region of the electronic spectrum. The direct method is unsuitable for copper(I) complexes with low extinction coefficients. This is not a problem with the displacement method if the copper(I) complex whose ligands are replaced has measurable absorbance.

The direct method was used by Hurst and Lane[31] to evaluate formation constant of copper(I) with $[(NH_3)_5Co(fumarate)]^{2+}$ and by Buxton et al.[32] for copper(I) with acrylamide. Meyerstein et al.[30b] also used the direct method to evaluate formation constants of copper(I) with fumaric and maleic acids, hydrogen -fumarate and -maleate and fumarate and maleate. Buxton et al.[32] and Meyerstein et al.[30c] have used the displacement method to evaluate formation constants, the former using copper(I)-acrylamide and the latter copper(I)-hydrogenfumarate.

Spectrophotometry data also can be used indirectly in the kinetic methods described below.

Electrochemical Methods. Cyclic voltammetry[30] and polarography[18a,22-24] utilize the effect of the ligand, L, on the reduction potential ($E_{1/2}$) of a metal ion to determine formation constants. Two consecutive single-electron processes are observed when aqueous copper(II) is reduced in the presence of ligands which form stable complexes with copper(I). If the reaction of the first wave is

$$\mathrm{Cu^{II}L + e^- + (n-1)L \rightleftarrows Cu^{I}L_n} \tag{1.5}$$

assuming only the mono ligand complex forms, then the difference between $E_{1/2}$ in the presence of L and with only solvent $(E_{1/2})_s$ is given by eq. 1.6,

$$\Delta E_{1/2} = -0.0591\left(\log K_{\mathrm{Cu^{II}}} - \log K_{\mathrm{Cu^{I}}}\right) - (1-\mathrm{n}) \times 0.0591 \log[\mathrm{L}] \tag{1.6}$$

where $K_{\mathrm{Cu^{I}}} = [\mathrm{Cu^{I}L_n}]/[\mathrm{Cu^{I}}][\mathrm{L}]^n$ and $K_{\mathrm{Cu^{II}}} = [\mathrm{Cu^{II}L}]/[\mathrm{Cu^{II}}][\mathrm{L}]$. A similar derivation can be done for the second wave.

$$\mathrm{Cu^{I}L_n + e^- \rightleftarrows Cu_{(s)} + nL} \tag{1.7}$$

$$\Delta E_{1/2} = 0.0591 \log K_{\mathrm{Cu^{I}}} - \mathrm{n} \times 0.0591 \log[\mathrm{L}] \tag{1.8}$$

Plots of $\Delta E_{1/2}$ versus log [L] can be used to determine $K_{Cu(I)}$. To use eq. 1.6, one needs to know the $K_{Cu(II)}$ value. As the stability constants are calculated from intercepts using published standard potentials, $(E_{1/2})_s$, which show a deviation of ±0.012, the error in the calculation is quite high since this small shift leads to an error of ~20% in the stability constants.[30b]

Using polarographic data, the effect of complexation on the cell potential can be summarized by eq. 1.9,

$$\Delta E = \frac{RT}{nF}\ln\left(1+\beta_1[\mathrm{Ligand}]+\beta_2[\mathrm{Ligand}]^2+\ldots+\beta_n[\mathrm{Ligand}]^n\right) \tag{1.9}$$

where ΔE is the difference between the half-wave potential of the free metal ion $(E_{1/2})_s$, and the half-wave potential of the metal-ligand complex, and β_n is the overall formation constant of ML_n.

In many cases, only small differences in the half-wave potentials occur in the presence of the ligand, so that the overall accuracy of the resulting stability constant is limited. As a result, in the copper(I)-allyl alcohol system the stability constant was evaluated with a large error as $(5.00 \pm 2.50) \times 10^4$ M^{-1}.[36]

Kinetic Methods. The most direct kinetic method determines formation constants from the ratio of the rates of formation and dissociation of a copper(I) complex. Meyerstein[30a] used pulse radiolysis to rapidly convert copper(II) to copper(I) in the presence of varying concentrations of maleic and fumaric acids and then observed the rate of formation of the copper(I)-olefin complex by spectrophotometry. The results gave the rate constants for the formation (k_f) and dissociation (k_r) of the complex, eq. 1.10, from which the complex formation constants were calculated as k_f / k_r.

$$\mathrm{Cu^I_{(aq)}} + \mathrm{L_{(aq)}} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{Cu^IL_{(aq)}} \tag{1.10}$$

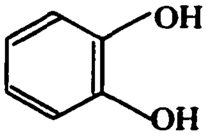
The direct method has a number of limitations. The most obvious limitation of this approach as used by Meyerstein[30a] is the cost and availability of pulse radiolysis equipment. It must be assumed that the radiolysis does not affect the olefin or produce any persistent products that absorb in the same region as the (LCu) complexes. The kinetic method (k_f/k_r) assumes that no side reactions are contributing to the disappearance of the complex (k_r). An inexpensive and clean way of producing copper(I) is the use of chromous method as described in Chapter 2. Copper(I) produced this way can be mixed with varying ligand concentrations on stopped-flow apparatus and the spectrum recorded. The problem here is that the ligand exchange reaction for a d^{10} system is fast and indeed the half-life values from Meyerstein's[30a] study are $< 3 \times 10^{-6}$ s whereas stopped-flow apparatus are good for reactions with half-times in the 10 ms to ~60 s range.[37] These limitations have led researchers to use indirect methods.

Indirect methods are based on the measurement of the rates of oxidation of copper(I) in the presence of some ligand, at varying ligand concentrations. Changes in concentration of the oxidant or copper(I) in these systems must be accurately measurable. Spectrophotometry as a method for monitoring this change is limited to systems that have species with good absorbance in some part of the electronic spectrum. It is also desirable to monitor these reactions where there is little or no other absorbing species, otherwise one needs to know the extinction coefficients of the other absorbing species in solution. Zuberbuhler and Mi[25] used the rate of oxidation of copper(I) by oxygen in aqueous acetonitrile to evaluate formation constants by monitoring the reaction with an oxygen sensitive electrode.[25]

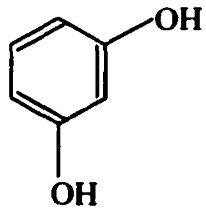
In general, the rate constants (pseudo-first-order or second-order) in varying amounts of the ligand are determined experimentally. Then a rate law is developed which relates the rate constant to the ligand concentration and the formation constant(s). Finally the experimental rate constants are fitted to the rate law to evaluate the formation constants.

Catechol

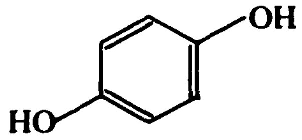
Catechol is the common name for 1,2-benzenediol. The other two family members are resorcinol (1,3-benzenediol) and hydroquinone (1,4-benzenediol). The catechols are components in a variety of important biomolecules, such as epinephrine, dihydroxyphenylalanine (DOPA), DOPamine, quercetin and rutin.



Catechol



Resorcinol



Hydroquinone

Copper(II) catechol complexes. The formation constants for the mono and bis complexes of copper(II) with catecholate are defined by eqs. 1.11 and 1.12, respectively.

$$K_1 = \frac{[\mathrm{CuL}]}{[\mathrm{Cu}^{2+}][\mathrm{L}^{2-}]} \tag{1.11}$$

$$K_2 = \frac{[\mathrm{CuL}_2^{2-}]}{[\mathrm{CuL}][\mathrm{L}^{2-}]} \tag{1.12}$$

pK_{a1} and pK_{a2} values of catechols and the log K_1 and log K_2 values of copper-catecholate complexes are summarized in Table 1.1. These values show that deprotonated catechols form very strong complexes with copper(II). At near neutral pH, as in the present study, the values predict that copper(II) will be significantly complexed by the catecholate anion as the mono and bis complexes.

The log K_1 and log K_2 values in Table 1.1 are approximately the same for the different ligands. The pK_{a1} values though change significantly for the ligands and can be correlated to an equilibrium constant value, K_1^*, for the complexation of copper(II) with the protonated ligands, eq. 1.13,

$$Cu^{2+}_{(aq)} + H_2L_{(aq)} \overset{K_1^*}{\rightleftarrows} CuL_{(aq)} + 2H^{+}_{(aq)} \tag{1.13}$$

where

$$K_1^* = \frac{[CuL][H^+]^2}{[Cu^{2+}][H_2L]} \tag{1.14}$$

and K_1^*, pK_{a1} and pK_{a2} are related by eq. 1.15,

$$\mathrm{Log}\, K_1^* = \mathrm{Log}\, K_1 - (\mathrm{p}K_{a1} + \mathrm{p}K_{a2}) \tag{1.15}$$

and similarly one can relate K_2, K_2^*, pK_{a1} and pK_{a2} by eq. 1.16.

$$\mathrm{Log}\, K_2^* = \mathrm{Log}\, K_2 - (\mathrm{p}K_{a1} + \mathrm{p}K_{a2}) \tag{1.16}$$

The log K_1^* values in Table 1.1 indicate that there is more complex formation i.e. less free copper(II) at a given pH, with Tiron (disodium 4,5-dihydroxy 1,3-benzene disulfonic acid) than with catechol. As a result of the high reduction potential of Tiron (0.955 V) compared to catechol (0.792 V), Tiron is not oxidized by copper(II).[38]

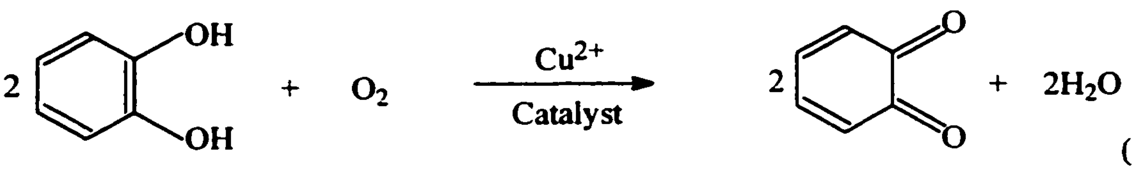
Table 1.1. Acid Dissociation Constants of Catechols and their Stability Constants with Copper(II).

Ligand	pK_{a1}	pK_{a2}	$\log K_1$	$\log K_2$	$\log K_1^*$	$\log K_2^*$
Catechol	9.25[a]	13.0	13.64	11.28	-8.61	-11.61
	9.195[b]	12.98	13.827	10.92	-8.35	-11.26
	9.23[c]	13.0	13.90	11.00	-8.33	-11.23
	9.13[d]	11.59	12.52	9.66	-8.20	-11.06
4-Carboxycatechol	8.67[d]	11.94	12.79	9.81	-7.82	-10.80
4-Chlorocatechol	8.522[b]	11.974	12.894	10.163	-7.60	-10.33
Catechol-4-sulfonate	8.26[d]	12.16	13.29	10.23	-7.13	-10.19
Tiron	7.62[c]	12.5	14.25	11.12	-5.87	-9.0
	7.54[d]	12.26	13.99	11.17	-5.81	-8.63
	7.66[e]	12.55	14.28	11.14	-5.93	-9.07
	7.69[f]	11.97	13.82	11.19	-5.84	-8.47
4-Nitrocatechol	6.701[b]	10.853	11.666	9.282	-5.89	-8.27

[a] Balla, J.; Kiss, T.; Jameson, R. F. *Inorg. Chem.* **1992**, *31*, 58. 25 °C and μ= 1.0 M. [b] Jameson, R. F.; Wilson, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, 2614-17. 25 °C and μ = 0.10 M. [c] Martell, A. E.; Smith, R. M. *NIST Critical Stability Constants of Metal Complexes Database* **1995**, U.S. Department of Commerce; μ = 0.1 and 25 °C. [d] Murakami, Y.; Nakamura, K.; Tokunaga, M. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 669. 30 °C and μ= 0.10 M. [e] Sigel, H.; Huber, P. R.; Griesser, R.; Prij, B. *Inorg. Chem.* **1973**, *12*, 1198. 25 °C and μ= 0.10 M. [f] Chakraborty, D.; Bhattacharya, P. K. *J. Chem. Soc., Dalton Trans.* **1990**, 3325. 30 °C and μ= 0.2 M.

It is then expected that for a given copper(II) and catechol concentration, the addition of Tiron, ([Tiron] < [catechol]) will slow down the copper(II) catalyzed oxidation of catechol, because the formation of unreactive copper(II)-Tiron complexes reduces the concentration of the active mono copper(II)-catecholate complex (Chapter 4).

Catechol Oxidation. The synthesis of organic ligands which incorporate many of the structural features thought to be present in naturally occurring metalloproteins has led to an increased understanding of a number of different proteins.[1b,c,39] Included among these are the Type III copper proteins tyrosinase and hemocyanin. Tyrosinase is capable of catalyzing the two electron oxidation of catechol to quinone as shown in eq. 1.17.



(1.17)

The simple aqueous copper(II) ion also catalyzes the oxidation of catechol by oxygen.

Rogic et al.[40] proposed that electron transfer between catechol and copper(II) only occurs after catechol and the copper(II) species form a copper(II)-catecholate intermediate. If other ligands are coordinated to copper(II) so tightly that they cannot be replaced by catechol, then the electron transfer does not occur.

Reduction potentials show that the oxidation of catechol by aqueous copper(II) is thermodynamically unfavorable. The auto-oxidation in the presence of dioxygen is driven to products by oxidation of copper(I) by dioxygen.

Jameson et al.[41] studied the copper(II) catalyzed oxidation of catechol by molecular oxygen in aqueous solutions at 25 °C. They found that the rates were inverse first-order in $[H^+]$, half-order with respect to oxygen concentration, but had no simple integral order with respect to copper(II) and catechol concentrations. The pH dependence of the kinetic data suggested the involvement of the species HA^- rather than H_2A in the chain propagation step. The active species was proposed to be the adduct CuO_2^+ which oxidized both free catechol and its copper(II) complexes.

There have been reports on copper(II) catalyzed oxidation of ascorbic acid, a system that is closely related to catechol.[42] In the presence of dioxygen, Martell and Khan[42a] observed that the reaction rates were inverse first-order with respect to [H^+] and first-order in copper(II) and dioxygen concentrations. This study and that by Jameson et al.[41] agree on reaction rates being inverse first-order in [H^+] and on the formation of copper(I) in the rate-determining step. They differ markedly in their reaction schemes since whereas Khan and Martell[42a] involve radicals, Jameson et al.[41] has no radicals formed. The CuO_2^+ adduct is first formed in the Jameson et al.[41] study and in turn oxidizes the copper(II) complexes. In the Khan and Martell[42a] study it is the formation of a copper(II)-ascorbate -dioxygen adduct that is perceived to be the reactive species.

Under anaerobic conditions, ascorbic acid oxidation was studied by Jordan and Xu[42b] and Jordan and Sisley[42c] who found that the rate has an inverse dependence on [H^+], is first-order in the copper(II) concentration, and has terms that are independent, first- and second-order in the chloride ion concentration. In the mechanisms proposed, the rate-determining step involves one-electron oxidation of the ascorbate anion (HA^-) by copper(II) chloride. The chloride ion served to catalyze the reaction by complexing with the copper(I) in the step involving the formation of the ascorbate radical. These studies and that by Khan and Martell[42a] agree on the dependence of the rate with respect to [H^+] and copper(II) albeit being under different conditions; anaerobically and aerobically, respectively.

Copper(II) is a one electron oxidant. Copper(II) catalyzed reactions involve one-electron-transfer steps, and formation of radical species is usually proposed in the rate determining step. The formation of the mono anion catecholate radical in our study of catechol is thought to be the rate determining step. Copper(I) is expected to be formed in the initiation step whether under aerobic or anaerobic conditions for both the catechol and ascorbic acid systems as discussed above. Different species are responsible for driving these copper(II) catalyzed oxidation processes forward; anaerobically, it is the formation of a copper(I) chloride complex in studies by Jordan and co-workers[42b,c] and the reaction between copper(I) and a pentaamminecobalt(III) complex in the present study. Aerobically, it is the oxidation of copper(I) back to copper(II) by dioxygen in the ascorbate study by Khan and Martell[42a] and the catechol study of Jameson et al.[41]

In light of Marcus, theory these studies have furnished the self-exchange rates for the copper(II)/copper(I) couple as well as for the organic species and our data is subjected to an analogous examination in Chapter 4.

The large majority of studies on oxidation of catechol by copper(II) though are in non-aqueous or mixed solutions.[43] For example, in pyridine, the oxidation of catechol takes place in the presence as well as in the absence of molecular oxygen. The overall anaerobic transformation of catechol to *cis,cis*-muconic acid monoethyl ester involves a two-electron oxidation of catechol to *o*-benzoquinone, followed by a second two electron oxidation of the *o*-benzoquinone to muconic acid ester.[43]

Other metals also have been employed in the oxidation of catechol in aqueous solutions. Pelizzetti et al.[44] studied the oxidation of catechol by aqueous manganese(III)[44a] and iron(III).[44b] The rates for the formation of the semiquinone were found to follow two pathways, a [H$^+$] independent reaction path and an inverse [H$^+$] dependent path. These were assigned to the oxidants $[M(OH_2)_6]^{3+}$ and $[M(OH_2)_5OH]^{2+}$, respectively.

The oxidation of various aromatic diols by tris(1,10-phenanthroline)iron(III) has been studied by Pelizzetti and Mentasti[44c] and by Kimura et al.[45] They agree that the rate is first-order in both oxidant and reductant and that semiquinone formation is rate controlling. However, their rate constants for the catechol oxidation in 1 M $HClO_4$ differ by a factor of ~4. For the various substituted catechols studied by Pelizzetti and

Mentasti[44c] the activation enthalpies are generally of the order of 5 kcal mol^{-1}. Kimura et al.[45] found 5.5 kcal mol^{-1} for catechol which seems more consistent with the general pattern than the -0.2 kcal mol^{-1} given by Pelizzetti and Mentasti.[44c] In both studies, the results were analyzed by Marcus theory with the conclusion that the self-exchange rate constant for catechol/cationic catechol radical is ~3 × 10^{7} M^{-1} s^{-1}. Pelizzetti et al.[44d] also studied the oxidation of catechol by hexachloroiridate(IV) and had similar findings reporting an activation enthalpy of 5.2 kcal mol^{-1} and self-exchange rate constant for catechol /cationic catechol radical of ~6 × 10^{7} M^{-1} s^{-1}. The details of these studies will be described later when comparisons are made to our results in Chapter 4.

Complete spectrophotometric studies of the oxidation of catechol by copper(II) in aqueous solutions are hindered by the formation of insoluble organic products. Previously the rates of such reactions have been followed by methods[41] where precipitation is not a problem or spectrophotometrically[41] in the early stages of the reaction before the precipitation significantly affects the absorbance readings.

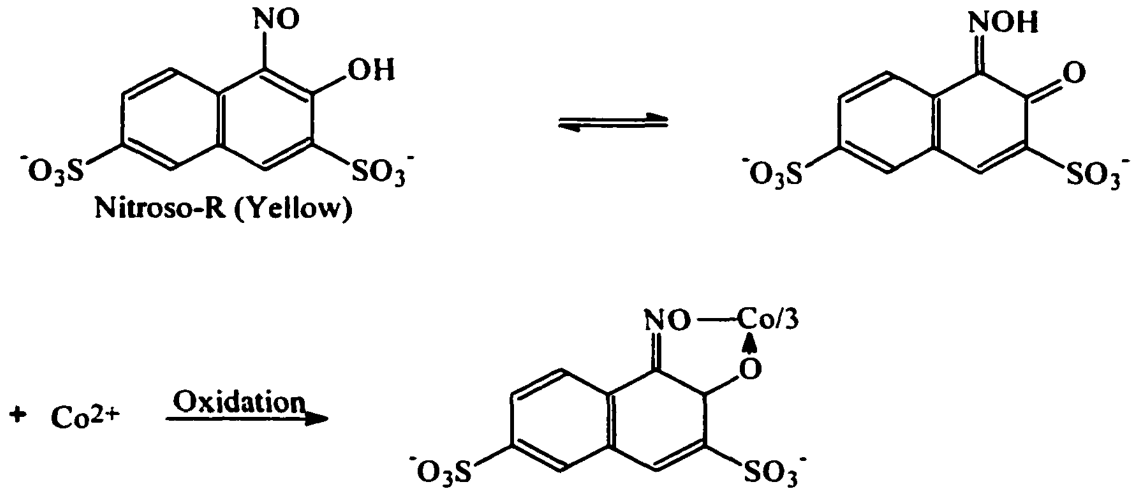
In the present study pentaamminecobalt(III) complexes are used to scavenge the copper(I) generated during the oxidation of catechol by copper(II). The resulting cobalt(II) is analyzed using the nitroso-R salt (NRS) method and details of this method are given in Chapter 4.

Nitroso-R

Nitroso-R (1-nitroso-2-napthol-3,6-disulfonic acid disodium salt) is a reagent that is specific for cobalt. The cobalt(III)-nitroso-R complex has a maximum[46] absorption at 420 nm but nitroso-R gives a large reagent blank making determination of cobalt at this wavelength troublesome. Measurements can be taken at 520-530 nm where there is little interference of the absorbance from the nitroso-R reagent.

The nitroso-R method for the determination of cobalt has been used extensively since Hoffman[47] first used it qualitatively. Determination of cobalt in bones and tissue and soil have been carried out by Shipman et al.[48] and McNaught.[49] Using nitroso-R, Omar et al.[50] determined cobalt as low as 0.1 mg/L in natural and waste water samples at pH 6.0. Wise and Brandt[51] also have used it for quantitative determination of cobalt in the presence of other metal ions. The chelation takes place at pH 5.5 - 6.5 and interference by other metal ions can be minimized by strong acidification with nitric or hydrochloric acids.

The chelation[52] is thought to take place by the reactions in, eq. 1.18.



Cobalt(III)-nitroso-R complex (Red) (1.18)

Cobalt(III) Complexes

It was felt both desirable and interesting to develop simple and accurate methods to study aqueous copper(I) chemistry. This was achieved by using pentaamminecobalt(III) complexes as oxidative scavengers for aqueous copper(I). These reactions have rather large second-order rate constants[53] (k_0 in Table 1.2) that depend on the heteroligand on the pentaamminecobalt(III) fragment.

Pentaamminecobalt(III) complexes have been the subject of numerous studies in the past.[54] These complexes are easy to prepare,[55] and colored, due to d-d transitions which makes them easy to follow spectrophotometrically in the visible region of the spectrum. They also have more intense charge transfer bands in the near uv region which allows them to be monitored under a wide range of concentration conditions. Since they are low spin d^6 systems, they are kinetically inert so that they do not complex with other species in solution. They are also rather unreactive oxidants, unless they can react by an inner-sphere mechanism, as in the case with copper(I).

Aqueous solutions of pentaamminecobalt(III) complexes undergo hydrolysis[54,56] by two pathways: aquation is first-order in the complex; base hydrolysis is also first order in $[OH^-]$. Typical rate constants for these pathways are given in Table 1.2. For pH ≤ 7, the hydrolysis has a half-time of > 25 hours at 25 °C for the bromo complex and $\sim 10^4$ hours for the azido complex. Nevertheless, stock solutions of these complexes should be made in acidic solution to suppress the base hydrolysis. Aqueous solutions of these cobalt(III) complexes also undergo photolysis and they should be protected from light by storage in the dark or in glassware covered with aluminum foil to optimize long time storage.

Table 1.2. Rate Constants for Hydrolysis of Pentaaminecobalt(III) Complexes and their Reduction by Copper(I) in Aqueous Solutions at 25 °C.

Cobalt complex	Acid Hydrolysis *k*, s^{-1}	Base Hydrolysis *k*, $M^{-1}s^{-1}$	Cu(I) Reduction k_0, $M^{-1}s^{-1}$
$[(NH_3)_5CoBr]^{2+}$	6.3×10^{-6}[a]	7.5[c]	4.46×10^{5}[d]
$[(NH_3)_5CoCl]^{2+}$	1.7×10^{-6}[a]	8.5×10^{-1}[c]	4.88×10^{4}[d]
$[(NH_3)_5CoN_3]^{2+}$	2.1×10^{-9}[b]	3.0×10^{-4}[c]	1.50×10^{3}[d]

[a] Basolo, F. *Chem. Rev.* **1953**, *52*, 459. Stranks, D. R. *Modern Coordination Chemistry*; New York, 1960; Chap. 2. [b] Lalor, G. C.; Moelyn-Hughes *J. Chem. Soc.* **1964**, 2375. [c] Lalor, G. C.; Lon, J. *J. Chem. Soc.* **1963**, 5620. Chan, S. C.; Hui, K. Y.; Miller, J.; Tsang, W. S. *J. Chem. Soc.* **1965**, 3207. [d] Parker, J. O.; Espenson, J. H. *J. Am. Chem. Soc.* **1968**, *91*, 1968.

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Chapter 2. A Kinetic Determination of Copper(I)-Acetonitrile (MeCN) Formation Constants in Aqueous Media

Background. Copper(I) is unstable with respect to disproportionation in aqueous solutions.[1] The equilibrium constant for eq. 2.1,

$$2\mathrm{Cu}^{+}_{(aq)} \underset{}{\overset{K}{\rightleftarrows}} \mathrm{Cu}^{2+}_{(aq)} + \mathrm{Cu}^{0}_{(s)} \qquad (2.1)$$

$K = 1.3 \times 10^{6}\,\mathrm{M}^{-1}$, lies far to the right, so that the equilibrium concentration of copper(I) in aqueous solutions is ~10^{-4} M for a typical copper(II) concentration of 1 × 10^{-2} M. Acetonitrile reduces this disproportionation to a great extent in water-acetonitrile solutions. Reduction potential values[2,3] for copper(I) and copper(II) in water-acetonitrile solutions indicate a decreasing trend on the equilibrium constant in eq. 2.1 as the amount of acetonitrile is increased in solution. In pure acetonitrile, polarographic studies[4] have shown that copper(I) is stable with respect to disproportionation, and the equilibrium constant for eq. 2.1 has been determined[5] potentiometrically to be 10^{-21} M^{-1}.

A number of salts of tetrakis(acetonitrile)copper(I), $\mathrm{Cu(NCCH_3)_4^+}$, have been prepared in the past.[6-9] Crystal structures have been done for the perchlorate,[10] hexafluorophosphate[11] and tetrafluoroborate[12] salts and all show essentially tetrahedral coordination of four acetonitriles to copper(I). These are generally stable solids and are useful starting materials for copper(I) chemistry. The bonding involves donation of the lone pair of electrons on the nitrogen of the nitrile to copper(I), and possibly back-bonding from the $3d^{10}$ orbitals to the π^* orbital of the nitrile group, as shown in Figure 2.1. This back-bonding aspect is somewhat controversial. Recent arguments[13,14] on copper(I) carbonyl coordination chemistry have shown non-classical trends in some of

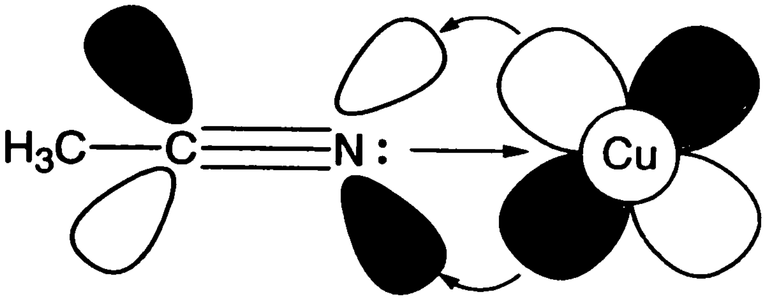

Figure. 2.1. Acetonitrile bonds to copper(I) via the end-on or σ fashion.

these complexes where the υ(CO) value increases instead of decreasing with respect to the uncoordinated υ(CO). Some of the C-O bond lengths also were non-classical in that the distance decreased instead of increasing on coordination. Since CO is a better π-acceptor than MeCN, one might expect less back bonding in $Cu(NCCH_3)_4^+$, but MeCN is a stronger σ-donor and this could increase the tendency for back-bonding. The C-N distances in representative copper(I) complexes[10-12,15] are of the same magnitude (1.11-1.14Å) as in free MeCN (1.12Å).[11,16]

The copper(I)-acetonitrile system serves as a stable source of univalent copper(I) in aqueous solutions. A number of studies have been done on copper(I) in acetonitrile-water mixtures. These range in diversity from the reconstitution[17] of apoceruloplasmin by following the kinetics of the oxidation of copper(I) by dissolved oxygen to the hydrometallurgical recovery and purification[18] of copper metal by distillation of acetonitrile from aqueous copper(I)-acetonitrile solution. Despite the amount of work involving copper(I)-acetonitrile in aqueous solutions, there are only a few studies on the copper(I)-acetonitrile formation constants. In solution, the mono, bis, and tris acetonitrile copper(I) complexes have been ascertained.[7, 19-21]

The formation constants of copper(I) with acetonitrile in aqueous solutions have been investigated previously by Hemmerich[7] using a dropping mercury electrode, and by Manahan[19], using a copper-amalgam electrode. Zuberbuhler,[20,21] studied the rate of reaction of copper(I) with dioxygen as a function of acetonitrile concentration with an oxygen specific electrode. The details of these studies will be described later when comparisons are made to our results. The disparity of the values of copper(I)-acetonitrile formation constants reported in the literature, and the importance of the system suggested the need for a simple and accurate method for their determination and prompted us to undertake this study.

The kinetic method developed here is based on the variation in the rate of reduction of a cobalt(III) complex by copper(I) in varying acetonitrile-water mixtures.

The method takes advantage of the fact that cobalt(III) complexes are stable, colored and reactive scavengers for aqueous copper(I).[22] The reduction appears to occur by an inner-sphere mechanism so that the reactivity changes with the nature of the bridging ligand(s) on the cobalt(III) complex. A wide range of second-order rate constants was reported by Espenson and Parker[22] for cobalt(III) complexes, with the values spanning about ten orders of magnitude; 4.46×10^5 to less than 4×10^{-4} $M^{-1}s^{-1}$ for the $[(NH_3)_5CoBr]^{2+}$ and $[Co(en)_3]^{3+}$, respectively. The method requires only standard laboratory equipment and a conventional ultra-violet-visible range spectrophotometer.

Experimental

Materials. Acetonitrile (specific gravity 0.777 g/cm^3, 99.5%, water 0.3%, BDH), copper foil (Matheson Coleman and Bell), silver nitrate (Johnson Matthey and Mallory Ltd.), copper nitrate trihydrate (Fisher Scientific), 30 mesh zinc granules (Fisher Scientific), copper oxide (Fisher Scientific), cobalt sulfate heptahydrate (Matheson Coleman and Bell), cobalt nitrate hexahydrate (Mallinckrodt), sodium azide (BDH), perchloric acid (Caledon), pre-purified argon (Praxair), and sodium perchlorate (Fisher Scientific) were used as received.

Pentaamminеazidocobalt(III) chloride, $[(NH_3)_5CoN_3]Cl_2$,[23] pentaamminebromocobalt(III) bromide, $[(NH_3)_5CoBr]Br_2$,[24] and pentaamminebromocobalt(III) perchlorate, $[(NH_3)_5CoBr](ClO_4)_2$,[25] were prepared by standard methods. Pentaammineazidocobalt(III) nitrate, $[(NH_3)_5CoN_3](NO_3)_2$, was prepared either by (i) the reaction of aqueous $[(NH_3)_5CoN_3]Cl_2$ with a stoichiometric amount of $AgNO_3$ and filtering off the AgCl precipitate through a 0.22 μm Millipore filter or (ii) through an adaptation of Linhard's synthesis of the chloride salt.[23] A solution of 12.2 g of $Co(NO_3)_2 \cdot 6H_2O$ dissolved in 25 mL of water was prepared and set aside. Then 29.9 g of ammonium nitrate and 10 g of sodium azide were dissolved in 60 mL of water in a 500 mL filter flask and 40 mL of concentrated aqueous ammonia added. The cobalt(II) nitrate solution was added to the second solution and air was drawn through the solution for 2 hours. The dark yellow-brown solution was placed on a steam bath for 1-2 hours, until it turned deep purple. The solution was cooled in ice/water for 3-4 hours and the product collected by filtration and washed with cold water, ethanol and ether. Yield 8.8 g. The product was dissolved in 1.0 L of water at 45-50 °C, filtered through a 0.2 μm filter and 10 g of ammonium nitrate was added and dissolved by stirring. The solution was cooled in ice/water for 4 hours and the product collected and washed as before. Yield 6.7 g.

Preparation of solutions. Stock solutions of $HClO_4$ were prepared by diluting 70% $HClO_4$ and analyzed by titration with standard NaOH. Stock solutions of $NaClO_4$ were made by dissolving reagent grade solid and analyzed by titrating the H^+ produced by an aliquot passed through an anion exchange column in the H^+ form with standard NaOH. Stock solutions of the acetonitrile were made by pipetting appropriate volumes of neat acetonitrile and diluting to the mark in a volumetric flask.

Stock solutions of $CuNO_3$ in acetonitrile-water for the kinetic runs were prepared by mixing appropriate volumes of 4.80×10^{-2} or 6.77×10^{-2} M aqueous silver nitrate and 9.46×10^{-1} or 9.46 M acetonitrile together with an appropriate volume of 1.28 M $HClO_4$ in the presence of copper metal and diluting to the mark in a 100 mL volumetric flask. The solution was transferred into a 250 mL Erlenmeyer flask with excess copper foil and deoxygenated for about an hour and left overnight[2] under pre-purified argon. A dirty white precipitate (colloidal silver) formed almost immediately and settled in about 15 to 20 minutes. The precipitated silver and excess copper metal were removed by filtration under argon. The total acetonitrile in these solutions ranged from 9.46×10^{-2} to 1.89 M. Portions of the copper(I) solution were air oxidized and analyzed for total copper via the potassium iodide/sodium thiosulfate method.[26] A portion of the solution was always tested by addition of sodium chloride to make sure that all the silver nitrate had reacted before they were used for the kinetic runs. Blank experiments indicate that silver chloride will precipitate even in 18.08 M acetonitrile with 7.7×10^{-5} M NaCl and 1.30×10^{-4} M $AgNO_3$. This is consistent with the small formation constants[27] of silver(I)-acetonitrile complexes.

Stock solutions of the cobalt(III) complexes were prepared by careful weighing of the solid and diluting to volume in a volumetric flask with doubly distilled water. In some cases these solutions were acidified to 3.33×10^{-2} M $HClO_4$ and the ionic strength was adjusted to 1.41×10^{-1} M by addition of appropriate volumes of stock $NaClO_4$ to the reaction mixture. Acidifying the solutions was necessary since the cobalt(III) solutions hydrolyzed in solutions that were not acidic. The time period for the hydrolysis varied with the complexes. For example, the absorbance at 252 nm of $[(NH_3)_5CoBr](ClO_4)_2$ decreased by 25% in a period of about 24 hours. Blank experiments show a decrease in absorbance with time of the cobalt(III) solutions that were stored exposed to light. To minimize these hydrolysis and photolysis effects the stock solutions (with the exception of $[(NH_3)_5CoN_3](NO_3)_2$ where the stock solution was sometimes not in acid) were prepared in acid and the volumetric flasks covered with aluminum foil. There was no hydrolysis of neutral solutions of $[(NH_3)_5CoN_3](NO_3)_2$ stored in the dark for a period of up to four days.

Values of the extinction coefficients and wavelengths where the reactions were monitored are given in Table 2.1. Acetonitrile shows no absorption over the range where the reactions were monitored. Copper(I)-acetonitrile absorbs in the uv but no experiments were done in acetonitrile in the uv region. At the concentrations of chromium(III) perchlorate used, its absorbance is negligible at 350 and 252 nm. Our values for the extinction coefficients of the cobalt(III) complexes in Table 2.1 are comparable to those reported in literature by Espenson and Parker[22] (bromo 16700 $M^{-1}cm^{-1}$, 253 nm; 52 $M^{-1}cm^{-1}$, 550 nm) and Linhard[23] (azido 281 $M^{-1}cm^{-1}$, 516 nm).

Table 2.1. Molar Extinction Coefficients of Reactants and Products.

	Observation Wavelength (nm)			
Species	546	516	350	252
$[(NH_3)_5CoN_3]Cl_2$[a]		2.60×10^2		
$[(NH_3)_5CoN_3](NO_3)_2$[a]		2.68×10^2	1.24×10^3	
$[(NH_3)_5CoBr]Br_2$[b]	55.2			
$[(NH_3)_5CoBr](ClO_4)_2$[c]	54.2			1.74×10^4
Co(II)[d]	3.2	6.18	5.81	
Cu(II)[e]			2.41	7.23
Cu(I)[f]				5.00×10^2
Cr(III)[g]	10.1	5.63	2.38	3.75

Extinction coefficients were determined with the solids dissolved: [a]in doubly distilled water; [b]in 3.24×10^{-2} M $HClO_4$; [c]in 2.19×10^{-1} M $NaClO_4$; [d]1.7×10^{-2} M $CoSO_4 \cdot 7H_2O$ in 2 M $HClO_4$; [e]8.31×10^{-2} M $Cu(ClO_4)_2$ in 3.08×10^{-2} M $HClO_4$; [f]9.42×10^{-4} M $Cu(ClO_4)$ in 0.19 M $HClO_4$ and 1.54×10^{-2} M $Cu(ClO_4)_2$; [g]4.00×10^{-2} M Cr(III) perchlorate in 7.94×10^{-2} M $HClO_4$.

Kinetic studies of copper(I)/acetonitrile with cobalt(III) complexes. The experiments were carried out with an excess of cobalt(III) over copper(I) so that the concentration of copper(I) could be determined from the change in absorbance of the cobalt(III) complex, as illustrated in Figure 2.2. Then this copper(I) concentration (when [Co(III)] > [Cu(I)]) was used to calculate a stock copper(I) concentration which then was used to work out the reaction concentration when the concentration of copper(I) was higher than that of cobalt(III) for a particular run in a given set of experiments. The reaction vessel was a 5.0 cm cylindrical optical cell with a total volume of 12 mL. Appropriate volumes of the cobalt(III) solution, stock acetonitrile solution and $HClO_4/NaClO_4$ to set the ionic strength at 1.41×10^{-1} M were deoxygenated in the serum-capped cell for about 10 minutes. Then the appropriate volume of copper(I)-acetonitrile was introduced via a 5 mL syringe. Immediately the cell was placed in the spectrophotometer and the recording started. The change of absorbance was monitored at 516 nm for the chloride and nitrate salts of $[(NH_3)_5CoN_3]^{2+}$ and 546 nm for the bromide and perchlorate salts of $[(NH_3)_5CoBr]^{2+}$. The reactant concentrations ranged from $(1.95 - 11.7) \times 10^{-4}$ M for cobalt(III), $(2.42 - 11.7) \times 10^{-4}$ M for copper(I) and $(2.37 - 204) \times 10^{-2}$ M for acetonitrile; the solution also contained 3.33×10^{-2} M $HClO_4$ and 1.09×10^{-1} M $NaClO_4$. The acidic conditions were necessary since a precipitate forms at pH values greater than 5.5.

The reactions were followed on a Cary 219 spectrophotometer at ambient temperature.

Kinetic studies of aqueous copper(I) with cobalt(III) complexes. Although these reactions have been studied previously,[22,28] it was necessary to obtain rate constants at the ionic strength of the present work. In water, copper(I) ion is unstable relative to disproportionation but this limitation can be overcome by preparing metastable solutions of aqueous copper(I) via eq. 2.2.[29-31]

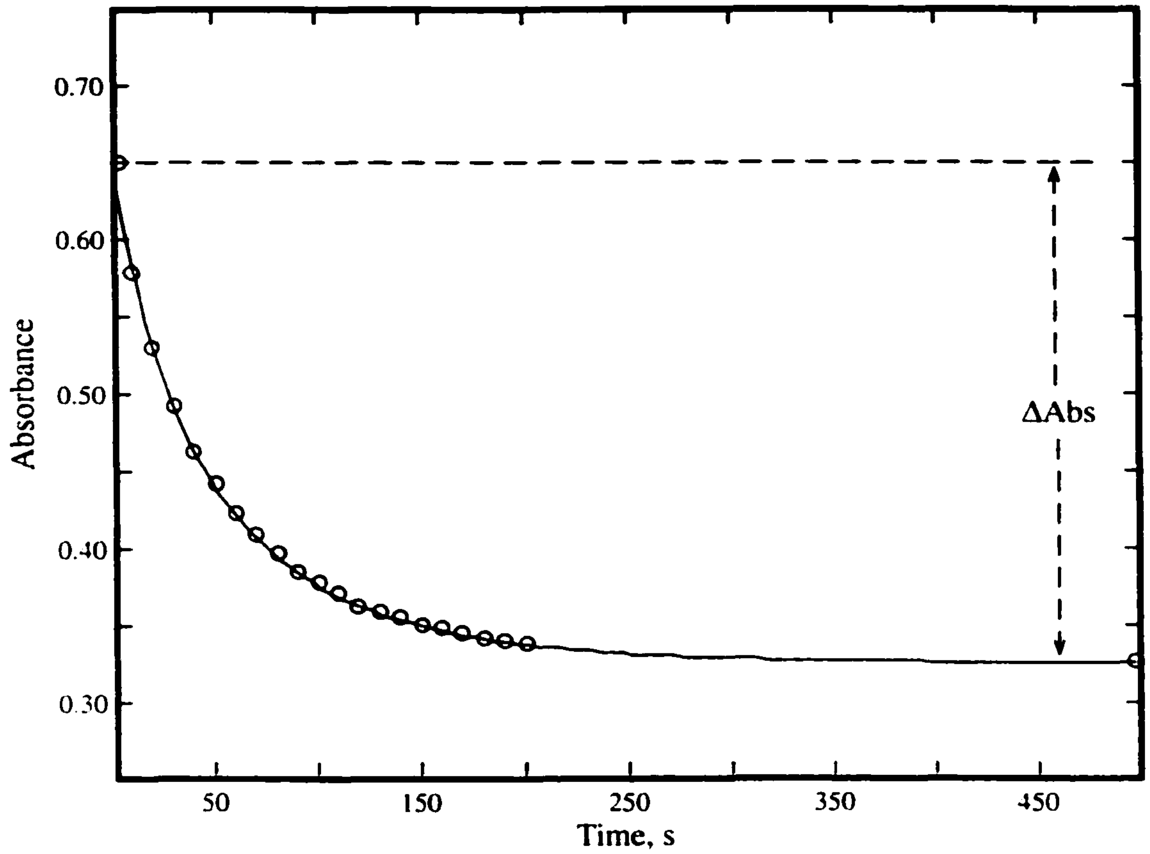

Figure 2.2. A reaction profile for the reduction of cobalt(III) by copper(I) in water-acetonitrile solution. Copper(I) reaction concentration is calculated from the relationship ΔAbs = $\varepsilon \Delta c l$. ΔAbs is the difference between the initial (I_0) and final (I_∞) absorbances obtained from the chart paper, ε is the extinction coefficient and l is the path length. Then $\Delta c = [\mathrm{Cu^I}]$.

$$\mathrm{Cr^{II}}_{(aq)} + \mathrm{Cu^{II}}_{(aq)} \longrightarrow \mathrm{Cr^{III}}_{(aq)} + \mathrm{Cu^{I}}_{(aq)} \qquad (2.2)$$

Solutions containing up to 8 mM copper(I) can be prepared easily and kept for several hours in acidic solution.

A 10 mL aliquot of 1.35 x 10^{-2} M chromium(III) perchlorate in 6.48 × 10^{-2} M $HClO_4$ was deoxygenated and mixed with an equal volume of deoxygenated doubly distilled water over amalgamated zinc. The reduction of chromium(III) was complete in ~ 1 hour. Then the solution was transferred under argon, through a 5 mL syringe packed with glass wool to remove zinc particles, to an Erlenmeyer flask containing 10 mL of 1.79 × 10^{-2} M copper(II) perchlorate, and an appropriate volume of 3.24 × 10^{-1} M $HClO_4$ and distilled water were added to give a final volume of 100 mL and 3.33 × 10^{-2} M $HClO_4$. About 15 minutes was allowed to generate copper(I). This gave a stock concentration of ~ 1.35 × 10^{-3} M copper(I) in 3.33 × 10^{-2} M $HClO_4$. The aqueous copper(I) solution was used first under pseudo-first-order conditions ([Cu(I)] >> [Co(III)]) for the reduction of $[(NH_3)_5CoBr](ClO_4)_2$. The same stock solution was used under second-order conditions ([Co(III)] > [Cu(I)]) for the reduction of $[(NH_3)_5CoN_3]^{2+}$. The absorbance change in the latter experiments gave the concentration of copper(I) in the stock solution.

The cobalt(III) stock solutions, in 3.33 × 10^{-2} M $HClO_4$ and 2.18 × 10^{-1} M $NaClO_4$, were prepared from weighed amounts of the cobalt(III) complex to give a final concentration of cobalt(III) of 2.0 × 10^{-3} M.

The cobalt(III) solution with appropriate dilution and copper(I) solution were transferred by syringe to separate serum-capped storage syringes on the stopped-flow system for thermostating at 25 ± 0.5 °C. The solutions were transferred via 3 way taps to the drive syringes and mixed in equal volumes on the stopped-flow system. The change of absorbance was monitored at 252 nm for $[(NH_3)_5CoBr](ClO_4)_2$ and 350 nm for $[(NH_3)_5CoN_3](NO_3)_2$. The amounts of $NaClO_4$ (1.09 × 10^{-1} M) and $HClO_4$ (3.33 × 10^{-2}

M) were maintained at the same concentrations as for the runs done on the Cary 219 spectrophotometer.

The reactions were monitored on a Tritech Dynamic Instruments stopped-flow system (Model IIA). Kinetic Version 1.2 IBM program was used to transfer the data from the transient recorder to the computer and for converting transmittance to absorbance with Beer's law correction.

It was felt that there was no need to examine the effect of acidity in our study since even in concentrated H_2SO_4 acetonitrile is not protonated.[32] Acid dependence is discussed in Chapter 3 in the determination of formation constants of copper(I) by unsaturated dicarboxylic acids and their derivatives in aqueous solutions.

Basic Equations. The following steps describe the derivation of the equations[33] necessary to fit the absorbance change as a function of time for pseudo-first-order and second-order reaction conditions. In the following steps, A is cobalt(III), B is copper(I), C is cobalt(II), and ε_A and ε_C are the extinction coefficients for cobalt(III) and cobalt(II) species respectively.

For a pseudo-first-order reaction, where B is in a large excess of A,

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \mathrm{C} \qquad (2.3)$$

the standard form of the integrated first-order rate law is given by eq. 2.3,

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k't} \qquad (2.4)$$

where A is the concentration at any time, A_0 is the initial concentration and k' ($k' = k[\mathrm{B}]_0$) is the pseudo-first-order rate constant. With this expression, the fact that $[\mathrm{C}]_\infty = [\mathrm{A}]_0$ at the end of reaction and Beer's law, one can develop the relationship for the time dependence of the absorbance (I) at zero time and at the end of the reaction. If the path length is 1.0 cm, then initially

$$I_0 = \varepsilon_A[A]_0 \tag{2.5}$$

and at the end of the reaction

$$I_\infty = \varepsilon_C[C]_\infty = \varepsilon_C[A]_0. \tag{2.6}$$

At any time the absorbance I is given by

$$I = \varepsilon_A[A] + \varepsilon_C[C] = \varepsilon_A[A] + \varepsilon_C([A]_0 - [A]) \tag{2.7}$$

since mass balance dictates that $[C] = [A]_0 - [A]$. Eq. 2.7 can be rearranged to the form below.

$$I = (\varepsilon_A - \varepsilon_C)[A] + I_\infty \tag{2.8}$$

Substitution for [A] from eq. 2.8 and $[A]_0$ from eq. 2.6 in terms of I and I_∞ into eq. 2.4 one gets eq. 2.9.

$$\frac{I - I_\infty}{\varepsilon_A - \varepsilon_C} = \frac{I_\infty}{\varepsilon_C} e^{-k't} \tag{2.9}$$

Rearranging eqs. 2.5 and 2.6 to get ε_A and ε_C in terms of A_0, I_0, and I_∞ and substituting for these expressions into eq. 2.9 gives eq. 2.10.

$$\frac{I - I_\infty}{I_0 - I_\infty} = e^{-k't} \qquad (2.10)$$

Rearrangement of eq. 2.10 gives eq. 2.11.

$$I = I_\infty - (I_\infty - I_0)e^{-k't} \qquad (2.11)$$

For a second-order reaction,

$$\mathrm{A + B} \xrightarrow{k} \mathrm{C} \qquad (2.12)$$

the standard form of the integrated second-order rate law is given by eq. 2.13,

$$kt = \frac{1}{\mathrm{B_0 - A_0}} \ln\left(\frac{\mathrm{A_0}}{\mathrm{B_0}} \times \frac{\mathrm{B}}{\mathrm{A}}\right) \qquad (2.13)$$

where A, B, and C represent the concentrations of the species at any time, subscript 0 denotes initial concentrations and *k* is the second-order rate constant.

The stoichiometry relationship that $\mathrm{A_0 - A = B_0 - B}$, can be solved for B in terms of A and then substituted into the integrated rate law to obtain the concentration of A at any time as eq. 2.14.

$$\mathrm{A} = \frac{(\mathrm{B_0 - A_0})}{\frac{\mathrm{B_0}}{\mathrm{A_0}} \exp\{(\mathrm{B_0 - A_0})kt\} - 1} \qquad (2.14)$$

The above expression for A can be substituted into the stoichiometry relationship $B = A + (B_0 - A_0)$, to obtain the concentration of B at any time as eq. 2.15.

$$B = \frac{(B_0 - A_0)\frac{A_0}{B_0}\exp\{(B_0 - A_0)kt\}}{\frac{B_0}{A_0}\exp\{(B_0 - A_0)kt\} - 1} \tag{2.15}$$

The stoichiometry gives $C = A_0 - A$, and substitution for A from eq. 2.14 gives eq. 2.16.

$$C = \frac{B_0[\exp\{(B_0 - A_0)kt\} - 1]}{\frac{B_0}{A_0}\exp\{(B_0 - A_0)kt\} - 1} \tag{2.16}$$

With these expressions for the concentrations and Beer's law, one can develop the relationship for the time dependence of the absorbance (*I*) under various conditions of observation.

When A and C are absorbing and A > B, then the initial absorbance is

$$I_0 = \varepsilon_A A_0 l \tag{2.17}$$

and the final concentration of C is $C_\infty = B_0$. The path length, *l*, was 5 cm in our copper(I)/acetonitrile studies. Then the final absorbance is given by eq. 2.18,

$$I_\infty = 5\varepsilon_C C_\infty + 5\varepsilon_A A_\infty = 5\varepsilon_C B_0 + 5\varepsilon_A(A_0 - B_0) = 5B_0(\varepsilon_C - \varepsilon_A) + I_0 \tag{2.18}$$

and rearrangement gives eq. 2.19.

$$B_0 = \frac{I_\infty - I_0}{5(\varepsilon_C - \varepsilon_A)} \tag{2.19}$$

The ratio B_0/A_0 can be expressed in terms of determinable parameters by substituting for A_0 from eq. 2.17 and B_0 from eq. 2.19 to give eq. 2.20.

$$\frac{B_0}{A_0} = \frac{5\varepsilon_A B_0}{I_0} = \frac{\varepsilon_A(I_\infty - I_0)}{I_0(\varepsilon_C - \varepsilon_A)} \tag{2.20}$$

The expression for I_∞, eq. 2.18, can also be used to obtain eq. 2.21.

$$B_0 - A_0 = \frac{5\varepsilon_C B_0 - I_\infty}{5\varepsilon_A} = \left(\frac{\varepsilon_C(I_\infty - I_0)}{5\varepsilon_A(\varepsilon_C - \varepsilon_A)}\right) - \left(\frac{I_\infty}{5\varepsilon_A}\right) \tag{2.21}$$

Then the absorbance at any time is

$$I = 5\varepsilon_A A + 5\varepsilon_C C + I_b \tag{2.22}$$

where I_b is a blank absorbance. Substituting for A (eq. 2.14), C (eq. 2.16), and adding an adjustment for dead time, t_d, which takes account of the time between the reaction start and the time the recording is started on the spectrophotometer, into eq. 2.22 gives the absorbance at any time as eq. 2.23.

$$I = \frac{5\varepsilon_A(B_0 - A_0) + 5\varepsilon_C B_0\left[\exp\{(B_0 - A_0)k(t + t_d)\} - 1\right]}{\frac{B_0}{A_0}\exp\{(B_0 - A_0)k(t + t_d)\} - 1} + I_b \qquad (2.23)$$

Substitution from eq. 2.20 and 2.21 gives the variation of I with t in terms of k, t_d, I_b, I_0, ε_A and ε_C. In the present application the latter three quantities are known and the first three were determined by least-squares fitting.

If ε_C is negligible in comparison to ε_A, and l is 1.0 cm as in our aqueous copper(I) studies, then eq. 2.23 can be expressed in terms of absorbances only by substituting for B_0/A_0 and B_0-A_0 from eqs. 2.20 and 2.21 to give eq. 2.24.

$$I = -\frac{I_\infty}{\left(\frac{I_0 - I_\infty}{I_0}\right)\exp\left\{-\left(\frac{I_\infty}{\varepsilon_A}\right)kt\right\} - 1} \qquad (2.24)$$

Kinetic data analysis. In the copper(I)/acetonitrile system the absorbance-time data points were manually read from the chart paper and stored in a BASIC data file. The copper(I) concentration for each kinetic run was calculated from the absorbance change (Figure 2.2) if the concentration of cobalt(III) was higher than that of copper(I), otherwise the copper(I) concentration was obtained as described previously under kinetic studies of copper(I)/acetonitrile with cobalt(III) complexes. This information along with the known cobalt(III) concentration also was stored in the data file. The absorbance-time data were fitted to eq. 2.23 by an iterative least-squares program. The program generated best-fit values of the second-order rate constant, the dead time, and the blank absorbance.

For the reduction of the bromo complex in aqueous solution, the concentration of copper(I) was ~10 times that of cobalt(III), so that the data were fitted to a first-order rate law (eq. 2.11) by an iterative least-squares program. The program generated the pseudo-first-order rate constant *k'*, the initial, and final absorbance for the best fit of the data.

The reduction of the azido complex in aqueous solution was carried out with an excess of cobalt(III) over copper(I). In the analysis, the concentration of the cobalt(III) complex and its extinction coefficient were known. The copper(I) concentration was obtained from the numerical analysis of the kinetic runs using eq. 2.19 with a path length of 1.0 cm, so that $[Cu(I)]_0 = (I_0 - I_\infty)\varepsilon_A^{-1}$, since $\varepsilon_C << \varepsilon_A$. The program generated values for the second-order rate constant, *k* by fitting the absorbance at any time to eq. 2.24.

Results

It has been shown previously[22] that the reaction of aqueous copper(I) with various cobalt(III) complexes is first-order in each reactant. The present observation with the azido and bromo complexes are consistent with this. The results are given in Table 2.2 and 2.3. The average rate constant (k_0) for the azido complex is 1.42×10^3 M^{-1}s^{-1}. These results also gave an average concentration of copper(I) of 1.36×10^{-4} M. The latter value was combined with the average first-order rate constants for the bromo complex, 54.8 s^{-1}, to obtain a k_0 value of 4.04×10^5 M^{-1}s^{-1}.

At constant acetonitrile and copper(I) concentrations, varying the cobalt(III) concentration gave constant second-order rate constants. Likewise constant second-order rates were obtained at constant acetonitrile and cobalt(III) concentrations and varying the copper(I) concentration. The rate of reaction was independent of whether nitrate or chloride salts of pentaammineazidocobalt(III) were used. These features are shown by data in Table 2.4.

The general trend observed is that reaction rate decreases smoothly as the acetonitrile concentration is increased, Table 2.4 and 2.5. In order to analyze the dependence of the observed rate constants on the acetonitrile concentration, a rate law for

Table 2.2. Second-Order Rate Constants for the Reduction of 2.26 × 10^{-4} M $[(NH_3)_5CoN_3](NO_3)_2$ by Aqueous Copper(I) at 350 nm in 1.09 × 10^{-1} M $NaClO_4$ and 3.33 × 10^{-2} M $HClO_4$ at 25 °C.

I_0	I_∞	$10^4[Cu^I]$,M	$10^{-3}k_{obsd}$, $M^{-1}s^{-1}$
0.291	0.122	1.360	1.419
0.314	0.143	1.377	1.369
0.297	0.128	1.367	1.391
0.307	0.149	1.272	1.404
0.300	0.137	1.320	1.337
0.280	0.091	1.533	1.459
0.276	0.101	1.410	1.424
0.293	0.136	1.269	1.457
0.315	0.171	1.157	1.380
0.310	0.130	1.454	1.435
0.302	0.134	1.354	1.351
0.301	0.141	1.287	1.445
0.304	0.126	1.434	1.449
0.279	0.103	1.424	1.414
0.296	0.131	1.331	1.452
		Ave. **1.36 ± 0.091**	Ave. **1.42 ± 0.04**

Where I_0 and I_∞ are the initial and final absorbances.

Table 2.3. Pseudo-First-Order Rate Constants for the Reduction of 3.78 × 10^{-5} M $[(NH_3)_5CoBr](ClO_4)_2$ by Aqueous Copper(I) at 252 nm in 1.09 × 10^{-1} M $NaClO_4$ and 3.33 × 10^{-2} M $HClO_4$ at 25 °C.

I_0	I_∞		k_{obsd}, s^{-1}
0.573	0.073		58.1
0.566	0.085		58.2
0.587	0.071		54.7
0.567	0.070		52.0
0.583	0.082		55.8
0.577	0.087		54.0
0.551	0.085		54.3
0.543	0.076		51.9
0.570	0.082		56.4
0.579	0.074		55.7
0.592	0.078		57.1
0.581	0.071		51.5
0.557	0.073		53.7
0.538	0.098		55.9
0.574	0.073		52.4
		Ave.	**54.78 ± 2.2**
		k_0	**(4.04 ± 0.2) × 10^5**

Where I_0 and I_∞ are the initial and final absorbances.

Table 2.4. Second-Order Rate Constants for the Reduction of $[(NH_3)_5CoN_3]^{2+}$ by Copper(I) in Water-Acetonitrile Solutions. Monitored at 516 nm, in 3.33×10^{-2} M $HClO_4$ and 1.09×10^{-1} M $NaClO_4$.

$10^4[Co^{III}]$,M	$10^4[Cu^I]$,M	10^2[MeCN],M	k, $M^{-1}s^{-1}$	
			Obsd.	Calcd.
5.84[a]	6.25	2.37	88.6	82.6
5.84[a]	5.00	2.37	84.2	82.6
5.84[b]	5.00	2.37	83.7	82.6
5.84[a]	3.50	2.99	53.8	60.4
5.84[a]	5.00	2.99	58.7	60.4
5.84[b]	5.00	3.63	47.3	45.8
5.84[a]	5.50	3.63	44.0	45.8
5.84[a]	4.75	4.26	34.7	36.1
5.84[b]	5.00	4.89	29.4	29.2
5.84[a]	4.00	4.89	26.6	29.2
5.84[a]	5.75	5.52	27.0	24.1
5.84[b]	5.50	5.52	25.6	24.1
5.84[a]	5.75	8.68	11.8	11.3
5.84[b]	4.00	8.68	11.2	11.3
1.95[b,e]	4.00	11.8	6.06	6.48
1.95[c,e]	7.50	11.8	7.13	6.48
3.89[b,e]	8.25	11.8	6.48	6.48
3.89[c,e]	7.50	11.8	7.59	6.48
3.89[a,e]	8.50	11.8	7.74	6.48
5.84[b,d,e]	8.75	11.8	6.04	6.48

Table 2.4. continued.

10^4[Co^{III}],M	10^4[Cu^{I}],M	10^2[MeCN],M	k, M^{-1}s^{-1}	
			Obsd.	Calcd.
5.84^{b,e}	3.38	11.8	6.21	6.48
5.84^{a,e}	5.88	11.8	6.40	6.48
5.84^{b,d,e}	8.75	11.8	6.42	6.48
5.84^{b,e}	8.75	11.8	6.63	6.48
5.84^{c,e}	8.25	11.8	7.37	6.48
5.84^{a,e}	8.25	11.8	7.82	6.48
7.78^{b,e}	7.75	11.8	6.48	6.48
7.78^{a,e}	8.75	11.8	7.27	6.48
5.84^{a}	6.50	15.0	3.46	4.18
5.84^{b}	3.63	15.0	3.96	4.18
5.84^{c}	2.42^{f}	15.8	4.01	3.81
5.84^{c}	5.34^{f}	15.8	3.44	3.81
5.84^{a}	5.51^{f}	15.8	3.48	3.81
5.84^{c}	7.25^{f}	15.8	3.79	3.81
5.84^{a}	9.50^{f}	15.8	3.26	3.81
5.84^{a}	11.7^{f}	15.8	3.86	3.81
5.84^{a}	5.00	18.1	3.25	2.94
5.84^{a}	3.65	21.3	2.62	2.17

[a] $[(NH_3)_5CoN_3](NO_3)_2$; [b] $[(NH_3)_5CoN_3]Cl_2$; [c] $[(NH_3)_5CoN_3](NO_3)_2$ prepared by stoichiometric reaction of $[(NH_3)_5CoN_3]Cl_2$ and $AgNO_3$. [d] NaCl added to $[(NH_3)_5CoN_3]Cl_2$; variation of [e] cobalt(III) and [f] copper(I) concentration as explained in the text.

Table 2.5. Second-Order Rate Constants for the Reduction of $[(NH_3)_5CoBr]^{2+}$ by Copper(I) in Water-Acetonitrile Solutions. Monitored at 546 nm, in 3.33×10^{-2} M $HClO_4$ and 1.09×10^{-1} M $NaClO_4$.

$10^4[Co^{III}]$,M	$10^4[Cu^I]$,M	$10^1[MeCN]$,M	k, $M^{-1}s^{-1}$	
			Obsd.	Calcd.
11.7	7.25	5.68	56.8	57.8
7.03	6.50	5.68	56.8	57.8
7.03	6.75	6.15	46.5	47.9
7.03	6.75	6.63	41.2	40.0
7.03	6.00	7.10	29.8	34.0
11.7	8.03	7.10	36.1	34.0
7.03	6.25	7.57	26.8	29.2
11.7	7.60	8.04	24.8	25.4
7.03	5.38	8.52	21.4	22.1
7.03	5.50	8.52	20.6	22.1
7.03	6.08	8.99	21.3	19.5
11.7	7.83	9.00	19.4	19.5
7.03	6.00	9.46	17.4	17.3
7.03	5.32	9.94	14.7	14.8
7.03	5.89	10.4	15.2	13.9
7.03	5.75	10.9	13.0	12.5
11.7	7.98	12.4	10.0	9.33
7.03	4.63	16.4	5.65	5.12
11.7	8.58	19.1	3.23	3.78
7.03	4.00	20.4	3.33	3.30

the system was derived based on the probable species present. These species, related by the successive formation constants for copper(I) coordination by MeCN, are defined by eq. 2.25, 2.26 and 2.27.

$$\mathrm{Cu^+ + MeCN} \overset{K_1}{\rightleftarrows} \mathrm{Cu(MeCN)^+} \tag{2.25}$$

$$\mathrm{Cu(MeCN)^+ + MeCN} \overset{K_2}{\rightleftarrows} \mathrm{Cu(MeCN)_2^+} \tag{2.26}$$

$$\mathrm{Cu(MeCN)_2^+ + MeCN} \overset{K_3}{\rightleftarrows} \mathrm{Cu(MeCN)_3^+} \tag{2.27}$$

The overall formation constants β_1, β_2 and β_3 are related to the equilibrium constants K_1, K_2 and K_3 by the following expressions, $\beta_1 = K_1$, $\beta_2 = K_1K_2$ and $\beta_3 = K_1K_2K_3$, so that β_1, β_2 and β_3 are given by eq. 2.28, 2.29, and 2.30.

$$\beta_1 = \frac{[\mathrm{Cu(MeCN)^+}]}{[\mathrm{Cu^+}][\mathrm{MeCN}]} \tag{2.28}$$

$$\beta_2 = \frac{[\mathrm{Cu(MeCN)_2^+}]}{[\mathrm{Cu^+}][\mathrm{MeCN}]^2} \tag{2.29}$$

$$\beta_3 = \frac{[\mathrm{Cu(MeCN)_3^+}]}{[\mathrm{Cu^+}][\mathrm{MeCN}]^3} \tag{2.30}$$

In acidic solution, the reduction of cobalt(III) by copper(I) species is given by the reaction in eq. 2.31.

$$\left[(NH_3)_5CoN_3\right]^{2+} + Cu(MeCN)_n^+ + 6H^+ \xrightarrow{k_n} Cu^{2+} + Co^{2+} + 5NH_4^+ + HN_3 + nMeCN \tag{2.31}$$

One can define the specific rate constants, k_0, k_1, k_2 and k_3, for the different copper(I) species with n = 0, 1, 2 and 3 respectively. Then the rate of disappearance of cobalt(III) is given by eq. 2.32.

$$\text{rate} = \left\{k_0\left[Cu^+\right] + k_1\left[Cu(MeCN)^+\right] + k_2\left[Cu(MeCN)_2^+\right] + k_3\left[Cu(MeCN)_3^+\right]\right\}\left[Co^{III}\right] \tag{2.32}$$

In order to use this expression, it is necessary to express the unknown concentrations of the copper(I) species in terms of the known total copper(I) and MeCN concentrations. The total copper (I) concentration, $[Cu^+]_t$ is given by eq. 2.33.

$$\left[Cu^+\right]_t = \left[Cu(MeCN)_3^+\right] + \left[Cu(MeCN)_2^+\right] + \left[Cu(MeCN)^+\right] + \left[Cu^+\right] \tag{2.33}$$

The individual concentrations for these copper(I) species can be obtained by rearrangement of eqs. 2.28, 2.29, and 2.30 for the conditions that $\left[MeCN\right] >> \left[Cu^+\right]_t$ and substituting these into eq. 2.33.

$$\left[Cu^+\right] = \left(\frac{1}{1 + \beta_1\left[MeCN\right] + \beta_2\left[MeCN\right]^2 + \beta_3\left[MeCN\right]^3}\right)\left[Cu^+\right]_t \tag{2.34}$$

$$\left[\mathrm{Cu(MeCN)^+}\right]=\left(\frac{\beta_1[\mathrm{MeCN}]}{1+\beta_1[\mathrm{MeCN}]+\beta_2[\mathrm{MeCN}]^2+\beta_3[\mathrm{MeCN}]^3}\right)\left[\mathrm{Cu^+}\right]_t \qquad (2.35)$$

$$\left[\mathrm{Cu(MeCN)_2^+}\right]=\left(\frac{\beta_2[\mathrm{MeCN}]^2}{1+\beta_1[\mathrm{MeCN}]+\beta_2[\mathrm{MeCN}]^2+\beta_3[\mathrm{MeCN}]^3}\right)\left[\mathrm{Cu^+}\right]_t \qquad (2.36)$$

$$\left[\mathrm{Cu(MeCN)_3^+}\right]=\left(\frac{\beta_3[\mathrm{MeCN}]^3}{1+\beta_1[\mathrm{MeCN}]+\beta_2[\mathrm{MeCN}]^2+\beta_3[\mathrm{MeCN}]^3}\right)\left[\mathrm{Cu^+}\right]_t \qquad (2.37)$$

Substitution of the copper(I) species (eqs. 2.34-37) into eq. 2.32, factoring out like terms, gives the rate of disappearance of cobalt(III) as eq. 2.38.

$$\frac{-d\left[\mathrm{Co^{III}}\right]}{dt}=\underbrace{\left(\frac{k_0+k_1\beta_1[\mathrm{MeCN}]+k_2\beta_2[\mathrm{MeCN}]^2+k_3\beta_3[\mathrm{MeCN}]^3}{1+\beta_1[\mathrm{MeCN}]+\beta_2[\mathrm{MeCN}]^2+\beta_3[\mathrm{MeCN}]^3}\right)}_{k_{\mathrm{obsd}}}\left[\mathrm{Cu^+}\right]_t\left[\mathrm{Co^{III}}\right] \qquad (2.38)$$

Where k_{obsd}, is the second-order rate constant for a particular run since the acetonitrile concentration was in large excess over the total copper(I) concentration.

$$k_{\mathrm{obsd}}=\left(\frac{k_0+k_1\beta_1[\mathrm{MeCN}]+k_2\beta_2[\mathrm{MeCN}]^2+k_3\beta_3[\mathrm{MeCN}]^3}{1+\beta_1[\mathrm{MeCN}]+\beta_2[\mathrm{MeCN}]^2+\beta_3[\mathrm{MeCN}]^3}\right) \qquad (2.39)$$

In principle the variation of k_{obsd} with [MeCN] can be fitted to eq. 2.39 to obtain k_n and β_n values (n = 1 to 3), with k_0 known as described above. However the large number of variables (k_n and β_n) that might be used to fit the observations presents a problem. Therefore it is useful to proceed with a qualitative examination of the data in order to determine which terms are probably significant.

If one assumes that only k_0 is significant in the numerator, then eq. 2.39 can be rearranged to give eq. 2.40.

$$\left(\frac{k_0}{k_{\text{obsd}}}-1\right)[\text{MeCN}]^{-1}=\beta_1+\beta_2[\text{MeCN}]+\beta_3[\text{MeCN}]^2 \qquad (2.40)$$

Then the left-hand-side can be plotted versus [MeCN]. Such a plot would be linear if the $\beta_3[\text{MeCN}]^2$ term is negligible and would have an intercept and slope of β_1 and β_2.

This plot is shown in Figure 2.3 for [MeCN] < 0.25 M and is linear as expected if the above assumption is realistic. However, if the plot is extended to higher [MeCN], as in Figure 2.4, then it is clear that the neglect of $\beta_3[\text{MeCN}]^2$ is not justified. As the [MeCN] increases, the data show increasingly positive deviation from the line predicted for [MeCN] < 0.25 M (Figure 2.4). If one does a least-squares fit of the data including β_1, β_2 and β_3, and assuming that only k_0 is important, then one obtains the dashed curve shown in Figure 2.4. This provides an adequate fit of the data for concentrations up to [MeCN] ~ 1.0 M, but higher concentrations show a significant negative deviation of the data from the curve. In other words, the data for [MeCN] > 1.5 M are not adequately fitted, and the nature of the deviation would not be improved by adding a β_4 term to the model.

The negative deviation from the curve in Figure 2.4 can be explained by the assumption that at least one of the copper(I)-acetonitrile complexes is kinetically active. A species distribution diagram, generated with approximate β values from the above analysis indicates that Cu(MeCN)_2^+ and Cu(MeCN)_3^+ are the dominant species for [MeCN] in the 1 to 2 M range. Therefore it seems reasonable to include the

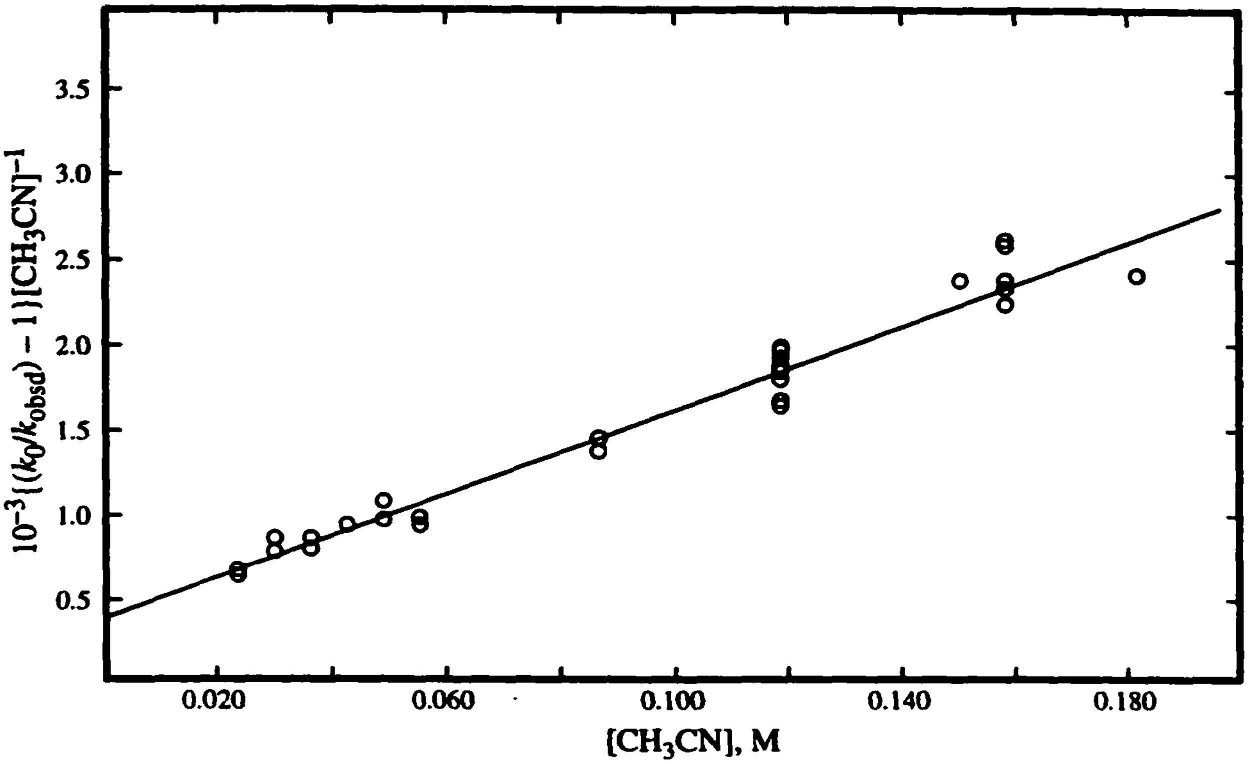

Figure 2.3. A plot of $\{(k_0/k_{obsd}) - 1\}[CH_3CN]^{-1}$ versus the acetonitrile concentration for the reduction of $[(NH_3)_5CoN_3]^{2+}$ by copper(I) in water-acetonitrile solutions. Monitored at 516 nm, in 3.33×10^{-2} M $HClO_4$ and 1.09×10^{-1} M $NaClO_4$.

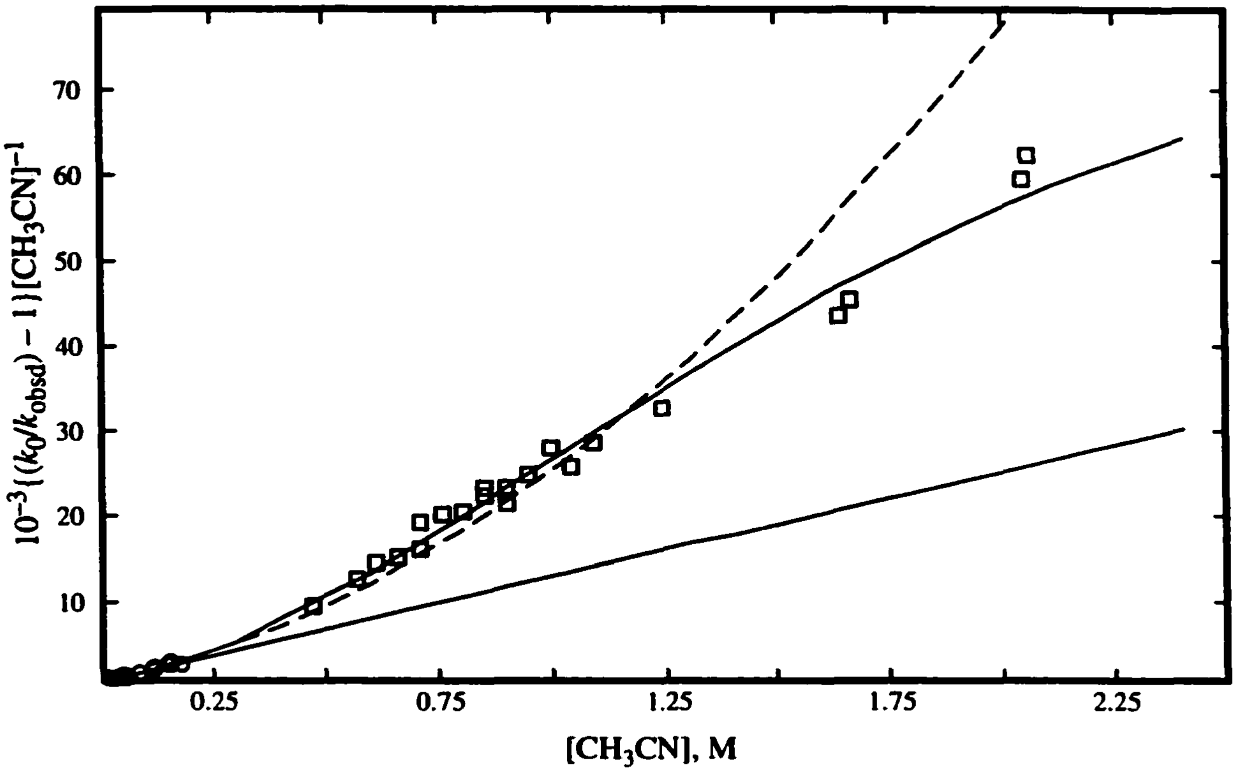

Figure 2.4. Plots of $\{(k_0/k_{obsd})-1\}[CH_3CN]^{-1}$ versus the acetonitrile concentration for the reduction of $[(NH_3)_5CoN_3]^{2+}$ (O) and $[(NH_3)_5CoBr]^{2+}$ (□) by copper(I) in water-acetonitrile solutions, in 3.33×10^{-2} M $HClO_4$ and 1.09×10^{-1} M $NaClO_4$. Calculated curves based on: Eq. 2.40 (___ linear); Eq. 2.39 (----) with k_0 as the only term in the numerator and the β_1, β_2 and β_3 terms in the denominator; Eq. 2.39 (___ curved) with k_0 and k_2 terms in the numerator and the β_1, β_2 and β_3 terms in the denominator.

$k_2\beta_2[\mathrm{MeCN}]^2$ term in the kinetic description of the system. If this is done, then the standard error of the fit is improved by a factor of ~2, and the data at high [MeCN] are adequately fitted, as shown by the solid curve in Figure 2.4.

K_i and k_i values obtained by a least-squares program using the k_0 for the cobalt complexes and eq. 2.40 are given in Table 2.6. A β_1 value of $(4.30 \pm 0.54) \times 10^2$ M^{-1}, β_2 of $(1.03 \pm 0.14) \times 10^4$ M^{-2} and β_3 of $(2.12 \pm 0.29) \times 10^4$ M^{-3} have been adopted for the discussion in this study.

Discussion

The rate of reaction for the reduction of cobalt(III) by copper(I) in aqueous solution is dependent on the ionic strength and our values are compared to literature values in Table 2.7. Our average value for the azido is in reasonable agreement with values determined by Espenson and Parker[22] and Sisley and Jordan[28] at different ionic strengths. The bromo value is consistent with that of Espenson and Parker.[22] Our values at $\mu = 0.141$ M are smaller than those of Espenson and Parker[22] at $\mu = 0.20$ M, by factor of 0.946 and 0.904 for the azido and bromo complexes, respectively.

It is commonly observed that stepwise formation constants slowly decrease in the order $K_1 > K_2 > K_3 \ldots > K_n$ and a number of factors[34] can rationalize this trend. Table 2.8 lists some formation constants for ammonia and their K_i/K_{i+1} ratios for metal ions in the same area of the periodic table as copper. The ratios for a particular metal ion are in the same order of magnitude. This generality holds true if there are no electronic or coordination changes as the ligands are complexed by the metal ion. The small K_1/K_2 value for silver(I) and the much larger K_2/K_3 value for mercury(II) may be attributed to coordination changes; from tetrahedral $\mathrm{Ag(OH_2)_4^+}$ to linear $\mathrm{Ag(NH_3)_2^+}$ and linear $\mathrm{Hg(OH_2)_2^{2+}}$ to tetrahedral $\mathrm{Hg(NH_3)_4^{2+}}$.

Table 2.6. Calculated Formation Constants for the Complexation of Copper(I) by Acetonitrile from Fitting Data Obtained from the Kinetic Runs of the Azido and Bromo Complexes to Various Forms of eq. 2.39.

K_1	K_2	K_3	$k_1(N_3^-)$	$k_2(N_3^-)$	$k_2(Br^-)$
379	29.9	1.16	0	0	0
485	17.5	2.82	0	0.04	11.2
488	17.2	2.87	0	0	11.4
430	23.8	2.07	0	0.51	7.98
409	28.6	1.59	3.38	0	5.80

Table 2.7. Second-Order Rate Constants for the Reduction of the $[(NH_3)_5CoN_3]^{2+}$ and $[(NH_3)_5CoBr]^{2+}$ by Aqueous Copper(I) at Various Ionic Strengths at 25 °C.

Ionic Strength	k_0, $M^{-1}s^{-1}$	
M	Azido	Bromo
0.141[a]	1.42×10^3	4.04×10^5
0.20[b]	1.50×10^3	4.46×10^5
1.00[c]	2.60×10^3	

[a] This study in $HClO_4/NaClO_4$. [b] Parker, J. O.; Espenson, J. H. *J. Am. Chem. Soc.* **1968**, *91*, 1968 in $HClO_4/LiClO_4$. [c] Sisley, M. J.; Jordan, R. B. *J. Chem. Soc., Dalton Trans.* **1997**, 3883 in $HClO_4/LiClO_4$.

Table 2.8. Representative Formation Constants for Metal Ions with Ammonia and their K_i/K_{i+1} Ratios.[a]

Metal ion	K_1	K_2	K_3	K_4	K_1/K_2	K_2/K_3	K_3/K_4
Cu^+	8.5×10^5	4.47×10^4			**1.90**		
Ag^+	2.2×10^3	7.76×10^3			**0.28**		
Cu^{2+}	1.4×10^4	3.0×10^3	7.4×10^2	1.1×10^2	**4.67**	**4.05**	**6.73**
Ni^{2+}	6.0×10^2	1.9×10^2	4.5×10^1	2.0×10^1	**3.16**	**4.22**	**2.25**
Zn^{2+}	2.1×10^2	3.1×10^2	2×10^2	1.6×10^2	**0.68**	**1.55**	**1.25**
Cd^{2+}	5.2×10^2	1.5×10^2	2.6×10^1	1.15×10^1	**3.46**	**5.76**	**2.26**
Hg^{2+}	6.3×10^8	4.0×10^8	1.0×10^1	5.0	**1.57**	**4.00×10^7**	**2.00**

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[a] Martel, A. E.; Smith, R. M. *Critical Stability Constants: Other Organic Ligands*; Plenum Press: New York, 1977; Vol.3.

Values for the formation constants of copper(I) by acetonitrile in aqueous solutions determined in this study, as well as those by other workers, are given in Table 2.9. The values of successive formation constants decrease in the expected order. Although the K_i/K_{i+1}, ratios are somewhat larger than the ammonia examples in Table 2.8, the changes are not so dramatic as to indicate any coordination changes.

The largest difference between the present and previous work lies in the value of K_1. At least part of this discrepancy may be traced back to the β_2 value reported by Hemmerich and Sigwart[7] in 1963. These authors reported that the reduction potential, measured polarographically at a dropping mercury electrode, did not change significantly between 0.10 and 2.0 M acetonitrile. They assumed that this represented the bis complex and therefore reported a β_2 value. However, subsequent potentiometric studies by Cox et al.[3] indicate that the potential change should vary from 0.09 to 0.31 V over this concentration range.

Polarography utilizes the effect of the ligand on the reduction potential of a metal at a dropping mercury electrode in determining formation constants, eq. 2.41.

$$\Delta E = \left(E_{1/2}\right)_{\mathrm{M}} - \left(E_{1/2}\right)_{\mathrm{M-L}} = \frac{RT}{zF}\ln\left(1+\beta_1[\mathrm{Ligand}]+\beta_2[\mathrm{Ligand}]^2+....\beta_n[\mathrm{Ligand}]^n\right) \quad (2.41)$$

$\left(E_{1/2}\right)_{\mathrm{M}}$ is the half-wave potential of the free metal ion, $\left(E_{1/2}\right)_{\mathrm{M-L}}$ is the half-wave potential of the metal-ligand complex, β_n is the overall formation constant of $[\mathrm{M(Ligand)}_n]$ and R, T and z have their usual meaning in the Nernst equation. ΔE values calculated using Hemmerich and Sigwart's[7] β_2 value are not in agreement with Cox's[3] ΔE values for the same acetonitrile concentrations.

There is also a problem with their assumption that only the bis complex is present between 0.1 and 2.0 M acetonitrile. A species distribution diagram, Figure 2.5, based on

Table 2.9. Comparison of K_1, β_2, and β_3 Values from Other Studies on Copper(I)-Acetonitrile in Aqueous Medium.

$10^{-3}\beta_1/K_1$	$10^{-3}\beta_2$	K_2	$10^{-3}\beta_3$	K_3	Method[a]
--	22.0		--		Pol.[b]
--	7.90		13.0	1.65	Pol.[c]
1.89	22.0	11.6			Kin.[d]
			24.0	1.10	Pol.[e]
			34-45		Kin.[f]
0.430	10.2	23.8	21.2	2.07	Kin.[g]

[a] Pol. is polarography and Kin. is kinetic study. [b] Hemmerich, P.; Sigwart, C. *Experientia* **1963**, *19*, 488. 0.1 - 2.0 M in MeCN. [c] Manahan, S. E.; Iwamoto, T. R. *J. Electroanal. Chem.* **1967**, *14*, 213. 0.001 - 1.00 M in MeCN, μ = 0.01 M, at 25 °C. [d] Gunter, A.; Zuberbuhler, A. *Chimia* **1970**, *24*, 340. 0.01 - 0.13 M in MeCN, ~ 10^{-6} M in Cu(I), μ = 0.2 M $NaNO_3$, 20 °C. [e] Zuberbuhler, A. *Helv. Chim. Acta* **1970**, *53*, 473. 0.19 - 1.22 M in MeCN, (0.13 - 3.2) × 10^{-3} M in Cu(I) μ = 0.2, at 20 °C. [f] Mi, L.; Zuberbuhler, A. *Helv. Chim. Acta* **1991**, *74*, 1679. 0.14 - 1.1 M in MeCN, (8.8 - 54) × 10^{-5} M in Cu(I) μ = 0.5 M KNO_3, at 25 °C, pH 0.28 - 5.1. [g] This study. 0.02 - 2.04 M in MeCN, ~ 10^{-4} M in Cu(I) μ = 0.141 M $HClO_4/NaClO_4$, at ambient temperature.

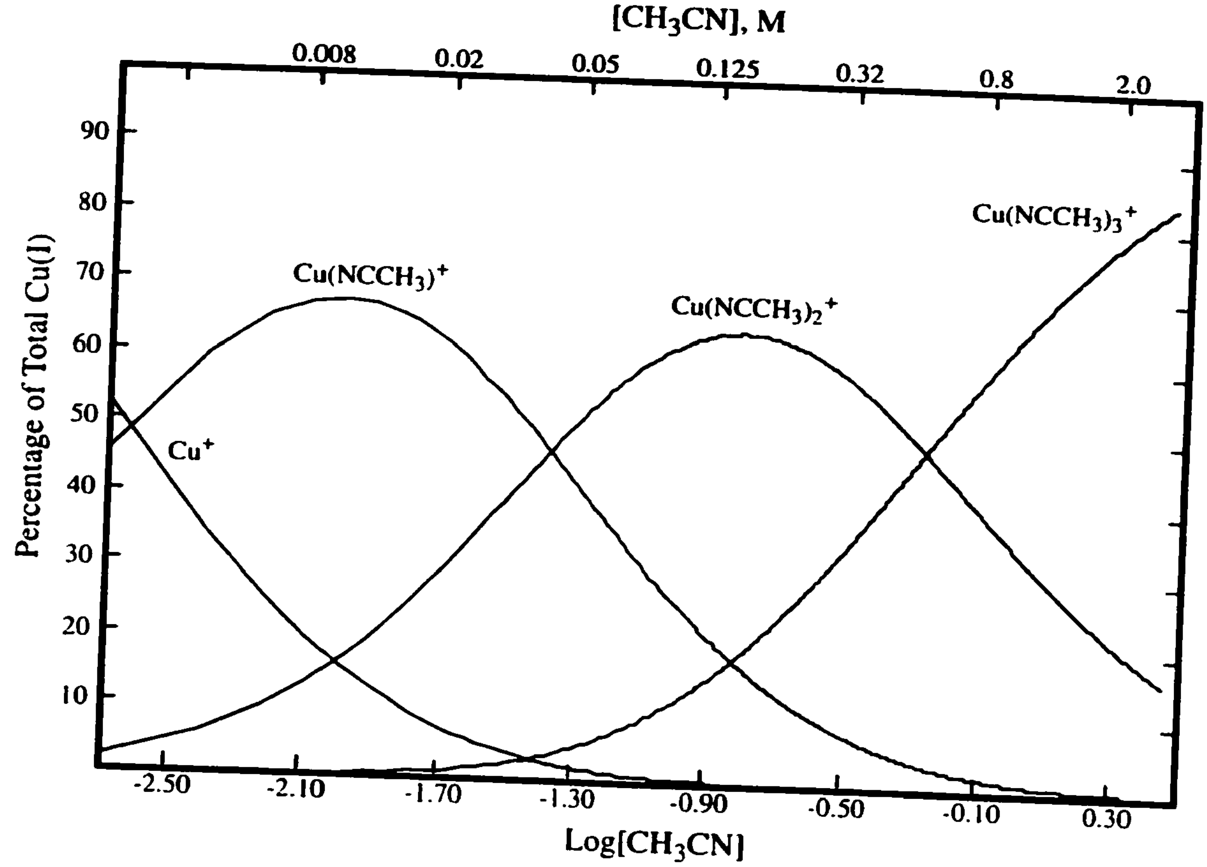

Figure 2.5. Speciation curves calculated from the formation constants from this work in Table 2.9.

the current β_i values, indicates that the bis complex is dominant at 0.1 M, but the tris complex is the major species at 2.0 M. Therefore the value of Hemmerich and Sigwart[7] is at best an estimate of some average of β_2 and β_3.

The β_2 value reported by Hemmerich and Sigwart[7] is best considered as an initial estimate from preliminary work. This would not be bad, except that Zuberbuhler and co-workers[20,21] took it as a fixed value in analyzing much of their kinetic work on the reaction of copper(I) with dioxygen. Thus the earlier value of β_2 was assumed as a fixed parameter in their kinetic determination of K_1 as given in Table 2.9. This assumption must skew the analysis used to determine K_1.

The value of β_3 determined polarographically by Zuberbuhler et al.[21a] is in reasonable agreement with the current work. However the more recent value from copper(I) and dioxygen kinetics[21b] is ~2 times larger. This may be due to higher ionic strength 0.5 M in KNO_3 compared to 0.2 M $NaNO_3$ in the earlier study.

The polarographic study of Manahan and Iwamoto[19] gives somewhat lower values than those found here. This may be again due to the ionic strength difference of 0.01 M versus 0.141 M used here. This would be consistent with the higher β_3 found by Zuberbuhler et al.[21b] at 0.5 M.

The magnitude of the K_i values show that aqueous copper(I) is complexed moderately strongly by acetonitrile. This is unusual because acetonitrile is usually considered as a weakly coordinating ligand. This probably is reflected in the fact that K_i values for acetonitrile in water are known only for silver(I) and copper(I). Normally weak complexation also is reflected in general measures of Lewis basicity such as Gutmann Donor Numbers; this value is 14.1 for acetonitrile, is smaller than dioxane (14.8), acetone (17) or methanol (19.1).

Complexation by copper(I) is often thought to be analogous to that of silver(I). Both are unipositive ions and with a filled nd^{10} electronic configuration so that there are no classical ligand field stabilization effects. With regard to acetonitrile coordination, both form tetrahedral $M(NCCH_3)_4^+$ ions, whose salts have been structurally characterized. For silver(I), only K_1 (2.63 M^{-1}) and K_2 (2.29 M^{-1}) values have been determined and they are smaller than those for copper(I) by factors of ~150 and 10, respectively. Thus silver(I) is rather weakly complexed by acetonitrile, but it should be noted that there is a similar difference for the complexation of ammonia by these two metal ions.

The difference in K_i values between copper(I) and silver(I) can be rationalized on several grounds. If the interaction is dominated by electrostatic ion-dipole forces, then the smaller copper(I) ion should give the stronger interaction. If acetonitrile is viewed as a hard base, then the expected increasing softness as one goes down a group also would predict a stronger interaction with the harder copper(I) ion.

However, the common rationalization of π-back-bonding does not seem to explain the observations. One might expect the 4d electrons of silver(I) to be more willing to donate to the π* orbital of acetonitrile than the 3d electrons of copper(I). The fact that complexation by ammonia, which cannot be a π-acid, shows features parallel to those of acetonitrile also argues against back-bonding as a major influence in the interaction of these ions with acetonitrile.

The method developed here is quite versatile because the reactivity of the scavenger can be adjusted to optimize the experiments depending on the β values for the copper(I)-ligand system. This is illustrated in Figure 2.6 for a range of k_0 and β_1 values. The range of k_{obsd} values plotted is typical of those in this work (2 - 90 $M^{-1}s^{-1}$) and provide a convenient experimental time for typical concentration of copper(I) and scavenger.

The plot with $k_0 = 2 \times 10^3$ $M^{-1}s^{-1}$ and $\beta_1 = 1 \times 10^3$ M^{-1} is representative of many of the systems studied here. When β_1 is increased to 5×10^3 M^{-1}, the useful concentration range is greatly reduced, as is shown by the lowest curve in Figure 2.6. But this can be overcome by choosing a more reactive scavenger, such as one with $k_0 = 2 \times 10^4$ $M^{-1}s^{-1}$, as shown in the Figure. If $\beta_1 = 2.5 \times 10^4$ M^{-1}, then a $k_0 = 4 \times 10^5$ $M^{-1}s^{-1}$ would be more

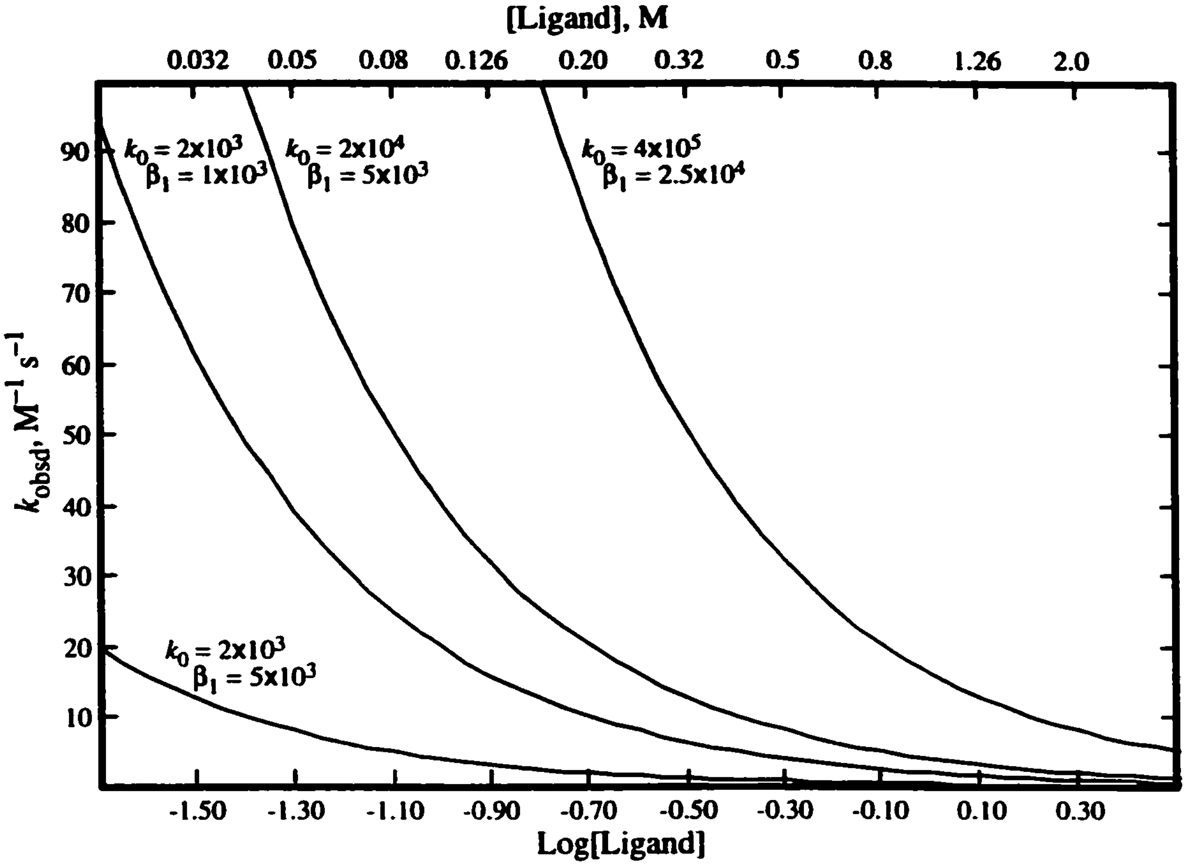

Figure 2.6. Calculated variation of k_{obsd} with ligand concentration for various k_0 and β_1 values.

suitable, as shown by the upper curve in Figure 2.6. Of course a wider range of ligand concentration can be studied if two scavengers are used, as was done here in the copper(I)-acetonitrile system.

Due to the second-order reaction conditions, the method developed here is limited to scavengers with high enough extinction coefficient values for one to obtain reasonable absorbances at low ($<10^{-3}$ M) scavenger concentrations. The method is limited to copper(I)-ligand systems that do not form precipitates in aqueous solutions and also to ligands that are soluble in aqueous solutions in the concentration range and reaction conditions that are of interest. The method is limited to systems where there is no reaction between cobalt(III) and the ligand. Complexation of the ligand by cobalt(II) or copper(II) can complicate the analysis by changing the free ligand concentration if the latter is not in large excess over the metal ions. This analysis would be more restricted if the copper(I)-ligand complex(es) absorb significantly relative to the scavenger at the monitoring wavelength. Then the total absorbance change will not give the copper(I) concentration.

Conclusion. Formation constants for copper(I) by acetonitrile in aqueous media have thus been redetermined using a simple method which is time and cost effective. This method was extended to a different aqueous copper(I) complexation system, namely the redetermination of formation constants for copper(I) by unsaturated dicarboxylic acids and their derivatives. These findings are discussed in the next chapter.

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Chapter 3. A Kinetic Determination of the Formation Constants of Copper(I) by Unsaturated Dicarboxylic Acids and Their Derivatives In Aqueous Media

Introduction

Although copper(I) is not stable in aqueous solution, it complexes strongly with olefins, eq. 3.1, and relatively stable solutions of these complexes can be prepared under anaerobic conditions.[1-4]

$$\mathrm{Cu^{+}_{(aq)} + (RR'C = CRR')_{(aq)} \rightleftharpoons Cu(RR'C = CRR')^{+}_{(aq)}} \qquad (3.1)$$

There are different methods[1-4] available for the preparation of copper(I)-olefin complexes in eq. 3.1. The copper(I)-olefin complexes were first prepared by saturating aqueous solutions of the olefins with copper(I) chloride.[1a-d] In general, copper(I)-olefin complexes have been prepared by deoxygenating aqueous copper(II)/olefin solutions in contact with copper metal[2c,3,5] or by introducing copper(I) into an aqueous olefin solution,[3,5] the copper(I) in this case being prepared via the chromous[6-8] reduction method, as described in Chapter 2, or via comproportionation of tetramminecopper(II) with copper metal.[2a] A less common method is the radiolysis of deoxygenated copper(II)/olefin solutions.[2b,4]

Crystal structures of several salts of copper(I) complexed to an unsaturated carbon-carbon bond have been determined.[9] It is commonly observed that the copper(I) binds with nearly equivalent distances to the olefinic carbon atoms and the copper(I) to carbon distances are about 2.0 Å.[9] In copper(I)-fumarate,[9a] $\mathrm{Cu_2(O_2CCH{=}CHCO_2)}$, these distances are 2.039 and 2.057 Å. Mostly, the carbon-carbon double bond in these copper(I)-olefin complexes is only slightly longer than that in uncomplexed ligands (1.348 Å).[10,11] The lengthening of the carbon-carbon double bond is typical for this class of ligands when η^2-bonded to low-valent, electron-rich transition metals,[9a,12] but a 1.488 Å[9a] distance reported for copper(I)-fumarate is unusual. The conventional explanation[13,14] of the bonding in metal-olefin complexes suggests that a sigma bond is formed by the donation of the pair of electrons in the π orbital on the olefin to an empty hybrid orbital on the metal. This is complemented by back-donation of the electron density from a filled hybrid orbital on the metal to the initially empty π^* orbital on the olefin, as shown in Figure 3.1. For a copper(I)-olefin complex, the metal orbitals most involved in bonding will be the 4s σ-acceptor and the 3d π-donor orbitals. No general agreement exists on the relative importance of the σ-bonding and π-back-bonding.

Experimental evidence has been used to suggest the significance of σ-bonding and π-back-bonding. Kochi et al.[15] inferred from ^{13}C and ^{1}H NMR shift data that the relative contributions of σ-bonding and π-back-bonding depends on the olefin involved. For complexes of the type Cu(polyolefin)$_n$OTf (OTf = $CF_3SO_3^-$ = triflate; polyolefin = 1,5-cyclooctadiene, 1,3,5,7-cyclooctatetraene, norbornadiene or 1,5,9- cyclododecatriene) deshielding was found for the sp^2 carbons and the olefinic protons, indicating predominant σ-donation. Complexes of CuOTf with monoolefins (e.g. norbornene, cyclooctene) exhibited the reverse trend, which was taken as evidence for predominant π-back-donation. An infrared spectrum of $CuCl(C_2H_4)$ has been interpreted as indicating significant π-back-bonding.[16]

Theoretical calculations on copper(I)-ethylene have been equivocal on the relative importance of σ-bonding and π-back-bonding. Using Hartree-Fock-Slater (HFS)[17] calculations, Ziegler et al.[18] concluded that π-back-bonding forms an important contribution to the total interaction energy. Later work,[19-21] using Restricted Hartree-Fock (RHF)[22] calculations indicated a negligible contribution of back-bonding. More recently

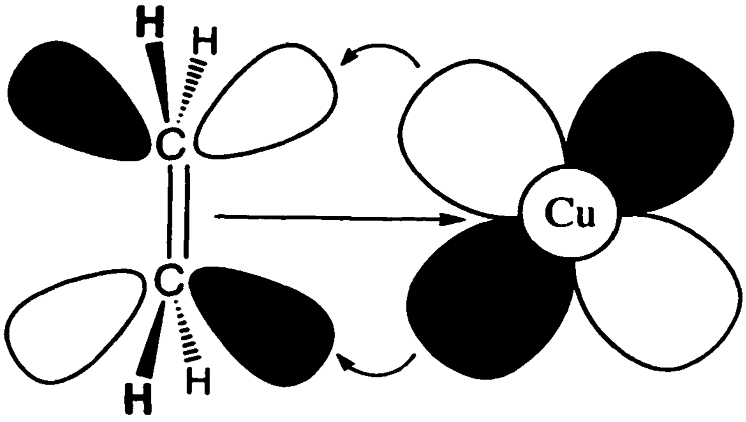


Figure 3.1. Conventional representation of the metal-alkene bond showing the alkene σ-donation and the metal π-back-donation.

an HFS calculation by Budzelaar et al.[23] found, in agreement with Ziegler et al.,[18] that π-back-bonding contributes about a third of the total interaction energy.

The chemistry of the organocopper species is of importance owing to their wide applications in organic chemistry.[24] Examples include copper(I) catalyzed acylation of terminal alkynes[24a], copper-mediated nucleophilic displacement reactions of 1-halo-alkynes[24b], and copper(I)-induced activation of dioxygen for the oxidation of organic substrates.[24c] The π-complexes of copper(I) occur as reaction intermediates in many of these organic reactions.[24] Meyerstein et al.[25] have reported the use of the copper(I)-fumaric acid complex to calculate copper(I) concentrations in aqueous solutions.

Previously, formation constants for copper(I) with olefins of carboxylic acids have been determined by Andrews et al.[1b,c] using the solubility method. Meyerstein et al.[25] determined these values by following the kinetics of the formation of copper(I) complexes with hydrogen -fumarate[2a,2b] and -maleate[2b] in pulse radiolysis studies and by cyclic voltammetry[2a] for fumaric and maleic acids and their monoprotonated and deprotonated forms. A more detailed review of these methods is given in Chapter 1.

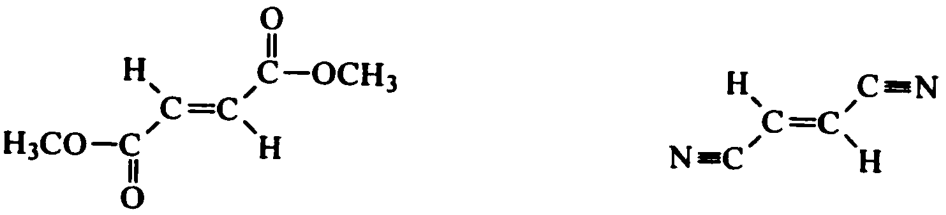
The kinetic method used for the copper(I)-acetonitrile system, described in Chapter 2, has been extended here to redetermine the formation constants of copper(I) with fumaric and maleic acids and to report for the first time the formation constants with dimethyl fumarate and fumaronitrile. The structures of the ligands are shown in Figure 3.2.

Experimental Section

Materials. Fumaric acid (Matheson Coleman and Bell), maleic acid (Eastman), dimethyl fumarate (Aldrich), nitric acid (Anachemia), sodium nitrate (ACP), copper nitrate trihydrate (Allied Chemical), benzene (Fisher Scientific), petroleum ether (35 - 60 °C, Mallinckrodt), and pre-purified argon (Praxair) were used as received.

Maleic Acid

Fumaric Acid



Dimethyl Fumarate

Fumaronitrile

Figure 3.2. Olefins used in this study.

Fumaronitrile (Fluka AG, Buchs SG) was purified by precipitation from hot benzene with petroleum ether.[26] Fumaronitrile (5g) was dissolved in 20 mL of hot benzene and the solution filtered into 50 mL of petroleum ether. A white suspension formed immediately and the petroleum ether was evaporated overnight, to leave a white crystalline powder, yield 2.7g. Anal. Calcd for $C_4H_2N_2$: C, 61.15; H, 2.582; N, 35.80. Found C, 61.66; H, 2.395; N, 36.09.

Preparation of solutions. Stock solutions of $HClO_4$ were prepared by diluting 70% $HClO_4$ and analyzed by titration with standard NaOH. Stock solutions of $NaClO_4$ were made by dissolving reagent grade solid and analyzed by titrating the H^+ produced by an aliquot passed through an anion exchange column in the H^+ form with standard NaOH. Stock solutions of nitric acid were prepared by pipetting the appropriate volume of concentrated acid (15.4 M), diluting to the mark in a volumetric flask and were analyzed by titration with standard NaOH. A stock solution of sodium nitrate was made by dissolving a weighed amount of the solid in doubly distilled water and diluting to volume in a volumetric flask. Stock solutions of fumaric acid, maleic acid, dimethyl fumarate and fumaronitrile were made similarly from weighed amounts of the solids. A stock solution of copper(II) nitrate, $Cu(NO_3)_2{\bullet}3H_2O$, was prepared by adding a weighed amount of the solid to a 500 mL volumetric flask and diluting to volume with doubly distilled water. Aliquots of the copper(II) solution were standardized by addition of excess potassium iodide and back titration with sodium thiosulfate.[27]

Stock solutions of the copper(I)-olefin complexes were prepared daily in doubly distilled water. Appropriate volumes of stock fumaric acid (4.00×10^{-2} M), maleic acid (2.00×10^{-1} M) or dimethyl fumarate (1.00×10^{-2} M) were made up to 25 or 50 mL in volumetric flask together with an appropriate volume of copper(II) nitrate (4.48×10^{-2} M). This solution was transferred into an Erlenmeyer flask containing copper foil, fitted with a serum cap and deoxygenated with pre-purified argon for about 2 hours. Within the first 10 minutes the solution turns to a yellow color that intensifies with time as more of the copper(I) complex is formed.

Copper(I)-fumaronitrile solutions (fumaronitrile stock concentration, 2.00 × 10^{-1} M) were made analogously to the other systems but were left overnight in an argon atmosphere because blank tests showed aliquots analyzed within a few hours had increasing copper(I) concentrations.

Aqueous solutions of the copper(I) complexes with fumaric acid, maleic acid, dimethyl fumarate and fumaronitrile were yellow in color, and their electronic spectra show absorption in the near uv region. The copper(I) complexes of fumaric and maleic acids show a maxima at 348 nm, and dimethyl fumarate at 359 nm. The copper(I) complex of fumaronitrile shows a shoulder between 300 and 310 nm. These absorption maxima for fumaric and maleic acids are in agreement with those reported by Andrews et al.[1a] and Meyerstein et al.[2a,b]

Stock solutions of pentaammineazidocobalt(III) nitrate, $[(NH_3)_5CoN_3](NO_3)_2$, were prepared by adding a weighed amount of the solid (see Chapter 2) to a volumetric flask and diluting to volume with doubly distilled water.

Preparations of the Solids: Cu(HOOCCHCHCOO). A solution containing 20 mL of 4.00 × 10^{-2} M fumaric acid and 5 mL of 4.48 × 10^{-2} M copper(II) nitrate was deoxygenated in contact with copper foil. After about 3 hours of deoxygenating, a fine yellow powder started to precipitate from the yellow solution and at this point the mixture was stored in a refrigerator overnight. The solution then was swirled and the yellow suspension decanted from the copper metal. The suspension was centrifuged and the clear solution decanted. This process was repeated two times with methanol. The damp, intensely yellow powder of copper(I)-fumarate was dried in the oven at 110 °C for 30 minutes. The dry powder is stable in air but damp powder turns greenish/blue with time. The yellow powder is insoluble in water but dissolves slowly in acidic solution. The product was formulated based on the elemental analysis. Anal. Calcd for $C_4H_3O_4Cu$: C, 26.90; H, 1.693; O, 35.83. Found C, 26.69; H, 1.543; O, 36.26.

$[Cu(NCCHCHCN)_{1.5}](ClO_4)$. A solution containing 20 mL of 2 × 10^{-1} M fumaronitrile and 5 mL of 8.96 × 10^{-3} M copper(II) nitrate in contact with copper metal was deoxygenated for ~ 6 hours. This solution was then mixed with 20 mL of deoxygenated 2.46 M sodium perchlorate solution. A whitish very fine suspension of copper(I)-fumaronitrile perchlorate formed instantaneously. This was separated from the copper foil by decanting the suspension and dried by vacuum filtration on a 0.22 μm filter paper. The product was formulated based on the elemental analysis. Anal. Calcd for $C_6H_3N_3O_4ClCu$: C, 25.70; H, 0.918; N, 15.00. Found C, 26.02; H, 1.079; N, 14.90.

$[Cu(NCCHCHCN)_2](NO_3)$. Yellow crystalline needles of bis(fumaronitrile)-copper(I) nitrate were prepared by deoxygenating 30 mL of 2.00 × 10^{-1} M fumaronitrile, 10 mL of 1.39 × 10^{-1} M nitric acid and 10 mL of 4.48 × 10^{-2} M copper(II) nitrate in contact with copper metal. After about 5 hours the yellow solution was stored in a bucket of crushed ice in the refrigerator overnight. The clear solution was swirled and the crystals quickly decanted from the copper metal. The yellow crystals were air dried on a filter paper. The product was formulated based on the elemental analysis and is in agreement with X-ray crystallography data. Anal. Calcd for $C_8H_4N_5O_3Cu$: C, 34.04; H, 1.43; N, 24.80. Found C, 33.38; H, 1.179; N, 24.16.

Elemental Analyses. The carbon, hydrogen, nitrogen and oxygen contents were determined in the MicroAnalytical Service Laboratory in the Department of Chemistry, University of Alberta.

Kinetic Studies of Copper(I)-Olefin with Pentaamminеazidocobalt(III) Nitrate. The experiments were carried out with an excess of cobalt(III) over copper(I) so that the concentration of copper(I) could be determined from the change in absorbance of the cobalt(III) complex, as illustrated in Figure 2.2. The reaction vessel was a 50 mm cylindrical optical cell with a total volume of 12 mL. Appropriate volumes of the stock cobalt(III) solution, stock olefin solution and stock $HClO_4/NaClO_4$ ($HNO_3/NaNO_3$ for the fumaronitrile runs) to set the ionic strength at 1.41×10^{-1} M were deoxygenated in the serum-capped cell for about 10 minutes. The reaction then was started by introducing the appropriate volume of copper(I)-olefin via a 5 mL syringe. Immediately the cell was placed in the Cary spectrophotometer and the recording started. The change of absorbance was monitored at 516 nm where $[(NH_3)_5CoN_3]^{2+}$ has an absorption maximum. The reactant concentrations ranged from 1.93×10^{-4} to 1.34×10^{-3} M for cobalt(III), 6.67 $\times 10^{-3}$ to 1.24×10^{-1} M for fumaronitrile, 5.00×10^{-4} to 2.10×10^{-2} M for fumaric acid, 5.00×10^{-4} to 6.00×10^{-3} M for dimethyl fumarate, and 5.00×10^{-4} to 8.38×10^{-2} M for maleic acid.

The reactions were followed on a Cary 219 spectrophotometer at ambient temperature.

Kinetic Data Analysis of the Copper(I)-Olefin Systems. The absorbance-time data points were manually read from the chart paper and stored in a BASIC data file. The copper(I) concentration for each kinetic run was calculated from the absorbance change (Figure 2.2). This information along with the known cobalt(III) concentration also was stored in the data file. The data points were fitted to a second-order rate law by an iterative least-squares program, using eq. 2.23 with substitution from eq. 2.20 and 2.21 to give the variation of I with t in terms of k, t_d, I_b, I_0, ε_A and ε_C. As in the case of acetonitrile, the latter three quantities are known and the first three were determined by least-squares fitting. The program generated best-fit values of the second-order rate constant, the dead time, and the blank absorbance.

Results

Crystal Structure Determination for Bis(fumaronitrile)copper(I) Nitrate. Yellow crystals of bis(fumaronitrile)copper(I) nitrate were obtained by cooling of an aqueous solution of the compound as detailed in the Experimental section. A crystal measuring 0.46 × 0.06 × 0.06 mm was selected and mounted on a glass fiber with Silastic adhesive for data collection. Data were collected on a Bruker P4/RA/SMART 1000 CCD diffractometer[28] using Mo $K\alpha$ (λ = 0.71073 A) radiation at -80 °C. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 2852 reflections from data collection. This yielded the following unit cell information; a = 5.3667 (5) Å, b = 22.228 (2) Å, c = 8.8952 (8) Å, β = 98.7072° (16), V = 1048.90 (17) Å^3, Z = 4, ρ = 1.784 g cm^{-3} and μ = 2.086 mm^{-1}. The space group was determined to be *C2/c* (No. 15). The data were corrected for absorption through use of the *SADABS*[28] procedure. Complete data tables are given in Appendixes 3.1-3.7.

The structure of bis(fumaronitrile)copper(I) nitrate was solved using direct methods (*SHELXS-86*)[29] and refinement was completed using the program *SHELXL-93*.[30] Hydrogen atoms were assigned positions based on the geometries of their attached carbon atoms, and were given thermal parameters 20% greater than those of the attached carbons. One set of fumaronitrile ligand atoms was found to be disordered in a 55:45 occupancy ratio, as indicated in the list of atomic coordinates, Appendix 3.7. The final model refined to values of $R_1(F)$ = 0.0266 (for 960 data with $F_0^2 \geq 2\sigma(F_0^2)$) and $wR_2(F^2)$ = 0.0682 (for all 1075 independent data).

A perspective view of the local coordination environment of the copper(I) center of bis(fumaronitrile)copper(I) nitrate with the atom labeling scheme is shown in Figure 3.3. Each copper atom is surrounded by a distorted tetrahedron of four nitrogen atoms, while each fumaronitrile molecule is coordinated to two copper ions. Macrocyclic Cu_6(fumaronitrile)$_6$ rings extend in three dimensions, forming an open structure within which the free nitrate anions are packed, as shown in Figure 3.4. Other reported complexes[31,32] similar to bis(fumaronitrile)copper(I) nitrate also show these extended networks. The structures of bis(succinonitrile)copper(I) perchlorate[31] and bis-(glutaronitrile)copper(I) nitrate[32b] consist of infinite two dimensional sheets,

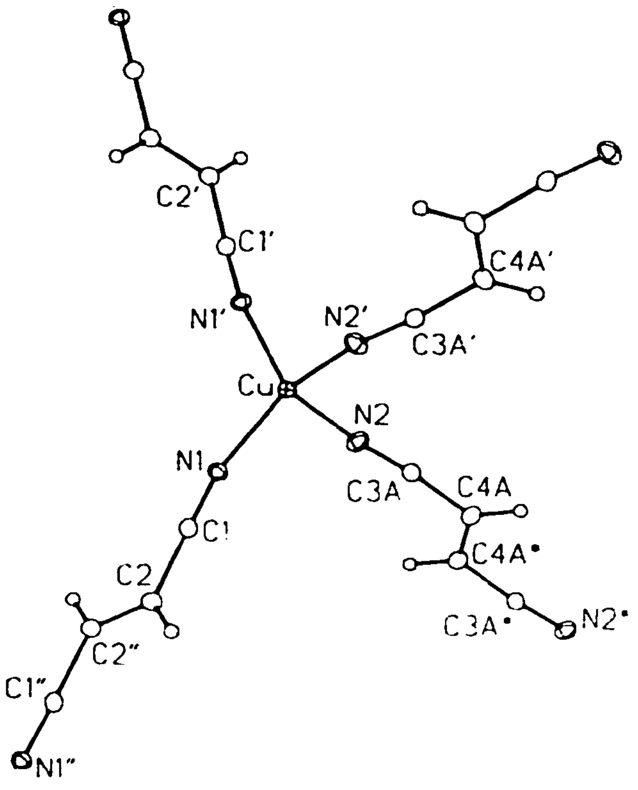


Figure 3.3. A perspective view of the local coordination environment of the copper(I) center of bis(fumaronitrile)copper(I) nitrate. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

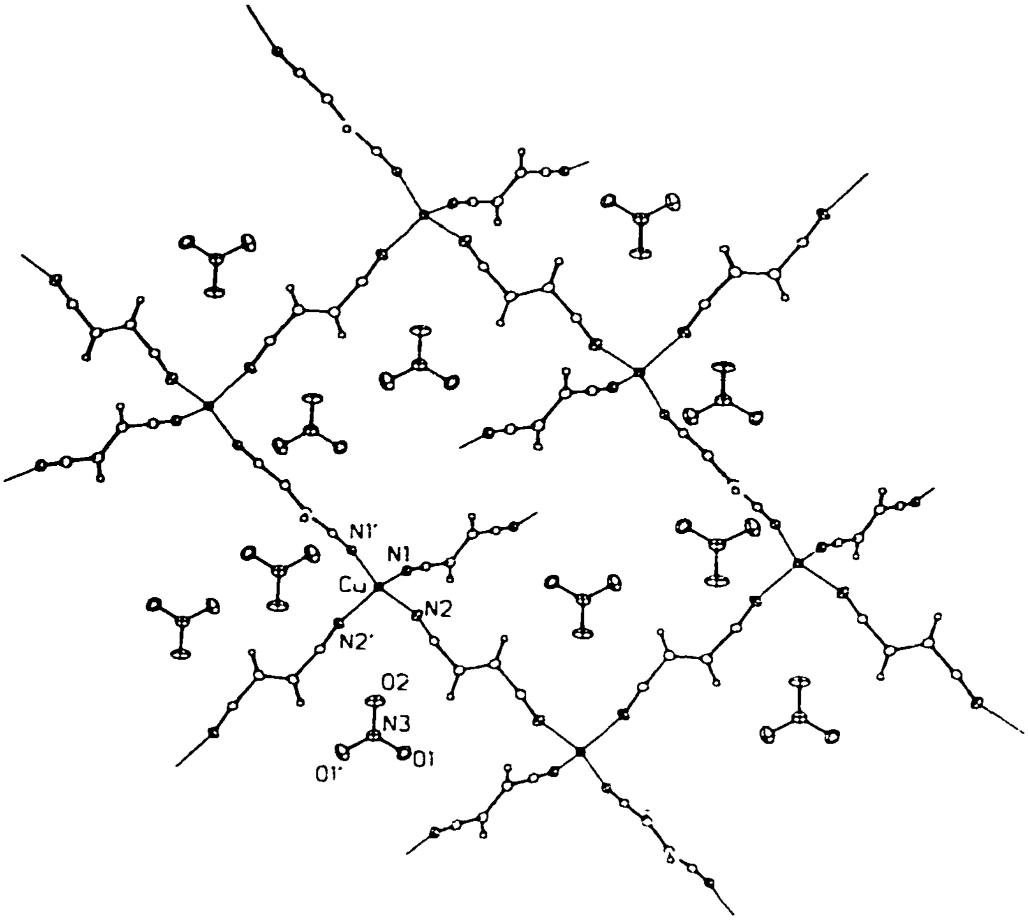


Figure 3.4. Illustration of the macrocyclic Cu_6(fumaronitrile)$_6$ unit upon which the extended structure is built. The Cu_6(fumaronitrile)$_6$ rings extend in three dimensions, forming an open structure within which the free nitrate anions are packed.

bis(succinonitrile)copper(I) nitrate[32a] has polymeric chains and bis(adiponitrile)copper(I) nitrate[32c] has an infinite three dimensional network. The nitrate or perchlorate anions are packed within spaces created in these extended network structures.

Some interatomic distances and angles for bis(fumaronitrile)copper(I) nitrate, together with values from similar copper(I) complexes, are presented in Table 3.1. In bis(fumaronitrile)copper(I) nitrate the $C \equiv N$ distances (1.138(3) - 1.165(8) Å) and the Cu-N distance (average 1.97 Å) are similar to those of the other[31-34] nitrile complexes of copper(I). The carbon-carbon double and single bond distances in bis(fumaronitrile)-copper(I) nitrate of 1.323 and 1.440 Å, respectively, are in the range found in similar complexes, and are similar to those in analogous uncomplexed ligands such as tetracyanoethylene[11a] or dichloro fumaronitrile.[11b]

The $N-Cu-N$ angles are distorted (103.8 - 118.9°) from a regular tetrahedron in bis(fumaronitrile)copper(I) nitrate, (Appendix 3.4) in comparison to tetrakis-(acetonitrile)copper(I) salts[34] which show an almost perfect tetrahedral geometry around the copper(I) centre. The $Cu-N \equiv C$ and the $N \equiv C-C$ angles in bis(fumaronitrile)-copper(I) nitrate are of similar magnitude to other reported values in Table 3.1.

Copper(I) complexes prepared in this study[35] as well as similar copper(I) complexes[31-33] are only moderately soluble in water. This property may be related to the fact that the copper atoms are bound in an infinite network. This may make them less susceptible to dissolution than monomeric complexes such as tetrakis(acetonitrile)-copper(I) complexes.[34] The later are useful starting materials in aqueous copper(I) chemistry.

The copper(I)-olefin complexes show some unusual and as yet unexplained variations in color. In the solid state, bis(fumaronitrile)copper(I) nitrate is yellow, but the perchlorate[35] salt complex is white. On the other hand, bis(succinonitrile)copper(I) nitrate[32a] is colorless, but the perchlorate[31] is pale grey-brown. Bis(adiponitrile)copper(I) nitrate[32c] is yellow like the fumaronitrile analogue. The fumarate,[9a] hydrogen -fumarate[1a]

Table 3.1. Selected Interatomic Distances and Angles of Copper(I) Complexes with Nitriles.

Compound	Bond	Bond lengths(Å)	Angle	Bond angles(°)
$[Cu(NC(CH)_2CN)_2]NO_3$[a]	Cu − N	1.964, 1.979	Cu − N ≡ C	168, 166
$[Cu(NC(CH)_2CN)_2]Cl$[b,c]		1.936		161
$[Cu(NC(CH)_2CN)_2]Cl$[b,d]		1.981		166
$[Cu(NC(CH_2)_2CN)_2]NO_3$[e]		1.96, 2.02		175, 177
$[Cu(NC(CH_2)_2CN)_2]ClO_4$[f]		1.99		170
$[Cu(NCCH_3)_4]ClO_4$[g]		1.99, 1.97		174
$[Cu(NC(CH)_2CN)_2]NO_3$[a]	N ≡ C	1.138, 1.164	N ≡ C − C	178
$[Cu(NC(CH)_2CN)_2]Cl$[b,c]		1.071		173
$[Cu(NC(CH)_2CN)_2]Cl$[b,d]		1.125		176.5
$[Cu(NC(CH_2)_2CN)_2]NO_3$[e]		1.14		175, 180
$[Cu(NC(CH_2)_2CN)_2]ClO_4$[f]		1.12		178
$(NC)_2(CH)_2(CN)_2$[h]		1.166		176
$NCCl(CH)_2ClCN$[i]		1.147		172
$[Cu(NC(CH)_2CN)_2]NO_3$[a]	C=C	1.323, 1.303		
$[Cu(NC(CH)_2CN)_2]Cl$[b,c]		1.282		
$[Cu(NC(CH)_2CN)_2]Cl$[b,d]		1.289		

Table 3.1. continued.

Compound	Bond	Bond lengths(Å)	Angle	Bond angles(°)
$(NC)_2(CH)_2(CN)_2$[h]		1.344		
$NCCl(CH)_2ClCN$[i]		1.350		
$Cu(NC(CH)_2CN)_2(NO_3)$[a]	C-C	1.429, 1.440		
$Cu(NC(CH)_2CN)_2Cl$[b,c]		1.513		
$Cu(NC(CH)_2CN)_2Cl$[b,d]		1.442		
$(NC)_2(CH)_2(CN)_2$[h]		1.438		
$NCCl(CH)_2ClCN$[i]		1.420		

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[a] This study. [b] Zavalii, P. Y.; Myskiv, M. G.; Fundamenskii, V. S. *Krystallografiya* **1984**, 2960: [c] Structure with an asymmetric bridging chloride. [d] Structure with symmetric bridging chloride. [e] Kinoshita, Y.; Matsubara, I.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 741. [f] Blount, J. F.; Freeman, H. C.; Hemmerich, P.; Sigwart, C. *Acta Cryst.* **1969**, *B25*, 1518. [f] Csoregh, I.; Kierkegaard, P.; Norrestam, R. *Acta Cryst.* **1975**, *B31*, 314. [h] Little, R. G.; Pautler, D.; Coppens, P. *Acta Cryst.* **1971**, *B27*, 1493. [i] Klewe, B.; Romming, C. *Acta Chem. Scand.* **1972**, *26*, 2272.

and -maleate[1a] solids also are yellow. In solution, the fumaronitrile complex is pale yellow, while the observations of Andrews et al.[1c] indicate that all the 1,2-dicarboxylic acid complexes are yellow, but all others are colorless. The color results from a band of moderate intensity that appears in the 270 - 360 nm region. All that can be said at this point is that the position of this band is dependent on the olefin, as might be expected, but also on the counter ion in the solid. Tetrakis(acetonitrile)copper(I) complexes[34] are colorless.

Formation Constants for Fumaronitrile with Copper(I). The kinetic results for the reaction of $[(NH_3)_5CoN_3]^{2+}$ with copper(I) in the presence of fumaronitrile are summarized in Table 3.2. The observations are consistent with the rate being first-order in cobalt(III) and copper(I) and independent of hydrogen ion concentration. The rate constant decreases smoothly as the fumaronitrile concentration is increased (see Table 3.2). The lack of hydrogen ion concentration dependence is expected because fumaronitrile lacks ionizable protons.

In order to analyze the dependence of the observed rate constants on the fumaronitrile concentration, a rate law for the system was derived based on the probable species present. The overall formation constants for copper(I) with fumaronitrile (L) are defined by eq. 3.2 and 3.3 for the mono and bis complexes, respectively.

$$\beta_1 = \frac{[\mathrm{CuL}]}{[\mathrm{Cu^+}][\mathrm{L}]} \tag{3.2}$$

$$\beta_2 = \frac{[\mathrm{CuL_2}]}{[\mathrm{Cu^+}][\mathrm{L}]^2} \tag{3.3}$$

Table 3.2. Second-Order Rate Constants for the Reduction of $[(NH_3)_5CoN_3](NO_3)_2$ by Copper(I) in Acidic Water-Fumaronitrile Solutions, Monitored at 516 nm.[a]

			k, $M^{-1}s^{-1}$	
$10^4[Co^{III}]$, M	$10^4[Cu^I]$, M	$10^3[L]$, M	Obsd.	Calc.
3.46	1.63	6.67[c]	247	210
3.41	0.906	6.67[b]	200	210
3.41	0.832	6.67	182	210
3.41	1.37	7.50	176	190
3.46	1.39	9.17[c]	166	159
3.41	1.17	9.17[b]	160	159
3.41	0.809	9.17	150	159
3.46	1.68	10.2[c]	156	145
3.46	3.06	13.3[c]	126	113
3.41	2.13	13.3	117	113
3.41	1.88	13.3	108	113
3.41	1.94	13.3[b]	104	113
3.41	1.75	13.3[b]	103	113
3.46	2.93	15.0[c]	94.7	101
3.46	2.97	16.6[c]	89.2	91.7
3.27	0.45	18.3[c]	83.3	82.2
3.60	0.69	20.0[c]	75.8	75.3
3.27	1.38	21.6[c]	72.4	69.8
3.46	3.28	25.8[c]	67.0	59.2
3.27	0.75	26.7[c]	67.6	56.4

Table 3.2. continued.

$10^4[Co^{III}]$, M	$10^4[Cu^I]$, M	$10^3[L]$, M	k, $M^{-1}s^{-1}$ Obsd.	Calc.
3.46	1.77	31.7[c]	53.4	48.0
3.41	1.06	31.7[b]	52.4	48.0
3.41	0.817	31.7	41.9	48.0
3.27	1.59	38.3[c]	38.5	38.8
3.27	1.96	45.0[c]	33.7	32.7
3.46	1.52	48.4[c]	28.2	30.6
3.60	1.22	61.7	21.3	23.2
6.57	4.00	70.0[b]	21.1	20.1
6.57	4.25	86.7[b]	15.6	15.8
6.57	4.68	103	13.1	12.9
6.57	4.75	103[c]	12.8	12.9
6.57	4.70	103[b]	12.5	12.9
3.46	1.83	124[c]	10.4	10.3
4.38	3.32	130[b]	9.86	9.75

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[a] The ionic strength is 1.41×10^{-1} M $HNO_3/NaNO_3$, and HNO_3 = 0.033 M unless otherwise indicated. [b] HNO_3 = 0.109 M. [c] HNO_3 = 0.141 M.

The derivation of the rate law is analogous to that followed in Chapter 2. The k_{obsd} then is given by eq. 3.4.

$$k_{obsd} = \frac{k_0 + k_1\beta_1[L] + k_2\beta_2[L]^2}{1 + \beta_1[L] + \beta_2[L]^2} \tag{3.4}$$

On the assumption that $k_0 >> k_1\beta_1[L] + k_2\beta_2[L]^2$ eq. 3.4 can be rearranged to eq. 3.5.

$$\frac{k_0}{k_{obsd}} - 1 = \beta_1[L] + \beta_2[L]^2 \tag{3.5}$$

Since k_0 is known (1.42×10^3 $M^{-1}s^{-1}$ for pentaamminеazidocobalt(III) nitrate, see Chapter 2) the left-hand-side of eq. 3.5 can be plotted versus the fumaronitrile concentration. If the $\beta_2[L]^2$ contribution is negligible then this plot would be linear with a slope of β_1. The plot, shown in Figure 3.5, shows upward curvature at the higher fumaronitrile concentrations and is consistent with a significant $\beta_2[L]^2$ contribution.

A non-linear least-squares program was used to fit the k_{obsd} values to eq. 3.5. The calculated rate constants are given in Table 3.2 and the best-fit curve is shown in Figure 3.5. The best-fit values of β_1 and β_2 are $(8.53 \pm 0.19) \times 10^2$ M^{-1} and $(2.00 \pm 0.39) \times 10^3$ M^{-2}, respectively. Least-squares fits to eq. 3.4 with the $k_1\beta_1[L]$ or $k_2\beta_2[L]^2$ terms retained did not improve the standard error of the fits.

Formation Constants for Fumaric Acid and Dimethyl Fumarate with Copper(I). Potentially fumaric acid might complex with copper(I) in the diprotonated, monoprotonated or deprotonated form(s). The first and second acid dissociation constants for fumaric acid are 1.45×10^{-3} M and 8.13×10^{-5} M, respectively.[36] These values indicate that very little of the acid is dissociated in the 0.033 and 0.109 M $HClO_4$

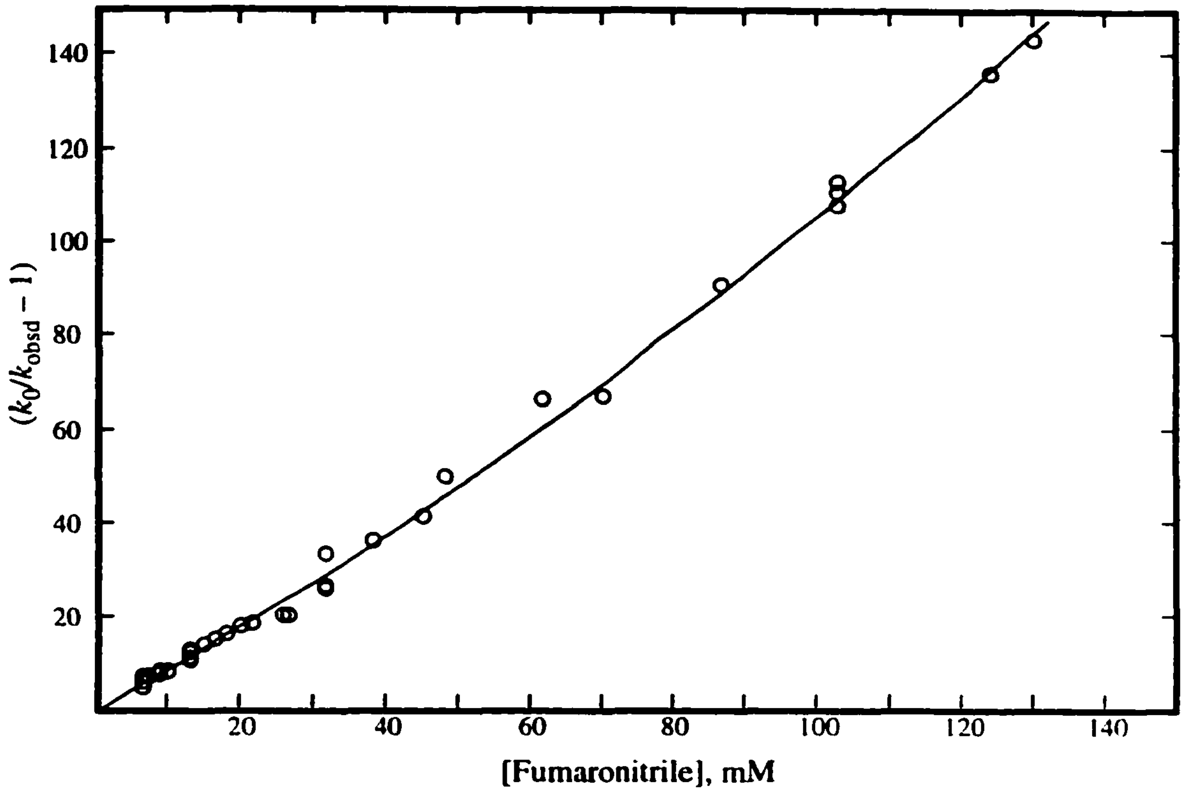

Figure 3.5. A plot of $(k_0/k_{obsd} - 1)$ versus the fumaronitrile concentration for the reduction of $[(NH_3)_5CoN_3](NO_3)_2$ by copper(I) in acidic water-fumaronitrile solutions.

solutions used in this study. In dimethyl fumarate there are no acidic protons. These two systems are considered together since the analysis is similar.

The kinetic results for the reaction of $[(NH_3)_5CoN_3]^{2+}$ with copper(I) in the presence of fumaric acid and dimethyl fumarate are summarized in Tables 3.3 and 3.4, respectively. The observations are consistent with the rate being first-order in cobalt(III) and copper(I) and independent of hydrogen ion concentration. The rate constant decreases smoothly as the fumaric acid and dimethyl fumarate concentrations are increased.

In order to analyze the dependence of the observed rate constants on the olefin (L) concentrations, a rate law for the system was derived based on the probable species present. The derivation of the rate law is analogous to that followed in the previous section with the assumptions that resulted in eq. 3.5, where L now is fumaric acid or dimethyl fumarate.

A plot of the left-hand-side of eq. 3.5 versus the olefin concentration should be linear with a slope of β_1 if the contribution of the $\beta_2[L]^2$ term is negligible. Such plots are linear, as shown in Figures 3.6 and 3.7. There is no hint of downward curvature that would indicate a $k_1\beta_1[L]$ term, nor of upward curvature that would indicate a $\beta_2[L]^2$ contribution. The least-squares best-fit values of β_1 for fumaric acid and dimethyl fumarate are $(7.34 \pm 0.15) \times 10^3$ M^{-1} and $(6.08 \pm 0.10) \times 10^3$ M^{-1}, respectively. The experimental and calculated values of k_{obsd} are given in Tables 3.3 and 3.4. From graphical simulations it is possible to estimate upper limits for K_2 of ≤ 5 and ≤ 20 M^{-1} for fumaric acid and dimethyl fumarate, respectively.

These β_1 values may be viewed as preliminary results since a closer look at Tables 3.3 and 3.4 reveals that the ligand concentrations are of the same magnitude as that of copper(I) for some experiments. If large amounts of the ligand are complexed, then the concentration of the free ligand would increase as the copper(I) complex is oxidized to copper(II) and free ligand. Then the k_{obsd} values would not be at a constant ligand concentration.

Table 3.3. **Second-Order Rate Constants for the Reduction of $[(NH_3)_5CoN_3](NO_3)_2$ by Copper(I) in Acidic Water-Fumaric Solutions, Monitored at 516 nm.**[a]

			k, $M^{-1}s^{-1}$	
$10^4[Co^{III}]$, M	$10^4[Cu^I]$, M	$10^4[L]$, M	Obsd.	Calc.
3.54	1.31	5.00[b]	271	300
1.93	1.75	8.33	238	199
3.54	2.21	10.0[b]	146	170
3.54	3.15	15.0[b]	121	119
3.54	2.96	20.0[b]	90.2	91.4
1.93	1.83	21.7	84.4	84.7
3.44	1.36	25.0[b]	67.5	74.2
3.22	1.34	25.0	62.8	74.2
3.22	1.70	33.0	59.1	57.0
3.44	3.12	33.3	57.0	56.5
3.44	3.05	33.3	54.7	56.5
3.54	2.43	43.3[b]	37.7	43.9
6.45	5.38	50.0	40.7	38.2
6.45	2.70	50.0	37.6	38.2
3.22	1.41	51.7	35.1	37.0
3.54	2.15	76.7[b]	22.9	25.2
3.22	1.55	78.3	24.8	24.7
3.22	1.87	100	21.2	19.4
3.22	1.16	105	22.3	18.5
13.4	0.97	125	15.8	15.6

Table 3.3. continued.

			k, $M^{-1}s^{-1}$	
$10^4[Co^{III}]$, M	$10^4[Cu^I]$, M	$10^4[L]$, M	Obsd.	Calc.
3.54	2.47	143[b]	13.6	13.6
13.4	11.3	186	10.7	10.5
5.16	4.15	203	11.0	9.64
3.54	2.44	210	9.30	9.32

[a] The ionic strength is 1.41 × 10^{-1} M $HClO_4/NaClO_4$, and $HClO_4$ = 0.033 M unless otherwise indicated. [b] $HClO_4$ = 0.109 M.

Table 3.4. Second-Order Rate Constants for the Reduction of $[(NH_3)_5CoN_3](NO_3)_2$ by Copper(I) in Acidic Water-Dimethyl Fumarate Solutions, Monitored at 516 nm.[a]

			k, $M^{-1}s^{-1}$	
$10^4[Co^{III}]$, M	$10^4[Cu^I]$, M	$10^4[L]$, M	Obsd.	Calc.
3.53	1.00	5.00	367	349
3.44	1.89	10.0[b]	193	203
3.34	0.598	13.3	166	159
3.53	1.75	15.0[b]	146	143
3.53	2.43	15.0	145	143
3.59	1.99	20.8	104	107
3.53	2.83	23.3	93.9	96.0
3.53	2.08	23.3[b]	89.8	96.0
3.44	2.55	31.7[b]	77.0	72.0
3.53	2.91	31.7	61.2	72.0
3.59	1.90	37.5	58.0	61.4
3.44	1.79	43.3[b]	52.4	53.6
3.53	3.28	48.3	51.4	48.2
3.44	1.64	51.7[b]	43.0	45.2
3.59	1.71	54.2	38.9	43.2
3.44	1.95	60.0	40.1	39.1

[a] The ionic strength is 1.41 × 10^{-1} M $HClO_4/NaClO_4$, and $HClO_4$ = 0.033 M unless otherwise indicated. [b] $HClO_4$ = 0.109 M.

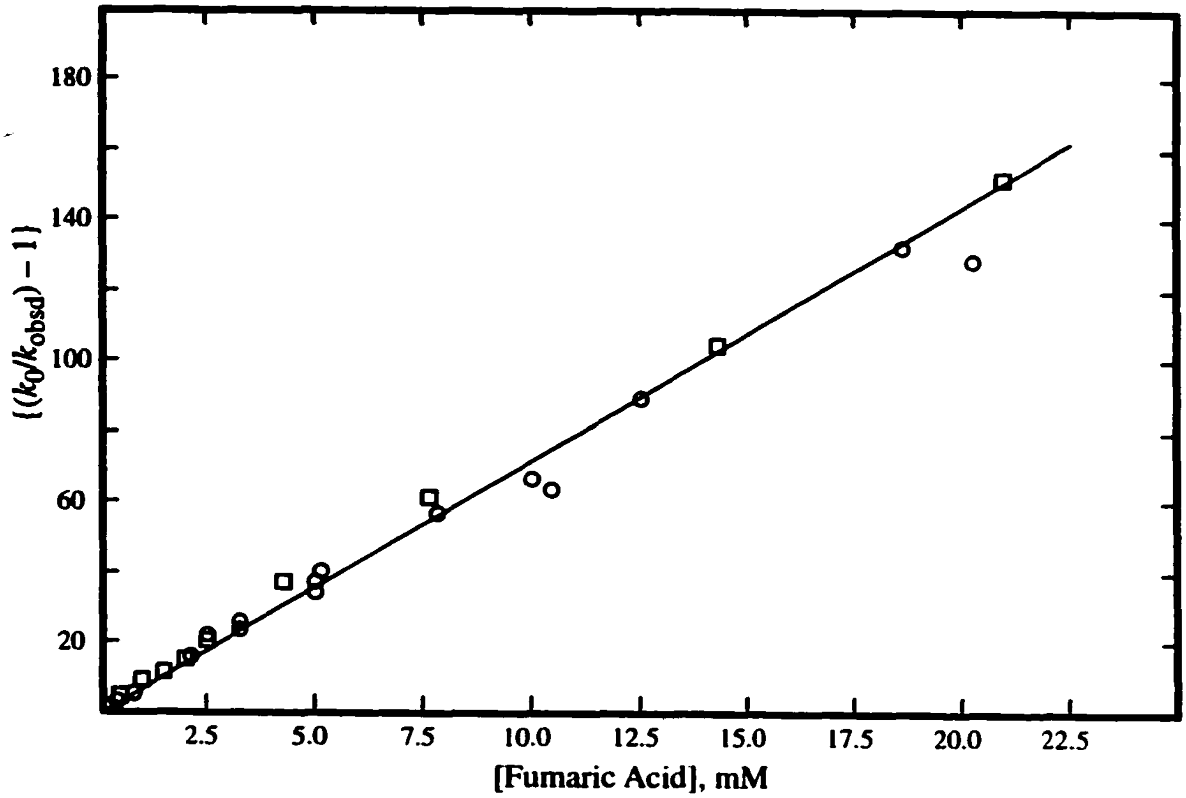

Figure 3.6. A plot of $(k_0/k_{obsd} - 1)$ versus the fumaric acid concentration for the reduction of $[(NH_3)_5CoN_3](NO_3)_2$ by copper(I) in acidic water-fumaric solutions: in 0.033 M (○) and 0.109 M (□) perchloric acid.

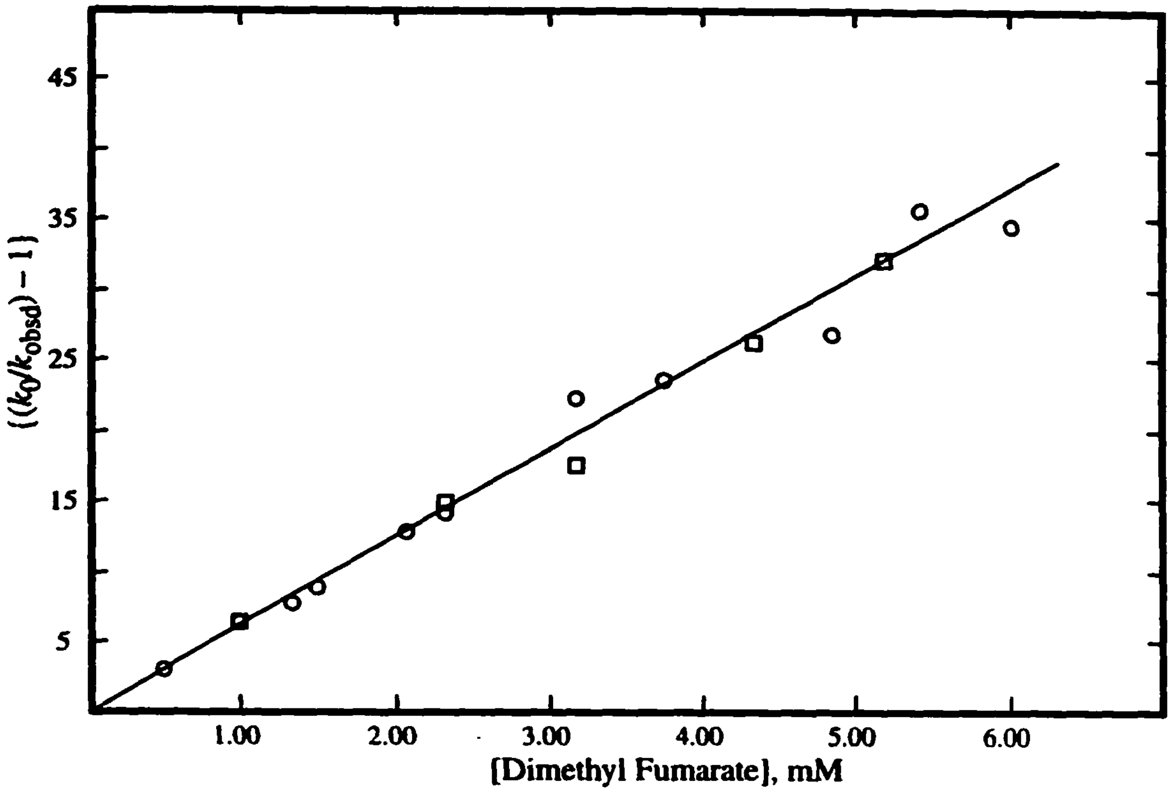

Figure 3.7. A plot of $(k_0/k_{\mathrm{obsd}} - 1)$ versus the dimethyl fumarate concentration for the reduction of $[(NH_3)_5CoN_3](NO_3)_2$ by copper(I) in acidic water-dimethyl fumarate solutions: in 0.033 M (○) and 0.109 M (□) perchloric acid.

In order to determine if the above factor is a significant complication, the free ligand concentration $[L]_f$ has been calculated at the time observation was started for runs with total ligand $[L]_0$ less than 10 times the total copper(I) concentration. These calculations were done using the expression for β_1 in eq. 3.6,

$$\beta_1 = \frac{[CuL^+]}{([Cu^+]_0 - [CuL^+])([L]_0 - [CuL^+])} \tag{3.6}$$

where $[CuL^+]$ is the complex concentration, $[Cu^+]_0$ is the concentration of copper(I) for the first absorbance recorded in the kinetic run, and β_1 values are known, at least to a first approximation, from the analysis described above. The equation can be rearranged to a quadratic form that can be solved for $[CuL^+]$, and the free ligand concentration can be obtained from $[L]_f = [L]_0 - [CuL^+]$.

The results given in Appendixes 3.8 and 3.9, show that > 87% of $[L]_0$ is present as $[L]_f$, so that the ligand concentration did not change appreciably during the kinetic run. Therefore, the fumaric acid and dimethyl fumarate concentrations can be taken to be constant and the k_{obsd} values are unaffected by these small changes in the ligand concentrations. Thus the β_1 values obtained using eq. 3.4 can be treated as the actual values and not as preliminary results.

Formation Constant for Maleic Acid with Copper(I). The kinetic results for the reaction of $[(NH_3)_5CoN_3]^{2+}$ with copper(I) in the presence of maleic acid are summarized in Tables 3.5. The observations are consistent with the rate being first-order in cobalt(III) and copper(I). The k_{obsd} is affected by changing the acidity from 0.033 to 0.109 M $HClO_4$ at constant maleic acid concentration, and is consistently higher at the higher acidity. The rate constant decreases smoothly at a given hydrogen ion concentration as the maleic acid concentration is increased.

Table 3.5. Second-Order Rate Constants for the Reduction of $[(NH_3)_5CoN_3](NO_3)_2$ by Copper(I) in Acidic Water-Maleic Solutions, Monitored at 516 nm.[a]

			k, $M^{-1}s^{-1}$	
$10^4[Co^{III}]$, M	$10^4[Cu^I]$, M	$10^4[H_2L]$, M	Obsd.	Calc.
3.32	1.39	5.00	310	295
3.32	1.62	5.00	314	295
3.62	2.13	5.00	288	295
3.62	2.21	5.00	279	295
3.62	2.16	5.00	260	295
3.32	1.75	10.0	172	166
3.62	2.63	10.0	162	166
3.62	2.43	10.0	154	166
3.32	1.51	10.0	151	166
3.62	2.06	10.0[b]	221	251
3.62	2.40	10.0[b]	258	251
3.62	2.25	13.3	129	129
3.62	2.55	13.3	146	129
4.02	2.68	21.7	85.5	83.2
3.32	1.83	55.0	37.8	35.6
3.32	1.62	55.0	39.9	35.6
4.02	2.50	55.0	32.7	35.6
4.02	2.63	88.3	22.5	23.4
3.62	1.91	88.3[b]	35.4	35.0
2.58	1.42	172	17.7	13.4

Table 3.5. continued.

			k, $M^{-1}s^{-1}$	
$10^4[Co^{III}]$, M	$10^4[Cu^I]$, M	$10^4[H_2L]$, M	Obsd.	Calc.
3.62	2.50	172[b]	19.1	18.9
2.58	2.12	338	9.05	8.04
2.58	2.50	505	7.36	6.14
4.05	2.75	505	6.25	6.14
3.62	2.55	505[b]	8.54	7.43
6.45	1.80	838	3.82	4.53
4.05	2.43	838	4.23	4.53

[a] The ionic strength is 1.41×10^{-1} M $HClO_4/NaClO_4$, and $HClO_4 = 0.033$ M unless otherwise indicated. [b] $HClO_4 = 0.109$ M.

The plot of $((k_0/k_{obsd}) - 1)$ versus maleic acid concentration, as described for fumaric acid and dimethyl fumarate systems, gives different slopes at low and high maleic acid concentrations (Figure 3.8). The results at low concentrations (< 10 mM maleic acid in 0.033 M H^+, upper line) give a higher slope (β_1) of ~7 × 10^3 M^{-1}, while those at higher maleic acid concentration in 0.109 M H^+ (lower line) have a lower slope of ~4 × 10^3 M^{-1}. Several possible explanations for this difference have been examined.

One possible complication is the complexation of copper(II) by maleate ion, since not all of the copper(II) is converted to copper(I). Maleate is a stronger complexing agent than fumarate because maleate can act as a bidentate chelate. Based on the total copper present and the amount of copper(I), one can estimate that the copper(II) concentration is $\leq 4.0 \times 10^{-4}$ M. Thus strong complexation by copper(II) could have a significant effect when the maleic acid concentration is $\leq 1.00 \times 10^{-3}$ M. The equilibrium constant for the complexation of copper(II) by maleate ion[36] is 2.60×10^3 M^{-1}. This value can be combined with the first and second dissociation constants[36] of maleic acid, 1.78×10^{-2} and 1.45×10^{-6} M, respectively, to obtain eq. 3.7,

$$\frac{[\mathrm{CuL}][\mathrm{H}^+]^2}{[\mathrm{Cu}^{2+}][\mathrm{H_2L}]} = 6.63 \times 10^{-5} \qquad (3.7)$$

where H_2L is maleic acid and L is the maleate dianion. With the relevant conditions of $H_2L = 1.00 \times 10^{-3}$ and $[H^+] = 0.033$ M, one can use eq. 3.7 to estimate that $[CuL]/[Cu^{2+}] \approx 6.1 \times 10^{-5}$. Therefore, if $[Cu^{2+}] \leq 4.00 \times 10^{-4}$ M, then $[CuL] \leq 2.5 \times 10^{-8}$ M and there is an insignificant amount of maleic acid tied-up as the copper(II) complex.

Another difference between maleic and fumaric acids is that intramolecular hydrogen bonding stabilizes the monoanion (HL^-) of maleic acid. This has the effect of making the first ionization constant of maleic acid (1.78×10^{-2} M) much larger than that

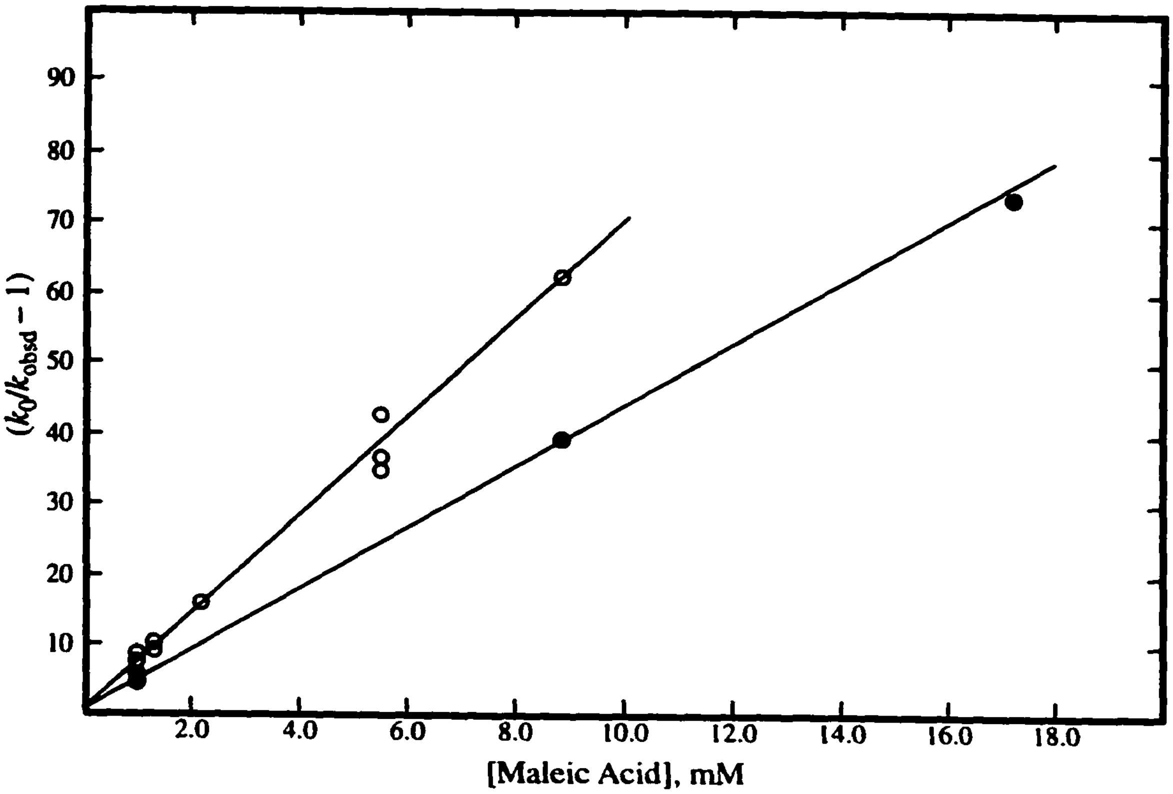

Figure 3.8 Plots of $(k_0/k_{obsd} - 1)$ versus maleic acid concentration for the reduction of $[(NH_3)_5CoN_3](NO_3)_2$ by copper(I) in acidic water-maleic solutions: in 0.033 M (○) and 0.109 M (●) perchloric acid.

of fumaric acid[36] (1.45×10^{-3} M). As a consequence, maleic acid exists as a mixture of the H_2L and HL^- forms, especially at the lower acidity (0.033M) of this study. A secondary consequence is that the acidity is actually higher than the nominal values, especially at the lower acidity and higher maleic acid concentrations. Then the dependence of the apparent formation constants on maleic acid concentration and acidity might be attributed to complexation of copper(I) by both the H_2L and HL^- forms of maleic acid.

Correction of the nominal acidity $[H^+]_0$ for that produced from ionization of maleic acid $[H^+]_i$ is straightforward, using the total maleic acid $[H_2L]_0$ and its first ionization constant.[36]

$$K_{a1} = \frac{[HL^-][H^+]}{[H_2L]} = \frac{[H^+]_i([H^+]_0 + [H^+]_i)}{[H_2L]_0 - [H^+]_i} = 1.78 \times 10^{-2}\,M \tag{3.8}$$

Eq. 3.8 can be rearranged to give a quadratic equation in $[H^+]_i$ that can be solved in the usual way. Then the final acidity is $[H^+]_f = [H^+]_0 + [H^+]_i$. The results indicate that this correction is only significant (> 5%) for $H_2L > 2.00 \times 10^{-3}$ M. This treatment has ignored the effect of complexation on the concentration and ionization of maleic acid. Sample calculations have shown that this is justified. This can be understood qualitatively because the maleic acid contribution to the acidity is significant only when its concentration is $> 2.00 \times 10^{-3}$ M and the copper(I) concentration is $\sim > 0.20 \times 10^{-3}$ M so that the amount of maleic acid complexed is $\leq$ 10% of the total.

The formation constants for the H_2L and HL^- complexes of copper(I) may be defined by eq. 3.9 and 3.10.

$$\beta_1 = \frac{\left[\mathrm{Cu(H_2L)^+}\right]}{\left[\mathrm{Cu^+}\right]\left[\mathrm{H_2L}\right]} \tag{3.9}$$

$$\beta_{12} = \frac{\left[\mathrm{Cu(HL)}\right]}{\left[\mathrm{Cu^+}\right]\left[\mathrm{HL^-}\right]} \tag{3.10}$$

The total copper(I) concentration at any time is given by eq. 3.11.

$$\left[\mathrm{Cu^+}\right]_T = \left[\mathrm{Cu^+}\right] + \left[\mathrm{Cu(H_2L)^+}\right] + \left[\mathrm{Cu(HL)}\right] \tag{3.11}$$

Substitution from the formation constant expressions gives eq. 3.12.

$$\left[\mathrm{Cu^+}\right]_T = \left[\mathrm{Cu^+}\right] + \beta_1\left[\mathrm{Cu^+}\right]\left[\mathrm{H_2L}\right] + \beta_{12}\left[\mathrm{Cu^+}\right]\left[\mathrm{HL^-}\right] \tag{3.12}$$

If the amount of ligand complexed is small relative to the total ligand, i.e. $[\mathrm{H_2L}]_0 >> [\mathrm{Cu(H_2L)^+}] + [\mathrm{Cu(HL)}]$, then

$$\left[\mathrm{H_2L}\right]_0 = \left[\mathrm{H_2L}\right] + \left[\mathrm{HL^-}\right] \tag{3.13}$$

and the expression for K_{a1} can be used to obtain eq. 3.14 and 3.15.

$$\left[\mathrm{HL^-}\right] = \frac{K_{a1}\left[\mathrm{H_2L}\right]_0}{K_{a1} + \left[\mathrm{H^+}\right]} \tag{3.14}$$

$$[\mathrm{H_2L}] = \frac{[\mathrm{H^+}][\mathrm{H_2L}]_0}{K_{a1} + [\mathrm{H^+}]} \tag{3.15}$$

Substitution into the expression of the free copper(I) and grouping terms gives eq. 3.16.

$$[\mathrm{Cu^+}]_T = [\mathrm{Cu^+}]\left\{1 + \left(\frac{\beta_1[\mathrm{H^+}] + \beta_{12}K_{a1}}{K_{a1} + [\mathrm{H^+}]}\right)[\mathrm{H_2L}]_0\right\} \tag{3.16}$$

Rearrangement gives the concentration of the free copper(I) in terms of the total copper(I) and ligand as eq. 3.17.

$$[\mathrm{Cu^+}] = \frac{[\mathrm{Cu^+}]_T}{1 + \left(\frac{\beta_1[\mathrm{H^+}] + \beta_{12}K_{a1}}{K_{a1} + [\mathrm{H^+}]}\right)[\mathrm{H_2L}]_0} \tag{3.17}$$

If the cobalt(III) complex is reduced only by free copper(I), then the rate is given by eq. 3.18.

$$-\frac{d[\mathrm{Co^{III}}]}{dt} = k_0[\mathrm{Cu^I}][\mathrm{Co^{III}}] = k_{obsd}[\mathrm{Cu^I}]_T[\mathrm{Co^{III}}] \tag{3.18}$$

Substitution for $[\mathrm{Cu^I}]$ from eq. 3.17 into eq. 3.18 shows that

$$k_{\mathrm{obsd}} = \frac{k_0}{1+\left(\frac{\beta_1[\mathrm{H^+}]+\beta_{12}K_{a1}}{K_{a1}+[\mathrm{H^+}]}\right)[\mathrm{H_2L}]_0}. \qquad (3.19)$$

This expression can be rearranged to a form analogous to that used for the other systems, and one obtains eq. 3.20.

$$\left(\frac{k_0}{k_{\mathrm{obsd}}}-1\right)\left(K_{a1}+[\mathrm{H^+}]\right)=\left(\beta_1[\mathrm{H^+}]+\beta_{12}K_{a1}\right)[\mathrm{H_2L}]_0 \qquad (3.20)$$

Unfortunately this does not lead to a simple plot because both $[\mathrm{H^+}]$ and $[\mathrm{H_2L}]_0$ are variables in eq. 3.20. However, it happens that a significant amount of the data are at $[\mathrm{H^+}]$ of ~0.035 ± 0.03 M and ~0.11 ± 0.006 M. Therefore, a plot of the left-hand-side of eq. 3.20 versus $[\mathrm{H_2L}]_0$ should be linear with a zero intercept and a larger slope for the higher-acidity set of data. The plots are linear with slopes of ~380 and ~560 based on visual inspection. These values give estimates for β_1 and β_{12} of 2.4×10^3 $\mathrm{M^{-1}}$ and 16.6×10^3 $\mathrm{M^{-1}}$ respectively.

The variation of k_{obsd} with $[\mathrm{H_2L}]_0$ was fitted to eq. 3.20 by least-squares and gave β_1 and β_{12} of $(2.16 \pm 0.60) \times 10^3$ $\mathrm{M^{-1}}$ and $(1.62 \pm 0.17) \times 10^4$ $\mathrm{M^{-1}}$, respectively. However, it was noted that this model did not provide a good fit for $[\mathrm{H_2L}]_0 > 3.00 \times 10^{-2}$ M, (Appendix 3.10). The calculated rate constants were persistently 20 - 30% smaller than the observed values for these 6 out of 27 data points.

This type of discrepancy might be ascribed to reduction by $\mathrm{Cu(H_2L)^+}$, as discussed in Chapter 2, but a model with this factor added did not improve the fit and typically led to a negative rate constant for this contribution. A consideration for the species present reveals that the extent of complexation is high for many data points even with $[\mathrm{H_2L}]_0 <$

3.00×10^{-2} M and the fit of these data is adversely affected by the addition of this new reduction pathway.

Species distribution using β_1 and β_{12} values obtained from least-squares fitting of the data with eq. 3.20 reveals that Cu(HL) is the dominant species. If Cu(HL) is acting as a reducing agent, with a specific rate constant of k_{12}, then the previous model in eq. 3.18 can be expanded to give eq. 3.21.

$$-\frac{d[\mathrm{Co^{II}}]}{dt} = k_0[\mathrm{Co^{III}}][\mathrm{Cu^{I}}] + k_{12}[\mathrm{Co^{III}}][\mathrm{Cu(HL)}] \qquad (3.21)$$

Substitution for [Cu(HL)] from eq. 3.10 into equation 3.21 and then substituting for [HL^-] and [Cu^I] from eqs. 3.14 and 3.17, respectively, one obtains the expanded version of eq. 3.19 as eq. 3.22.

$$k_{\mathrm{obsd}} = \frac{k_0 + k_{12}\beta_{12}K_{a1}[\mathrm{H_2L}]_0\left(K_{a1} + [\mathrm{H^+}]\right)^{-1}}{1 + \left(\frac{\beta_1[\mathrm{H^+}] + \beta_{12}K_{a1}}{K_{a1} + [\mathrm{H^+}]}\right)[\mathrm{H_2L}]_0} \qquad (3.22)$$

A least-squares fit to this model gives $\beta_1 = (2.68 \pm 0.43) \times 10^3$ M^{-1}, $\beta_{12} = (1.69 \pm 0.12) \times 10^4$ M^{-1} and $k_{12}\beta_{12}K_{a1} = (8.07 \pm 1.3) \times 10^2$, and adequately fits all of the data. The overall standard error of the fit is improved by 70% and the points at $[H_2L]_0 > 3.00 \times 10^{-2}$ M now are adequately fitted, Table 3.5. The value of $k_{12}\beta_{12}K_{a1}$ can be used to obtain k_{12} = 2.7 M^{-1} s^{-1}. This value seems reasonable since it is of the same magnitude as the values obtained for the bis(acetonitrile)copper(I) complex reacting with the azido and bromo complexes, 0.51 and 7.98 M^{-1} s^{-1}, respectively.

Another model that fits all of the data is based on the possibility of ion pairing between $[(NH_3)_5CoN_3]^{2+}$ and HL^-. This is the only system studied here in which the ligand is present in significant amounts as an anion. Previous work[37] on the ion-pairing of $[Co(en)_3]^{3+}$ with acetate ion gives an ion-pair formation constant of ~40 M^{-1} and differences in charge type and ionic strength indicate that this may reduce by a factor of ~ 6 for $[(NH_3)_5CoN_3]^{2+} + HL^-$ at $\mu = 0.1$ M, so that a value of ~7 M^{-1} is expected.[38]

The ion-pair formation constant (K_{ip}) is given by eq. 3.23.

$$K_{ip} = \frac{\left[(NH_3)_5CoN_3{}^{2+} \cdot HL^-\right]}{\left[(NH_3)_5CoN_3{}^{2+}\right]\left[HL^-\right]} \tag{3.23}$$

If the ion-pair reacts with copper(I) with a specific rate constant k_{ip}, then the overall rate of reaction is given by eq. 3.24,

$$-\frac{d\left[Co^{III}\right]}{dt} = k_0\left[Co^{III}\right]\left[Cu^I\right] + k_{ip}\left[Co^{III} \cdot HL^-\right]\left[Cu^I\right] \tag{3.24}$$

where Co^{III} is $[(NH_3)_5CoN_3]^{2+}$ and $Co^{III}{\bullet}HL$ is the ion-pair. The total cobalt(III) in the reaction mixture is given by eq. 3.25,

$$\left[Co^{III}\right]_T = \left[Co^{III}\right] + \left[Co^{III} \cdot HL^-\right] \tag{3.25}$$

and the individual cobalt(III) species in terms of the total cobalt(III) concentration can be worked out in an analogous way to that of the copper(I) species in Chapter 2. The overall rate of reaction is given by eq. 3.26.

$$-\frac{d[\mathrm{Co^{III}}]}{dt} = \left\{\frac{k_0 + k_{ip}K_{ip}[\mathrm{HL^-}]}{1 + K_{ip}[\mathrm{HL^-}]}\right\}[\mathrm{Co^{III}}]_T[\mathrm{Cu^I}] \tag{3.26}$$

If $K_{ip} \approx 7\ \mathrm{M^{-1}}$, then $1 > K_{ip}[\mathrm{HL^-}]$ in the denominator of eq. 3.26. Substituting for $[\mathrm{HL^-}]$ and $[\mathrm{Cu^I}]$ from eq. 3.14 and 3.17, respectively, into eq. 3.26, gives k_{obsd} as eq. 3.27.

$$k_{obsd} = \frac{k_0 + k_{ip}K_{ip}K_{a1}[\mathrm{H_2L}]_0\left(K_{a1} + [\mathrm{H^+}]\right)^{-1}}{1 + \left(\frac{\beta_1[\mathrm{H^+}] + \beta_{12}K_{a1}}{K_{a1} + [\mathrm{H^+}]}\right)[\mathrm{H_2L}]_0} \tag{3.27}$$

This expression is mathematically identical to eq. 3.22, so that it is not surprising that it gives an equivalent and adequate fit of the data. A least-squares fit to this model gives $\beta_1 = (2.68 \pm 0.43) \times 10^3\ \mathrm{M^{-1}}$, $\beta_{12} = (1.69 \pm 0.12) \times 10^4\ \mathrm{M^{-1}}$ and $k_{ip}K_{ip}K_{a1} = (8.07 \pm 1.3) \times 10^2$. If $K_{ip} \approx 7\ \mathrm{M^{-1}}$, then $k_{ip} \approx 7 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$. This value seems reasonable since it is of the same magnitude as the value obtained for aqueous copper(I) reacting with the azido complex of $1.42 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$.

Attempts to Evaluate the Formation Constants for Copper(I) with Benzoic Acid and p-Toluenesulfonic Acid Sodium Salt. A solution of benzoic acid (6.00×10^{-3} M) together with copper(II) nitrate (2.00×10^{-2} M) was deoxygenated in contact with copper metal for an hour, sealed and left overnight. 6 mL of this solution were mixed under argon atmosphere with 6 mL of 6.00×10^{-4} M $[(\mathrm{NH_3})_5\mathrm{CoN_3}]^{2+}$ in 6.00×10^{-3} M benzoic acid in a 5.0 cm spectrophotometric cell. The absorbance of $[(\mathrm{NH_3})_5\mathrm{CoN_3}]^{2+}$ at 516 nm showed no significant decrease other than that due to the copper(I) from the comproportionation of copper(II) and copper metal for the test solution compared to a blank containing 6.00×10^{-3} M benzoic acid, 1.00×10^{-2} M copper(II) nitrate and 3.00 ×

10^{-4} M $[(NH_3)_5CoN_3]^{2+}$. A solution containing 2.50×10^{-1} M p-toluenesulfonic acid sodium salt, 4.48×10^{-2} M copper(II) nitrate and 0.033 M $HClO_4$ was deoxygenated in contact with copper metal. Visual inspection of the solution after staying overnight shows that there was no disappearance of the blue color of copper(II) nor formation of the yellow color seen in the studies of the olefins systems discussed above. Based on the fact that a 25% color change would be visually noticeable, the β_1 value for p-toluenesulfonic acid is estimated to be $\leq 3 \times 10^2$ M^{-1}.

Introducing the copper(I) via the chromous reduction method (see Chapter 2) also was unsuccessful in our attempts to form copper(I)-benzene system complexes since these solutions disproportionated fast (in about an hour) just like solutions of aqueous copper(I). The silver(I) nitrate method (see Chapter 2) also was unsuccessful in our attempts to form copper(I)-benzene system complexes.

Kinetic runs for the reaction between $[(NH_3)_5CoN_3]^{2+}$ and copper(I) (made via the chromous method) in the presence of benzoic acid and p-toluenesulfonic acid sodium salt were monitored at 350 and 516 nm, respectively, on a Tritech Dynamic Instruments stopped-flow system (Model IIA). In ~0.033 M $HClO_4$, the benzoic acid concentration was varied from $(3.93 - 98.5) \times 10^{-4}$ M. The k_{obsd} values gave an average value of 1.36×10^3 $M^{-1}s^{-1}$ for the 3.93×10^{-4} M and averaged 1.12×10^3 $M^{-1}s^{-1}$ for the $(9.85 - 98.5) \times 10^{-4}$ M benzoic acid. The β_1 values obtained from these average k_{obsd} values are 112 M^{-1} and 27.2 - 272 M^{-1} for the lowest concentration and the ten fold increase from 9.85×10^{-4} M benzoic acid, respectively. Analogous experiments in 0.033 M $HClO_4$ were done with p-toluenesulfonic acid sodium salt, except that the greater solubility allowed higher concentrations of $(2.06 - 20.6) \times 10^{-3}$ M to be used. The k_{obsd} values show no trend with p-toluenesulfonic acid concentration and had an average value of 1.26×10^3 $M^{-1}s^{-1}$. This value, like the ones from the benzoic acid study, is close to the one observed for aqueous copper(I) with $[(NH_3)_5CoN_3]^{2+}$ (1.42×10^3 $M^{-1}s^{-1}$) as reported in Chapter 2. The β_1 values obtained from these average k_{obsd} values for the p-toluenesulfonic acid system are

6.16 - 61.6 M^{-1}. We can speculate here that only small amounts of the copper(I) are complexed for these benzene systems.

Discussion

Before discussing the variations in the formation constants with the nature of the olefin, it is of some interest to describe the various methods that have been used to determine these constants. Some assessment of the strengths and weakness of the methods also will be given.

The first quantitative measurements were presented in a series of papers by Andrews et al.[1b-d] in 1949. They studied the effect of various olefins (L) and chloride ion on the solubility of copper(I) chloride. They determined the total dissolved copper(I) as a function of olefin and chloride ion concentrations, and then determined, apparently by trial and error, the values of the formation constants for (LCu^+) and (LCuCl) that most closely predicted the observed total copper(I). In the analysis, they used literature values for the solubility product (K_{sp}) of $CuCl_{(s)}$ and for the formation constant of $CuCl_2^-$. With the assistance of modern computers, it is possible to use least-squares analysis to provide more objective values of the formation constants and to evaluate uncertainties in the values. The results of such analyses produce generally minor changes in the equilibrium constants, but reveal that some have substantial uncertainties. The latter result in part from the limited data sets and correlations between the two formation constants being evaluated, rather than from poor fits of the data. This method has the advantage of requiring no special apparatus, other than that required to ensure anaerobic conditions. The analysis was formerly complex, tedious, and subjective, but that need no longer be the case. The complexity added by the formation of (LCuCl) is a weakness that could not be avoided because chloride ion is always present from the dissolution of $CuCl_{(s)}$. The method also relies heavily on knowing the K_{sp} and the formation constant of $CuCl_2^-$. A potential error will result if an insoluble copper(I) complex is formed. This might not be noticed because of the $CuCl_{(s)}$ and would deplete the copper(I) in solution and cause low formation constants.

In a series of papers from 1974 - 99, Meyerstein and co-workers[2] have used pulse radiolysis[2a,b] of aqueous-methanol (~1 M) solutions of copper(II) and olefin. Through a complex series of reactions copper(II) reacts with •H and $^{\bullet}CH_2OH$ to produce copper(I), which then complexes with the olefin. The products are observed by spectrophotometry in the 250 - 400 nm region. Buxton et al.[4] also studied several olefins in this way. Most commonly, the variation of absorbance with olefin concentration is used to determine the formation constant. However, in the first paper, Meyerstein[2b] also measured the rate of formation of LCu^+ as a function of [L] and found that the pseudo-first-order rate constant is given by $k_{obsd} = k_f[L] + k_r$. Then the ratio of k_f/k_r was used to calculate the equilibrium constant. The most obvious limitation of this approach is the cost and availability of pulse radiolysis equipment. It must be assumed that the radiolysis does not affect the olefin or produce any persistent products that absorb in the same region as the (LCu) complexes, since the latter have rather modest extinction coefficients of $\sim 2 \times 10^3$ M^{-1} cm^{-1}. Since the copper(I) concentration is in the $1 - 5 \times 10^{-5}$ M range, the absorbance changes are rather small, even when multiple-pass spectrophotometer cells are used. The kinetic method (k_f/k_r) assumes that no side reactions are contributing to the disappearance of the complex (k_r).

Meyerstein and co-workers have also applied cyclic voltammetry[2a,c] to this problem. The method is based on the shift in the Cu(II)/Cu(I) potential as the copper(I) is complexed. The authors have acknowledged the various problems including uncertainties in the standard Cu(II)/Cu(I) potential, drifts in potentials during experiments and the problem of complexation of copper(II) and solubility at the rather high L concentrations (0.05 - 0.3 M) required. In the most recent study, problems with the slope of $E_{1/2}$ versus log [L] plots being lower than the expected 0.059 also are noted. This method gave values in reasonable agreement with earlier results[2b] for the maleic acid system, but substantially different with fumaric acid.

Finally Meyerstein et al. have used a spectrophotometric displacement method[2c] in which the spectrum of the fumarate complex was measured in the presence of varying concentrations of substituted benzoic acids and phenols. The decrease in absorbance at 346 nm with increasing concentration of the aromatic species was attributed to displacement of fumaric acid by the aromatic species. This method gave formation constant values that typically were within a factor of 4 of those determined by cyclic voltammetry.[2c] In the paper, the formation constant and extinction coefficient of the fumarate complex are given at pH 3, but most of the measurements were at pH 4 and 5. It is not clear that allowance was made for the pH dependence of the fumarate system. There also is a potential problem with the way the displacement reaction was set-up. A solution of copper(II), fumarate and the aromatic compound was allowed to stand in contact with copper metal for 24 hours and then the spectrum was taken and compared to that of a solution that contained no aromatic compound. If the aromatic species complexes with copper(II), then it will have the effect of displacing the comproportionation equilibrium towards copper(II) and copper metal and decrease the amount of copper(I). Then the absorbance will decrease even if there is no complexing of copper(I) by the aromatic species.

Our kinetic method for the determination of the formation constant (β) values for copper(I) with olefins and benzene systems is described in Chapter 2. In our method the copper(I) complexes were simply prepared by deoxygenating copper(II)/olefin solutions in contact with copper metal. Unlike the method of Andrews et al., where chloride ion was always present, our preparative method has the olefin as the only species in solution capable of complexing with aqueous copper(I).

The method takes advantage of the fact that cobalt(III) complexes are stable, colored and reactive scavengers for aqueous copper(I).[40] Solutions of $[(NH_3)_5CoN_3]^{2+}$

have absorption maxima in the visible region (λ = 516 nm, $\varepsilon = 2.68 \times 10^2\ M^{-1}\ cm^{-1}$) where the olefins, copper(II) and the reaction products show little or no absorption and also absorb in the near uv region (λ = 350 nm, $\varepsilon = 1.24 \times 10^3\ M^{-1}\ cm^{-1}$) where the olefins and copper(II) and absorption of the copper(I)-olefin complex can be taken into account. The kinetics for the reaction of $[(NH_3)_5CoN_3]^{2+}$ with copper(I) in the presence of the olefins were followed by monitoring the disappearance of cobalt(III) at 350 or 516 nm. Reaction conditions were second-order with an excess of cobalt(III) over copper(I). The change in absorbance and the extinction coefficient of cobalt(III) were used to determine the copper(I) concentration from the relationship $\Delta Abs = \varepsilon_{Co(III)} \times [Cu(I)] \times l$, where l is the path length. Least-squares analysis of the absorbance-time data gave second-order rate constants (k_{obsd}) which were progressively smaller with increasing olefin concentration. If the rate constant (k_0) for the reaction of $[(NH_3)_5CoN_3]^{2+}$ with aqueous copper(I) is known then plots of (k_0/k_{obsd} - 1) versus the olefin concentration are indicative of a number of possible situations. Linear plots show that only a mono complex is present. Bis complex formation is manifested by upward curvature, whereas kinetically active copper(I) complexes are indicated by a downward curvature. Least-squares analysis of the k_{obsd} values (using k_0 for [olefin] = 0) was used to determine the β values. Standard laboratory equipment suffices to determine formation constants values using our method.

Our method relies on the difference between k_{obsd} values at different ligand concentrations and the k_0 value. Eq. 3.5 can be rearranged to eq. 3.28 to illustrate this for the mono copper(I)-olefin complex.

$$\beta_1 = \left(\frac{k_0}{k_{obsd}} - 1\right) \times \frac{1}{[L]} \tag{3.28}$$

In order to estimate the lower limit on β_1 that can be determined by this method, one expects that a difference of >15% between k_0 (assigned 100%) and k_{obsd} can be reliably determined by the stopped-flow method. Then $k_0/k_{obsd} \approx 1.18$, and if [L] = 0.1 M, the value of β_1 is 1.8 M^{-1}. Therefore the smallest β_1 value that could be determined is ~2 M^{-1}.

Values for the formation constants for the complexation of copper(I) in aqueous solutions by various olefins determined in this study, as well as those by other workers, are given in Table 3.6. Values for fumaric and maleic acids and for hydrogenmaleate anion have been reported by Andrews et al.[1b,c] and Meyerstein et al.[2a,b] We are reporting for the first time formation constant values for dimethyl fumarate and fumaronitrile. A literature survey[1b,c,2a,b,39] of formation constant values of copper(I) with olefins reveals only β_1 values reported. We report here a β_2 value for the fumaronitrile and an estimated upper limit on β_2 values for fumaric acid and dimethyl fumarate.

A number of factors can affect the bonding between a metal center and the ligand(s). At the beginning of this chapter, the predominance of σ-donation relative to π-back-bonding in copper(I)-olefin complexes was noted both from experimental data and theoretical considerations. The electronic nature of substituent groups on the olefinic carbons can affect the electron density on the double bond and in turn the magnitude of the formation constants.

A comparison of the β values for the neutral and charged species for fumaric and maleic acids serves here to illustrate one aspect of these electronic effects on formation constants. Values of formation constants for copper(I) with fumaric and maleic acids and their anions are given in Table 3.6. The trend in the magnitude of the β values, $L^{2-} > HL^- > H_2L$, would suggest predominant σ-donation for the bonding in these complexes. As the negative charge increases (acid < anion < dianion) one expects more electron density at the double bond and consequently stronger bonds to the copper ion, leading to larger β values. If π-backbonding was the dominant mode, one would expect the opposite trend in β values.

Another aspect of electronics can be demonstrated through electrostatic forces. Electrostatic forces bring about a stronger interaction between the positively charged copper(I) and the negatively charged anion or dianion. Reports[40] on ion-pair formation constants (K_i) in various solvents indicate that the K_i values depend on cation-anion charge product and ionic strength and this has been extended for use in the present case. Using calculated[40] ion-pair formation constants values at 298 °K, the ratio of the K_i values for ion charge product values of -1 and -2 at 0.141 M ionic strength used in this study is 2.53. Although obviously crude, this estimate indicates that successive changes in β values for H_2L, HL^- and L^{2-} of ≤ 2 might be largely due to increased electrostatic interactions. This is the type of change observed in the fumaric acid system and also between the HL^- and L^{2-} forms of the maleic acid. Thus the general trend might not be due to the better π-backbonding mentioned in the previous paragraph. The exception is the ~6 fold increase from maleic acid to hydrogen maleate. In this case, the β value for maleic acid appears to be unusually small compared to that of the fumaric acid, for reasons that remain unclear.

The electronic influence of substituent groups on the formation constant values for a series of related substrates may be correlated using Hammett sigma constant (σ) values. A large positive σ-value implies high electron-withdrawing power by inductive and/or resonance effects relative to H and a large negative σ-value implies high electron releasing power relative to H. Since the σ-values[41] are approximately additive, a plot of log β versus Σσ is shown in Figure 3.9 for the neutral olefins listed in Table 3.6.

The general trend of the β values in Figure 3.9 is a gradual decrease as the σ value increases. This indicates that more electron withdrawing substituents give smaller β values, as expected if σ-donation is more important than π-back-bonding. A correlation line is possible for entries (1-10), but there seems to be no apparent correlation for entries (11-18). The ligands (1-10) all have at least one hydrogen on each of the olefinic carbons,

Table 3.6. Formation Constants for Copper(I)-Olefin Complexes in Aqueous Media.

		$10^{-3}\beta$, M^{-1} (H_2L)	$10^{-4}\beta$, M^{-1} (HL^-)	$10^{-4}\beta$, M^{-1} (L^{2-})	Method[a]
Fumaric Acid	(i)	9.20			Sol.[b]
	(ii)	7.30	1.16	1.50	Spec.[c]
	(iii)	7.34 ($K_2 < 5$ M^{-1})			Kin.[d]
Maleic Acid	(i)	1.13	2.02		Sol.[e]
	(ii)	2.30	1.20	2.80	C.V.[c]
	(iii)	2.68	1.69		Kin.[d]
Dimethyl Fumarate		6.08 ($K_2 < 20$ M^{-1})			Kin.[d]
Fumaronitrile		0.853 ($K_2 = 2.34$ M^{-1})			Kin.[d]
Mesaconic		0.41			Sol.[b]
Citraconic		0.022			Sol.[b]
Allyl Alcohol		52.0			Sol.[f]
β-Methallyl Alcohol		9.20			Sol.[g]
Ethylvinylcarbinol		39.0			Sol.[g]
Methylvinylcarbinol		33.0			Sol.[g]
α,α-Dimethylallyl alcohol		25.0			Sol.[g]
4-methyl-4-penten-2-ol		16.0			Sol.[g]
3-Methyl-3-buten-2-ol		4.00			Sol.[g]
Crotyl Alcohol		10.0			Sol.[g]
2-Methyl-2-buten-1-ol		3.50			Sol.[g]
β-Chloroallyl Alcohol		0.22			Sol.[g]

Table 3.6. continued

	$10^{-3}\beta$, M^{-1} (H_2L)	$10^{-4}\beta$, M^{-1} (HL^-)	$10^{-4}\beta$, M^{-1} (L^{2-})	Method[a]
Ethylene	222			Spec.[h]
Isobutene	27.0			Spec.[h]
Acrylamide	21.0			Spec.[h]

[a]The abbreviations for the various methods are: Sol. is solubility method, Spec. is a spectrophotometric method, C.V. is cyclic voltammetry method and Kin. is kinetic method. [b]Keefer, R. M.; Andrews, L. J.; Kepner, R. E. *J. Am. Chem. Soc.* **1949**, *71*, 2381; $\mu = 0.1$ M in $HClO_4$ or HCl, 25 °C, [fumaric] = 0.0182-0.0465 M, [mesaconic] = 0.113-0.151 M, [citraconic] = 0.345-0.459 M. [c]Navon, N.; Masarwa, A., Cohen, H.; Meyerstein, D. *Inorg. Chim. Acta* **1997**, *261*, 29; $\mu = 0.1$ M in KNO_3, 22 ± 2 °C, [fumaric] and [maleic] = 0.05-0.3 M. [d]This study, $\mu = 0.141$ M in $HClO_4/NaClO_4$ or $HNO_3/NaNO_3$, ambient temperature. [e]Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1949**, *71*, 2379; $\mu = 0.01\text{-}1.0$ M in $HClO_4$ 25 °C, [maleic] = 0.0503-0.202 M. [f]Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1949**, *71*, 1723. $\mu = 0.10$ M in $HCl/HClO_4$ or $NaClO_4$ 25 °C, [allyl alcohol] = 0.010-0.081. [g]Keefer, R. M.; Andrews, L. J.; Kepner, R. E. *J. Am. Chem. Soc.* **1949**, *71*, 3906. $\mu = 0.10$ M in $HCl/HClO_4$ or $NaClO_4$ 25 °C,[crotyl alcohol] = 0.034-0.14, [β-methallyl alcohol] = 0.024-0.071, [ethylvinylcarbinol] = 0.012-0.93, [methylvinylcarbinol] = 0.018-0.73, [3-methyl-3-buten-2-ol] = 0.038-0.050, [β chloroallyl alcohol] = 0.5 [α,α-dimethylallyl alcohol] = 0.23-0.91, [4-methyl-4-penten-2-ol] = 0.009-0.034, M. [h]Buxton, G. V.; Green, J. C.; Sellers, R. M. *J. Chem. Soc., Dalton Trans.* **1976**, 2160. pH 3.00 using $HClO_4$ or H_2SO_4.

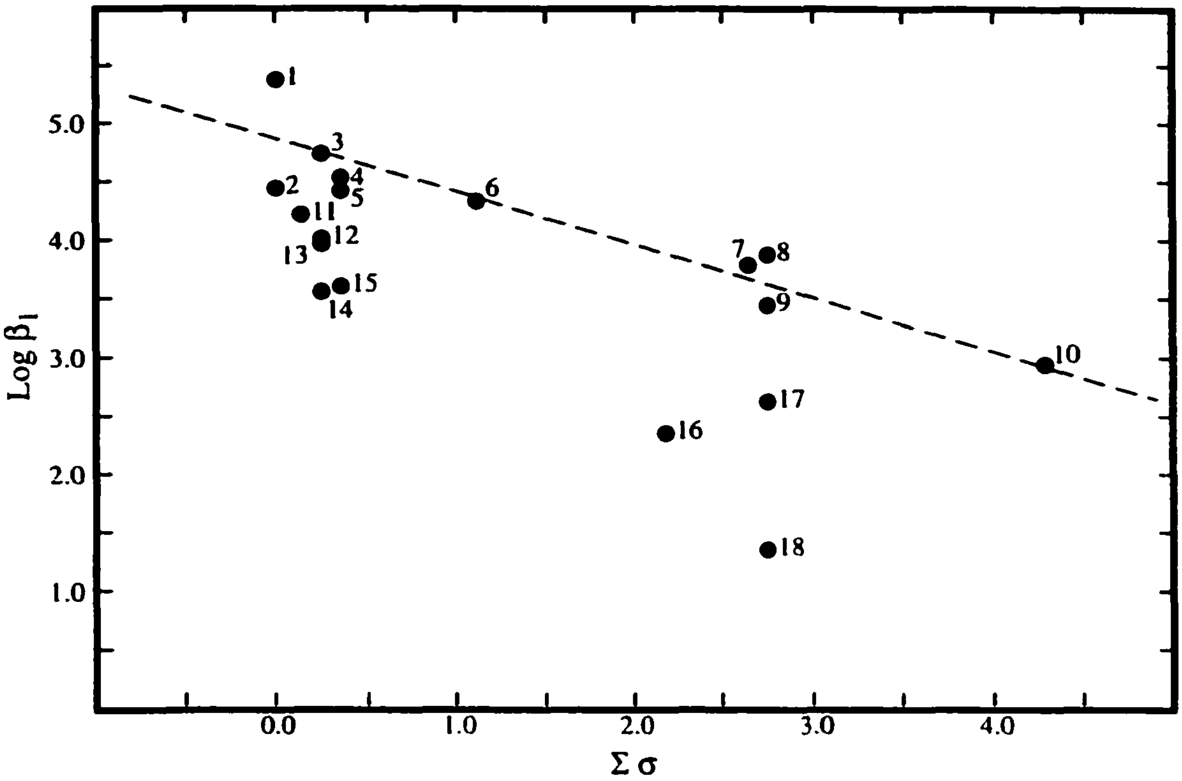

Figure 3.9. Variation of log β_1 for complexation of copper(I) by olefins (R'R"C=CR'"R"") versus the sum of the σ values of the R substituents. 1. ethylene, 2. isobutene, 3. allyl alcohol, 4. methylvinylcarbinol, 5 α,α-dimethyl allyl alcohol, 6. acrylamide, 7. dimethyl fumarate, 8. fumaric acid, 9. maleic acid, 10. fumaronitrile, 11. 4-methyl-4-penten-2-ol, 12. crotyl alcohol, 13. β-methallyl alcohol, 14. 2-methyl-2-buten-1-ol, 15. 3-methyl-3-buten-2-ol, 16. β-chloroallyl alcohol, 17. mesaconic acid and 18. citraconic acid.

whereas the others (11-18) have at least one of these hydrogen's replaced by a methyl or chloride substituent.

The correlation for ligands (1-10) provides some assistance in determining whether fumaronitrile in solution bonds through the double bond or through the nitrile, as found in bis(fumaronitrile)copper(I) nitrate. There is little doubt that ligands (1-9) coordinate to copper(I) through the double bond. The fact that fumaronitrile, (entry 10), lies close to the line defined by entries 1-9 is consistent with the bonding in fumaronitrile being through the double bond.

Arguments based on successive formation constants also are indicative of bonding in fumaronitrile being through the double bond. Successive formation constants decrease by an order of magnitude between K_1 and K_2 for the copper(I)-acetonitrile system (Chapter 2). The K_2 value for the fumaronitrile system and the estimated upper limits of the K_2 values for fumaric acid and dimethyl fumarate systems are three orders of magnitude less than their respective K_1 values. Again fumaronitrile shows trends similar to the other olefins bonded through the double bond, suggesting that copper(I) bonding in fumaronitrile is not through the nitrogen of nitrile as in acetonitrile.

In Chapter 2, the K_1/K_2 ratios for a number of metal ions were shown to be about an order of magnitude. Since copper(I) is a d^{10} system we do not anticipate electronic changes, but possibly the structure changes from tetrahedral to linear geometry in the bis(olefin)-copper(I) complexes, resulting in the small K_2 values. The geometry changes could be attributed to the steric requirements of two olefin ligands.

Sterics could be responsible for the entries in Figure 3.9 that do not fit with the general linear plot. Table 3.7 lists some ratios of the formation constants for similar ligands where a hydrogen on the olefinic carbons is substituted with a methyl group. On average the ratios are < 10 except for the larger ratios for citraconic and mesaconic acids. Substitution of a second hydrogen by a methyl on the olefinic carbons seems not to have as big an effect as the first substitution. This is illustrated by the values for allyl alcohol

Table 3.7. Ratio of Formation Constants where a Hydrogen is Substituted by a Methyl Group.[a]

Hydrogen	Methyl	Ratio (β_H / β_{CH_3})
Crotyl Alcohol	2-Methyl-2-buten-1-ol	2.86
Allyl Alcohol	β Methallyl Alcohol	5.65
Methylvinylcarbinol	3-Methyl-3-buten-2-ol	8.25
Ethylene	Isobutene	8.22
Fumaric Acid	Mesaconic Acid	17.9[b]
Maleic Acid	Citraconic Acid	122[b]

[a]Data from Table 3.6 where original references are given. [b]Ratios obtained using values obtained in this study for fumaric and maleic acids and Andrews et al.[1b,c] values for mesaconic and citraconic acids.

(5.2×10^4 M^{-1}), β-methallyl alcohol (9.2×10^3 M^{-1}) and 2-methyl-2-buten-1-ol (3.5×10^3 M^{-1}). Similarly substitution of a hydrogen by a methyl group away from the double bond has less effect on the β values; compare allyl alcohol (5.2×10^4 M^{-1}), ethylvinylcarbinol (3.9×10^4 M^{-1}) and methylvinylcarbinol (3.3×10^4 M^{-1}). Andrews et al. attributed the smaller β values where a hydrogen had been substituted with a methyl to steric effects. The β values for mesaconic and citraconic acids are lower than would be expected based on the other ratios in Table 3.7. These β values might be explained if there was precipitate formation of the copper(I) complex in solution as discussed previously in the method of Andrews et al.

The steric influence of a methyl group can be assessed from a computer model of a hypothetical copper(I)-olefin complex with a methyl on an olefinic carbon, assuming three water molecules and an olefin in a tetrahedral arrangement around copper(I), as shown in Figure 3.10. The model reveals that the hydrogens on the methyl group interact sterically with the hydrogens on the water molecules only for very specific orientations of the methyl and water molecules. Since both of these groups are conformationally flexible, there seems to be no reason for them to adopt unfavorable conformations and steric effects are hard to rationalize for such systems.

Absorption in the uv for unsaturated carbon-carbon double bonds is attributed to the π - π^* transition. The electronic spectra of the copper(I)-olefin complexes show maxima in the uv region. The maxima for some copper(I) complexes are ethylene (270 nm), isobutene (270 nm), allyl alcohol (270 nm), fumaronitrile (305 nm), acrylamide (315 nm), fumaric and maleic acids (348 nm) and dimethyl fumarate (359 nm). Copper(I) complexes with conjugated ligands have their maxima at lower energy. For the homologous series of fumaronitrile, fumaric and maleic acids and dimethylfumarate, there is a trend of decreasing energy of this electronic transition with decreasing electron withdrawing power of the substituents, as measured by their σ values.

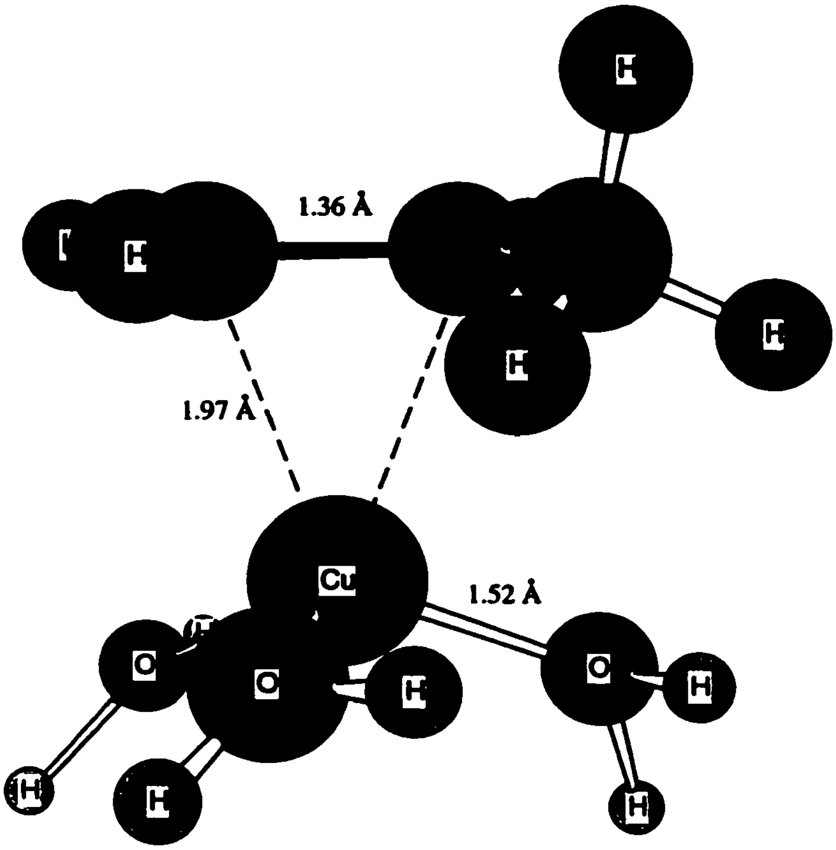

Figure 3.10. Spatial arrangement of a model tetrahedral triaquacopper(I)-propylene complex.

Our method was unable to detect any significant complexation between copper(I) and benzoic acid up to (9.85×10^{-3} M) or p-toluenesulfonate (0.021 M) in 0.033 M H^+. Using the analysis described previously, these observations give upper limits for the formation constants with benzoic acid and p-toluenesulfonate of $\leq 3 \times 10^2$ and ≤ 62 M^{-1}, respectively. However, Meyerstein et al.[2c] have recently reported $\beta_1 = 1.0 \times 10^4$ M^{-1} at pH 4.00 for benzoic acid by both the spectrophotometric displacement and cyclic voltammetry methods. They gave values of similar magnitude for other aromatic systems. This disagreement can be explained either by the thus far unprecedented fact that solvated copper(I) and the benzoic acid complex react at the same rate with $[(NH_3)_5CoN_3]^{2+}$, or by some error in the determination of the reported values.

Approximate values for the complexation of copper(I) by benzoic acid can be derived from the observations of Hurst and Lane.[3] They were unable to detect any complexation of copper(I) with $[(NH_3)_5Co(benzoate)]^{2+}$ and suggest an upper limit of $\beta_1 < 10^2$ M^{-1}. On the other hand, they found that $[(NH_3)_5Co(fumarate)]^{2+}$ has a $\beta_1 = 4.4 \times 10^3$ M^{-1}. Comparison of the latter value to that obtained here for fumaric acid, combined with the upper limit for $[(NH_3)_5Co(benzoate)]^{2+}$ suggest an upper limit of $\leq 1.7 \times 10^2$ M^{-1} for the complexation of copper(I) with benzoic acid.

A similar argument can be based on the relative complex formation constants of silver(I) and copper(I). The complexation of unsaturated alcohols[1d] indicates that β_1 is ~ 10^3 times larger for copper(I) than for silver(I). A value of $\beta_1 = 2.4$ M^{-1} has been reported[42] for the aqueous silver(I)-benzene system, and this leads to an estimate of ~ 2.5×10^3 M^{-1} for the copper(I)-benzene system. To take into account electronic factors to extend this to benzoic acid, one may note that the σ value for $-C(O)NH_2$ and $-CO_2H$ are similar and that β_1 with copper(I) is 10 times smaller for acrylamide than for ethylene. This yields an estimate for the copper(I)-benzoic acid system of $\beta_1 \approx 2.5 \times 10^2$ M^{-1}. Using this value for copper(I)-benzoic acid and the ratio between the β values for maleic and hydrogen maleate with copper(I) of ~6, one obtains a value of 1.5 × 10^3 M^{-1} for the formation constant of copper(I)-benzoate.

Both of these methods of estimation lead to β_1 values ~10 - 50 times smaller than those reported by Meyerstein et al.[2c] Some possible explanations for this seemingly large difference are discussed in the following paragraphs.

One possible complication in the ligand displacement method used by Meyerstein et al.[2c] involves complexation of copper(II) by the added ligand. If this occurs, then the disproportionation equilibrium will shift so that copper(I) is converted to copper(II). The result will be a decrease in the absorbance due to the copper(I)-hydrogenfumarate complex that really has nothing to do with complexation of copper(I) by the added ligand. In the specific case of benzoic acid as the added ligand, at pH 4.00 there is close to a 1:1 mixture of benzoic acid and benzoate and the formation constant, K_f, for copper(II)-benzoate has been determined to be 57.5 M^{-1} by Dubler et al.[43] A qualitative analysis of the copper(I)-hydrogenfumarate, copper(II)-benzoate system is given in the following development.

For a system starting with copper(II), copper metal and ligand (L = hydrogenfumarate) eq. 3.29,

$$Cu^{2+}_{(aq)} + Cu_{(s)} + 2L_{(aq)} \rightleftharpoons CuL^{+}_{(aq)} \qquad (3.29)$$

the equilibrium system can be described by eq. 3.30,

$$K = K_D \times \beta_1^2 = \frac{[CuL^+]^2}{[Cu^{2+}][L]^2} \qquad (3.30)$$

where K_D (7.69 × 10^{-7} M) is the comproportionation constant for copper(II)/copper metal and β_1 (1.00 × 10^4 M^{-1}) is the formation constant for the copper(I)-hydrogenfumarate complex.

If another ligand HL', such as benzoic acid is added, and it is assumed that its conjugate base (L') complexes only with copper(II), then there is the following additional equilibrium, eq. 3.31.

$$Cu^{2+}_{(aq)} + L'_{(aq)} \rightleftarrows Cu^{II}L'_{(aq)} \qquad K_f = \frac{[Cu^{II}L']}{[Cu^{2+}][L']} \tag{3.31}$$

The total initial copper(II) is given by eq. 3.32.

$$[Cu^{II}]_0 = [Cu^{II}] + [Cu^{I}L] + [Cu^{II}L'] \tag{3.32}$$

Substitution for $[Cu^{I}L]$ and $[Cu^{II}L']$ from eqs. 3.30 and 3.31, respectively, and equating $\sqrt{Cu^{II}}$ to x, results in eq. 3.33, a quadratic in x that can be solved in the usual way to give equilibrium concentration of copper(II).

$$(1 + K_f[L'])x^2 + (\sqrt{K}[L])x - [Cu^{II}]_0 = 0 \tag{3.33}$$

From eq. 3.33 it can be seen that addition of L' will affect the system only if $K_f[L'] \geq 1$. Using $K_f = 57.5\ M^{-1}$ from Dubler et al.[43], then only concentrations less than ≤ 0.017 M benzoate can be used without concern that complexation from copper(II) will affect the copper(I) concentration.

Since it is not necessarily true that [L] >> $[Cu^{I}L]$, one must take into account the stoichiometric balance of the L concentration as shown in eq. 3.34.

$$[L]_0 = [L] + [Cu^IL] \tag{3.34}$$

Substituting for [Cu^{I}L] from eq. 3.30 and rearrangement, one gets eq. 3.35.

$$[L] = \frac{[L]_0}{\left(1+\sqrt{K}\left[Cu^{II}\right]\right)} = \frac{[L]_0}{\left(1+\sqrt{K}x\right)} \tag{3.35}$$

Substitution for [L] in eq. 3.33 and rearrangement gives a cubic in x, eq. 3.36, that can be solved by iteration.

$$\sqrt{K}(1+K_f[L'])x^3 + (1+K_f[L'])x^2 + \sqrt{K}\left([L]_0 - \left[Cu^{II}\right]_0\right)x - \left[Cu^{II}\right]_0 = 0 \tag{3.36}$$

We have used here reasonable values for the benzoate concentration in solving eq. 3.35 since Meyerstein et al.[2c] have not given them in their report. In analogous experiments, they report typical concentrations of 1.00 × 10^{-4} and 5.00 × 10^{-3} M for copper(II) and fumaric acid, respectively, and these concentrations have been used in calculating equilibrium concentrations of copper(II) at various benzoate concentrations given in Table 3.8. From Table 3.8 one can observe that the concentration of copper(I)-hydrogenfumarate gradually decreases as the benzoate concentration increases. Maybe the decreasing copper(I)-hydrogenfumarate concentration trend with increasing benzoate concentration calculated in Table 3.8 is what Meyerstein et al.[2c] attributed to copper(I) complexation by benzoic acid. This decrease though is small and is probably not responsible for the large β value for copper(I)-benzoic acid obtained by Meyerstein et al.[2c] using eq. 3.37,

Table 3.8. Equilibrium Concentrations of Copper(II) and Copper(I)-hydrogenfumarate (Cu^IHL) at Various Benzoate Concentrations at pH 4.00 and 1.00 × 10^{-4} and 5.00 × 10^{-3} M Copper(II) and Fumaric Acid, Respectively.[a]

10^3[Benzoate]	10^6[Cu(II)]	10^3[HL^-]	10^5[Cu^IHL]	10^6[Copper(I)]
0.00	4.89	4.90	9.51	1.94
1.00	4.86	4.91	9.49	1.93
2.00	4.84	4.91	9.46	1.93
5.00	4.76	4.91	9.39	1.91
7.50	4.70	4.91	9.33	1.90
10.0	4.64	4.91	9.27	1.89
20.0	4.42	4.91	9.05	1.84
50.0	3.88	4.92	8.50	1.73
100	3.26	4.92	7.80	1.58

[a] Equilibrium concentrations based on Meyerstein et al.[2c] β_1 value of 1.00 × 10^4 M^{-1} and Dubler et al.[43] K_f value of 57.5 M^{-1}.

$$\beta = \beta_1 \times \frac{[\mathrm{Cu^I(L')}][\mathrm{L}]}{[\mathrm{Cu^I(L)}][\mathrm{L'}]} \tag{3.37}$$

where $[\mathrm{Cu^I(L')}] = [\mathrm{Cu^I(L)}]_0 - [\mathrm{Cu^I(L)}]$, $[\mathrm{L}] = [\mathrm{L}]_0 - [\mathrm{Cu^I(L)}]$, $[\mathrm{L'}] = [\mathrm{L'}]_0 - [\mathrm{Cu^I(L')}]$, $[\mathrm{Cu^I(L)}] = \mathrm{Abs_{346}} / \varepsilon_{346}$, and $\varepsilon_{346}(\mathrm{Cu^IL}) = 1.60 \times 10^3\ \mathrm{M^{-1}\ cm^{-1}}$.

Other factors that we are unable to pinpoint at this juncture must have come into play for Meyerstein et al.[2c] to get their β value which is far greater than our observations and estimates from other sources discussed above for complexation of copper(I) by benzoic acid.

Conclusion. We have successfully employed our kinetic method here for the determination of formation constants for copper(I) with unsaturated carbon-carbon systems. The method is simple, quick, inexpensive and uses standard laboratory equipment. We anticipate that our method can be used successfully for many other similar systems. Our method is applicable with any colored complex that is a good scavenger for aqueous copper(I). Complexes with higher ε values than $[(\mathrm{NH_3})_5\mathrm{CoN_3}]^{2+}$ would be more sensitive to small concentration changes in copper(I) and act as better probes for copper(I) complexation.

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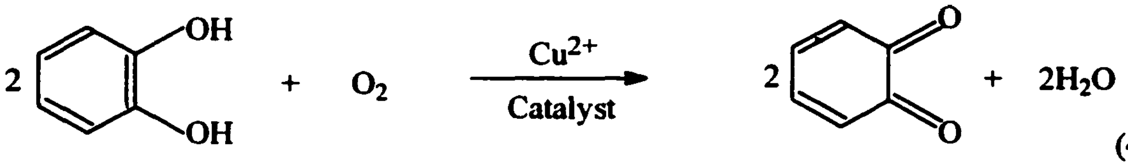
Chapter 4. Copper(II) Catalyzed Oxidation of Catechol in Aqueous Solutions

Introduction

The biological functions of copper proteins and enzymes are many.[1] They participate in reactions in which the oxygen molecule is directly or indirectly involved. One such activity is by tyrosinase and one of its functions is to catalyze the oxidation of catechol, H_2A, to quinone, Q, eq. 4.1.



(4.1)

Interest in studying small molecular weight copper(II) complexes as models for copper oxidase enzymes has led to the synthesis of many mononuclear[2] and dinuclear[3] copper(II) complexes, with the idea that these complexes might mimic the reaction of several copper-containing proteins, such as that of tyrosinase. These model complexes, unlike the case of the simple aquated copper(II) complex discussed below, have the high reduction potential values necessary to drive eq. 4.1 forward under the experimental conditions of the individual studies.[2a,3]

Copper(II) usually is a one electron oxidant and hence oxidation of catechol would take place through two successive one-electron steps as follows, where SQ is the semiquinone radical.

$$Cu^{2+}_{(aq)} + H_2A \rightleftarrows Cu^{+}_{(aq)} + SQ + H^+ \qquad (4.2)$$

$$\mathrm{Cu^{2+}_{(aq)} + SQ \longrightarrow Cu^{+}_{(aq)} + Q + H^{+}} \qquad (4.3)$$

The copper(II)/(I) reduction potential is invariant at 0.153 V with increasing pH up to weakly alkaline solutions. Cerium(IV) and thallium(III) oxidize catechol with known stoichiometry to the quinone. The quinone/catechol reduction potential has been unequivocally determined from potentiometric data using these two oxidants at pH 0.0 as 0.792 V.[4,5a] The one electron reduction potential for semiquinone has only been estimated since direct experimental determination is hindered due to the unstable nature of the catechol radicals in aqueous solutions. For a series of quinols and catechols, Pelizzetti and co-workers[5b,c] found that there was a fairly constant difference of ~0.38 V between the reduction potential of the semiquinone radical ($\mathrm{SQ + H^{+} + e \rightleftharpoons H_2A}$) and the two-electron reduction of the quinone ($\mathrm{Q + 2H^{+} + 2e \rightleftharpoons H_2A}$). From this they estimated a reduction potential of ~1.2 V for $\mathrm{SQ/H_2A}$. These reduction potential values for copper(II/I) and $\mathrm{SQ/H_2A}$ show that the first step in the oxidation of catechol by aqueous copper(II) is thermodynamically unfavorable in 1 M $\mathrm{H^{+}}$. From the Nernst equation, it can be shown that $\Delta E = -(\Delta \mathrm{pH} \times 0.0592)$[6] and thus the reduction potential for $\mathrm{SQ/H_2A}$ is ~ 0.79 V at pH 7.0, and the oxidation in eq. 4.2 still is thermodynamically unfavorable. Pathways by which aqueous copper(II) oxidizes catechol under anaerobic conditions despite the unfavorable reduction potential are presented in the Discussion section. The simple aquated copper(II) ion has been shown to catalyze the oxidation of catechol[7] by dioxygen and aqueous copper(II) nitrate has been used in this study.

The rate limiting step in the catechol oxidation is usually proposed to be the formation of the semiquinone and it is evident from the potentials above that the barrier for this step is less at pH 7.00 than at pH 0.0. The lower potentials at high pH maybe the reason why studies of copper(II) catalyzed oxidation of 3,5-di-tert-butylcatechol and catechol have been carried out in weakly acidic solutions.[3b,7] The near neutral pH values used in this study also are closer to physiological pH of 6.8 - 8.0.[8]

catechol have been carried out in weakly acidic solutions.[3b,7] The near neutral pH values used in this study also are closer to physiological pH of 6.8 - 8.0.[8]

Many mechanistic studies of the catalytic catechol oxidation by copper complexes have appeared,[7,9] with a copper(I)-dioxygen species often postulated as being responsible for formation of quinone and H_2O_2, with the general reactions described by eqs. 4.2 - 4.6.

$$Cu^+ + O_2 \rightleftarrows Cu(O_2)^+ \tag{4.4}$$

$$Cu(O_2)^+ + SQ \xrightarrow{2H^+} Cu^{2+} + H_2O_2 + Q \tag{4.5}$$

$$Cu^+ + \text{Oxidizing Scavenger} \longrightarrow Cu^{2+} + \text{Reduced Scavenger} \tag{4.6}$$

Low concentrations of copper(I) (due to steady-state considerations) and dioxygen (pure dioxygen saturated aqueous solutions contain only 1.3×10^{-3} M)[7] make it difficult to determine the rate controlling step in eqs. 4.2 - 4.6. If oxygen was eliminated from the above system of equations, then the reaction would be described by eqs. 4.2, 4.3 and 4.6. Then oxidizing scavengers which will react rapidly with copper(I) would help in determining the rate constant for eq. 4.2, which is rate-determining.

A previous study[10] has shown that several pentaamminecobalt(III) complexes react rapidly with copper(I) in aqueous solution. The second-order rate constant values in 0.200 M $LiClO_4$ at 25 °C are 1.50×10^3, 4.88×10^4 and 4.46×10^5 $M^{-1}s^{-1}$ for the azido ($[(NH_3)_5CoN_3](ClO_4)_2$), chloro ($[(NH_3)_5CoCl](ClO_4)_2$) and bromo ($[(NH_3)_5CoBr](ClO_4)_2$) complexes, respectively. The magnitude of these rate constants indicate that these cobalt(III) complexes would serve as good copper(I) scavengers in eq. 4.6. In the present study, only solutions of the azido complex are used as the oxidizing scavenger. Though better scavengers than the azido complex, the chloro and bromo complexes could not be used for reasons given later.

The only reported kinetic study of the oxidation of catechol by aqueous copper(II) ion is by Jameson et al.[7] They studied the copper(II) catalyzed oxidation of catechol by molecular oxygen between pH 4.60 and 5.70. Jameson et al.[7] monitored the reaction either by use of a Clark-type oxygen electrode, or by spectrophotometric detection of the quinone for up to ~35% of the reaction. They proposed the following reaction mechanism to explain their kinetic data.

Initiation:

$$Cu^{2+} + CuA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cu^{+} + Q \tag{4.7}$$

Chain propagation:

$$Cu^{+} + O_2 \overset{K}{\rightleftharpoons} Cu(O_2)^{+} \tag{4.8}$$

$$Cu(O_2)^{+} + HA^{-} \xrightarrow{k_2} Cu^{+} + HO_2^{-} + Q \tag{4.9}$$

$$Cu(O_2)^{+} + CuA \xrightarrow{k_3} Cu^{+} + O_2^{2-} + Q + Cu^{2+} \tag{4.10}$$

$$Cu(O_2)^{+} + CuA_2^{2-} \xrightarrow{k_4} Cu^{+} + O_2^{2-} + Q + CuA \tag{4.11}$$

Termination:

$$Cu(O_2)^{+} + Cu^{+} \xrightarrow{k_5} 2Cu^{2+} + O_2^{2-} \tag{4.12}$$

A major difference in their proposed reaction mechanism is the absence of radical formation as in reactions described by eqs. 4.2 and 4.3.

Details and analysis of their findings are compared to our results in the Discussion section. The present work is similar in that it is in purely aqueous media and the pH is just slightly higher, but here the conditions are anaerobic and a cobalt(III) complex is used as a scavenger for copper(I).

There have been reports on the copper(II) catalyzed oxidation in aqueous solutions of other systems closely related to catechol, and of particular interest is the oxidation of ascorbic acid. There have been both aerobic and anaerobic studies and a comparison of these reports might give some insight with regard to common mechanistic features of the aerobic study of Jameson et al.[7] and our anaerobic study.

Khan and Martell[11] followed the rate of production of dehydroascorbic acid under anaerobic conditions between pH range 2.0 - 5.5. They proposed a metal ion independent pathway in which molecular oxygen directly oxidizes the ascorbate anion. For the copper(II) catalyzed pathway, they observed that the reaction rates were inverse first-order in $[H^+]$ and first-order in the dioxygen and copper(II) concentrations.

Under anaerobic conditions, Jordan and Xu[12] monitored the reaction in $(0.50\text{-}10) \times 10^{-3}$ M H^+ by following the disappearance of ascorbic acid. Jordan and Sisley[13] studied this reaction at ambient temperature in 0.01 M H^+ both by monitoring the disappearance of copper(II) and by monitoring the disappearance of pentaammineazidocobalt(III) due to its reduction by copper(I). The results from these two monitoring methods were found to be in good agreement. The general observation from these studies is that the rate has an inverse dependence on $[H^+]$ and is first-order in the copper(II) concentration, and has terms that were independent, first- and second-order in the chloride ion concentration.

These aerobic and anaerobic studies agree on a number of points. In the mechanisms proposed,[11,12,13] the rate-determining step involves one electron oxidation of the ascorbate anion, HA^- in a copper(II)-ascorbate-dioxygen species and by copper(II) and its chloride complexes in aerobic and anaerobic conditions, respectively. The large equilibrium constant in the formation of copper(II)-ascorbate complex with dioxygen serves to drive forward the reaction in the study by Khan and Martell.[11] Analogous driving force effect is observed in the anaerobic studies[12,13] where the chloride ion served to catalyze the reaction by complexing with the copper(I) (the large equilibrium constant value here being the driving force for the catalysis) in the step involving the formation of the ascorbate radical. These comparisons will be revisited in more detail in the Discussion section.

The large majority of studies on the oxidation of catechol by copper(II) are in non-aqueous or mixed solutions.[9c,f,g] For example, in pyridine[9c] the oxidation of catechol takes place in the presence as well as in the absence of molecular oxygen. The overall anaerobic transformation of catechol to cis,cis-muconic acid monoethyl ester involves a two-electron oxidation of catechol to *o*-benzoquinone, followed by a second two electron oxidation of the *o*-benzoquinone to muconic acid ester.[9c] The active species is thought to be a dicopper(II) complex and thus the oxidation still is a one electron process from each copper(II) center.

Acetonitrile is known to inhibit the oxidation of aqueous copper(I) by coordination, forming complexes that take progressively longer time periods in getting oxidized (refer to Chapter 2 for detailed mechanism) with increasing acetonitrile concentration.[14] In acetonitrile-water solutions the catalytic effect of copper(II) is progressively reduced as the amount of acetonitrile is increased for both the ascorbic acid[15] and catechol[7] systems. An initial increase in rate of oxidation is observed with up to ~0.1 and ~0.6 M acetonitrile for the ascorbic acid and catechol systems, respectively. Shtamm et al.[15] suggested that the increase of the overall rate at low acetonitrile concentrations was an effect of acetonitrile on the rate of copper(I) production in the initiation-step reaction via the formation of an intermediate copper(II)-ascorbate-acetonitrile complex. In this complex, the electron transfer from ascorbate to copper(II) was assumed to be more favored. Jameson et al.[7] agree that such complexation also is possible for the initial increase in their catechol study. The assertion that the rate of oxidation of ascorbic acid by dioxygen practically falls to zero in 2.0 M acetonitrile by Shtamm et al.[15] is not what has been observed in this thesis (Chapter 2) and from other studies.[7,14]

More strongly oxidizing metal ions than copper(II) have been used to oxidize catechol in acidic solutions. Pelizzetti et al.[16] studied the oxidation of catechol by aqueous manganese(III)[16a] and iron(III),[16b] at [H$^+$] between 0.50 and 3.0 M and 0.10 and 1.0 M, respectively. The rates were followed by monitoring the formation of *o*-benzoquinone on a stopped-flow spectrophotometer. The rate of formation of the semiquinone was found to have an [H$^+$] independent path and an inverse [H$^+$] dependent path. These were assigned to the oxidants $[M(OH_2)_6]^{3+}$ and $[M(OH_2)_5OH]^{2+}$, respectively. Copper(II) is not hydrolyzed under our reaction conditions and any pH dependence can be attributed to anionic forms of catechol.

Pelizzetti and Menstati[16c] studied the oxidation of catechol by tris(1,10-phenanthroline)iron(III) and its derivatives, and Kimura et al.[16] used only tris(1,10-phenanthroline)iron(III). In the former study, the acidity was held at 1.0 M and between 0.055 and 1.0 M in the later. The rate of reaction was determined by monitoring the formation of the tris(1,10-phenanthroline)iron(II) complexes by stopped-flow spectrophotometry. Pelizzetti et al.[5c] also studied the oxidation of catechol by hexachloroiridate(IV). The acidity range was between 0.03 and at 1.0 M and the rate was determined from the disappearance of hexachloroiridate(IV). Results from these studies agree that the rate is first-order in both oxidant and reductant and that semiquinone formation is rate controlling. Similar to our aquated copper(II), these oxidants are not hydrolyzed and at the respective [H$^+$] in these studies[5c,16c,17] catechol is essentially in the protonated form. Pelizzetti and co-workers[5c,16c] have attributed the slight increase in rate of reaction with decrease in [H$^+$] to a salt effect. However, the rate constants for the oxidation of catechol by tris(1,10-phenanthroline)iron(III) in 1.0 M $HClO_4$ differ by a factor of ~4 in the studies by Pelizzetti and Mentasti[16c] and Kimura et al.[17] An average self-exchange rate value for catechol/cationic catechol radical from these studies is used to test an outer-sphere reaction mechanism for the present study (Discussion section).

A discussion of the copper(II) catalyzed oxidation of catechol would be incomplete without a review of the formation constants between copper(II) and deprotonated catechol. Table 4.1 summarizes acid and copper(II) equilibria values for catechol and for Tiron.[18] The log K_1 and K_2 values in Table 4.1 indicate that copper(II) forms strong complexes with deprotonated catechol and Tiron. The log K_1^* values (see development in Chapter 1) show that, at a given pH, Tiron complexes more strongly to copper(II) than catechol does. It is expected that most of the copper(II) will be complexed under our reaction conditions and such complexation is evident in the observed rates of oxidation for catechol.

Nitroso-R (disodium 1-nitroso-2-hydroxy-naphthalene-3,6-disulfonate) salt (NRS) Method.[19] Spectrophotometric studies of aqueous solutions in the scheme represented by eqs. 4.2 - 4.6 are hindered by the formation of insoluble products, eq. 4.5. Previously the rates of such reactions have been followed by an oxygen analyzer,[7] where precipitation is not a problem or spectrophotometrically[7] by following the reaction in the early stages before the precipitation significantly affects the absorbance readings. In the present study, the rates are followed by monitoring the formation of cobalt(II) resulting from the reduction of cobalt(III) by copper(I) using the NRS method.

The reaction between nitroso-R-salt and cobalt(II) has been extensively used for the determination of cobalt since Hoffmann[20a] and later Klooster[20b] used it about a century ago. NRS (yellow in acid solution) was used because it is soluble in aqueous media due to the sulfonate groups and complexes strongly with cobalt(II) which oxidizes to give the cobalt(III) (red in acid solution) complex. The cobalt(III)-nitroso-R complex has an absorbance maximum at 420 nm; however, the reagent also absorbs

Table 4.1. Acid Dissociation Constants of Catechol and Tiron and Their Stability Constants with Copper(II).

Ligand	pK_{a1}	pK_{a2}	log K_1	log K_2	log K_1^*	log K_2^*
Catechol	9.25[a]	13.0	13.64	11.28	-8.61	-10.97
	9.195[b]	12.98	13.827	10.92	-8.35	-11.26
	9.23[c]	13.0	13.90	11.00	-8.33	-11.23
	9.13[d]	11.59	12.52	9.66	-8.20	-11.06
Tiron	7.62[c]	12.5	14.25	11.12	-5.87	-9.0
	7.54[d]	12.26	13.99	11.17	-5.81	-8.63
	7.66[e]	12.55	14.28	11.14	-5.93	-9.07
	7.69[f]	11.97	13.82	11.19	-5.84	-8.47

[a] Balla, J.; Kiss, T.; Jameson, R. F. *Inorg. Chem.* **1992**, *31*, 58. 25 °C and μ= 1.0 M. [b] Jameson, R. F.; Wilson, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, 2614-17. 25 °C and μ = 0.10 M. [c] Martell, A. E.; Smith, R. M. *NIST Critical Stability Constants of Metal Complexes Database* **1995**, U.S. Department of Commerce; μ = 0.1 and 25 °C. [d] Murakami, Y.; Nakamura, K.; Tokunaga, M. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 669. 30 °C and μ= 0.10 M. [e] Sigel, H.; Huber, P. R.; Griesser, R.; Prij, B. *Inorg. Chem.* **1973**, *12*, 1198. 25 °C and μ= 0.10 M. [f] Chakraborty, D.; Bhattacharya, P. K. *J. Chem. Soc., Dalton Trans.* **1990**, 3325. 30 °C and μ= 0.2 M.

strongly in this region and the optimum wavelength to monitor the reaction between nitroso-R salt and cobalt(II) is between 520 and 530 nm. At 525 nm the molar absorptivity is 1.34×10^4 M^{-1} cm^{-1} for the cobalt(III)-nitroso-R complex and there is negligible absorption from the NRS reagent.[21]

Under anaerobic conditions, the following reactions, eqs. 4.13 - 4.15, have been proposed by Lalor[22] from studies on the reactivity of pentaamminecobalt(III) complexes with nitroso-R in aqueous solutions.

$$Co^{2+} + 2NRS \longrightarrow Co^{II}(NRS)_2 \qquad \text{fast} \qquad (4.13)$$

$$Co^{II}(NRS)_2 + NRS \rightleftarrows Co^{II}(NRS)_3 \qquad \text{fast} \qquad (4.14)$$

$$Co^{II}(NRS)_3 + (NH_3)_5Co^{III}X \longrightarrow Co^{III}(NRS)_3 + Co^{2+} + 5NH_3 + X \qquad (4.15)$$

Aerobically, Lalor[22] found out that tris(nitroso-R)cobalt(II) is oxidized by dioxygen, eq. 4.16.

$$Co^{II}(NRS)_3 \xrightarrow{O_2} Co^{III}(NRS)_3 \qquad (4.16)$$

For application of the NRS method to solutions containing cobalt(II) and $[(NH_3)_5CoX]^{2+}$, the rate of eq. 4.16 must be faster than the rate of eq. 4.15. Lalor[22] found that this was the case for $[(NH_3)_6Co]^{3+}$ and $[(NH_3)_5CoNO_2]^{2+}$ and thus these complexes are unreactive in the presence of dioxygen. However, complexes such as $[(NH_3)_5CoCl]^{2+}$ and $[(NH_3)_5CoBr]^{2+}$ have significant reactivity with nitroso-R in the presence of cobalt(II) even under aerobic conditions.[22]

In the study by Jordan and Sisley,[13] discussed above, the copper(II) catalyzed oxidation of ascorbic acid was monitored by the disappearance of pentaammineazido-cobalt(III) complex when it reacts with copper(I). The findings from this method were in good agreement with those from direct monitoring of the disappearance of copper(II).[13] It is expected that pentaaminecobalt(III) complexes can be used in an analogous way in the present study, but it is the formation of cobalt(II) that is monitored here from the reaction between cobalt(III) and copper(I). The analytical procedure is explained in the Experimental section.

Experimental

Materials. Catechol (Fisher Scientific), Tiron (Aldrich Chemicals), sodium acetate (BDH), HEPES (Fisher Scientific), PIPES (Aldrich Chemicals), pre-purified argon (Praxair), cobalt(II) sulfate heptahydrate (Anachemia Chemicals), phosphoric acid (Fisher Scientific, 85% assay), hydrochloric acid (Anachemia Chemicals, 36.5 - 38%, specific gravity 1.18), disodium 1-nitroso-2-hydroxy-naphthalene-3,6-disulfonate (Aldrich), and sodium chloride (BDH), were used as received.

Pentaammineazidocobalt(III) chloride $[(NH_3)_5CoN_3]Cl_2$,[23] pentaammine-bromocobalt(III) bromide $[(NH_3)_5CoBr]Br_2$,[24] pentaamminebromocobalt(III) perchlorate $[(NH_3)_5CoBr](ClO_4)_2$,[25] and pentaamminechlorocobalt(III) perchlorate $[(NH_3)_5CoCl](ClO_4)_2$[25] were prepared by standard methods. Pentaammineazidocobalt(III) nitrate $[(NH_3)_5CoN_3](NO_3)_2$, was prepared through an adaptation of Linhard's synthesis of the chloride salt[23], as described in Chapter 2.

Preparation of solutions. Stock solutions of $HClO_4$ were prepared by diluting 70% $HClO_4$ and analyzed by titration with standard NaOH. The sodium hydroxide solutions were prepared by dilution of ampoules of concentrated reagent. Stock solutions of $NaClO_4$ were made by dissolving reagent grade solid and analyzed by titrating the H^+

produced by an aliquot passed through a cation exchange column in the H^+ form with standard NaOH. Stock solutions of hydrochloric acid were prepared by diluting the concentrated acid (12.4 M) and analyzed by titration with standard NaOH. Stock solutions of phosphoric acid were prepared by pipetting the appropriate volume of concentrated acid (14.7 M), and diluting to the mark in a volumetric flask.

Stock solutions of the cobalt(III) complexes were prepared by weighing the solid and diluting to volume in a volumetric flask with doubly distilled water and appropriate volumes of stock $NaClO_4$ to adjust the ionic strength. Blank experiments show a decrease in absorbance with time of the cobalt(III) solutions that were stored exposed to light. To minimize these photolysis effects the containers of the stock solutions were covered with aluminum foil. There was no hydrolysis of neutral solutions of $[(NH_3)_5CoN_3](NO_3)_2$ stored in the dark for a period of up to four days. Stock solutions of nitroso-R were prepared by weighing the solid and diluting to volume in a volumetric flask with doubly distilled water. The nitroso-R solutions were stored in brown bottles.

The buffer solutions were prepared by weighing of the solid (HEPES or PIPES) and diluting to volume with doubly distilled water after adjusting the pH with NaOH or $HClO_4$ as appropriate. Stock solutions of catechol were prepared daily by weighing of the solid and diluting to volume in a volumetric flask with the buffer solution, and the flasks were covered with aluminum foil. A stock solution of copper(II) nitrate, $Cu(NO_3)_2{\bullet}3H_2O$, was prepared by adding a weighed amount of the solid to a 500 mL volumetric flask and diluting to volume with doubly distilled water. Aliquots of the copper(II) solution were standardized by addition of excess potassium iodide and back titration with sodium thiosulfate.[26]

Analytical procedure for the determination of cobalt(II) using NRS method. The analytical procedure involves mixing a sample containing cobalt(II) in phosphoric acid with nitroso-R, followed by addition of a sodium acetate solution and then finally acidification with hydrochloric acid. The phosphate/acetate buffer provides the medium for the complexation and oxidation of the cobalt(II) complex is effected by molecular oxygen. The last step, acidification, destroys other metal complexes of nitroso-R, thereby minimizing interference from other metals and also serves to stabilize with time the color of the cobalt(III)-nitroso-R complex. In this study acidification also served to dissolve the insoluble organic products in eq. 4.5.

Concentrations of reagents used in the NRS method. Determination of the concentrations of reagents needed in this study was worked out through a series of experiments. In solutions containing 1.36×10^{-5} M cobalt(II) sulfate, the nitroso-R concentration was varied and the absorbance at 525 nm recorded. The absorbance values are invariant, $(2.30 \pm 0.019) \times 10^{-1}$, as the amount of nitroso-R was increased, Figure 4.1. A value of 3.18×10^{-4} M nitroso-R was chosen as the final working concentration.

The effect of the phosphoric acid concentration on the observed absorbances due to the cobalt(II) present was determined. The phosphoric acid serves to quench the oxidation of the catechol by copper(II) and to reduce interference from iron.[27] As shown in Figure 4.2, the absorbances rose gently and then dipped steeply as the concentration of phosphoric acid was increased. From this observation, it was decided to use a final concentration of 2.30×10^{-2} M phosphoric acid in order to maximize the observed absorbances. Sodium acetate was introduced to make a phosphate/acetate buffer ca. pH 5.94 which is in the optimum range pH 5.5 - 6.5 for cobalt(II)-nitroso-R complex formation.[28] A final concentration of 7.32×10^{-1} M sodium acetate was adopted based on the resulting buffer pH of 5.94 being in the optimum pH range above.

Tests showed that samples from the reaction mixture quenched in phosphoric acid were stable with respect to the cobalt(II) concentration. The absorbances were the same whether the sodium acetate and hydrochloric acid were added immediately or 10, 20 or 30 minutes after quenching.

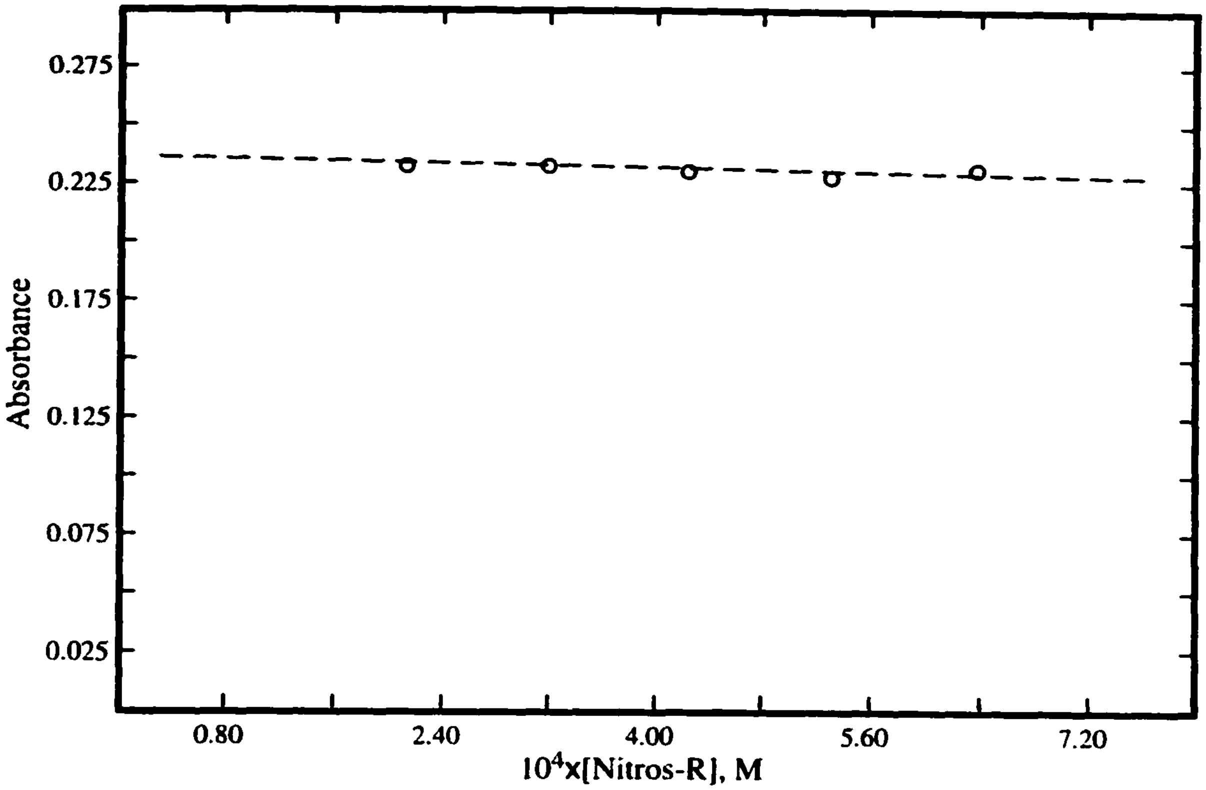


Figure 4.1. Dependence of cobalt(III)-nitroso-R complex absorbances on nitroso-R concentration: 1.36 × 10^{-5} M cobalt(II), 1.43 × 10^{-5} M copper(II), 2.30 × 10^{-2} M phosphoric acid, 7.32 × 10^{-1} M sodium acetate and 1.86 M hydrochloric acid, monitored at 525 nm.

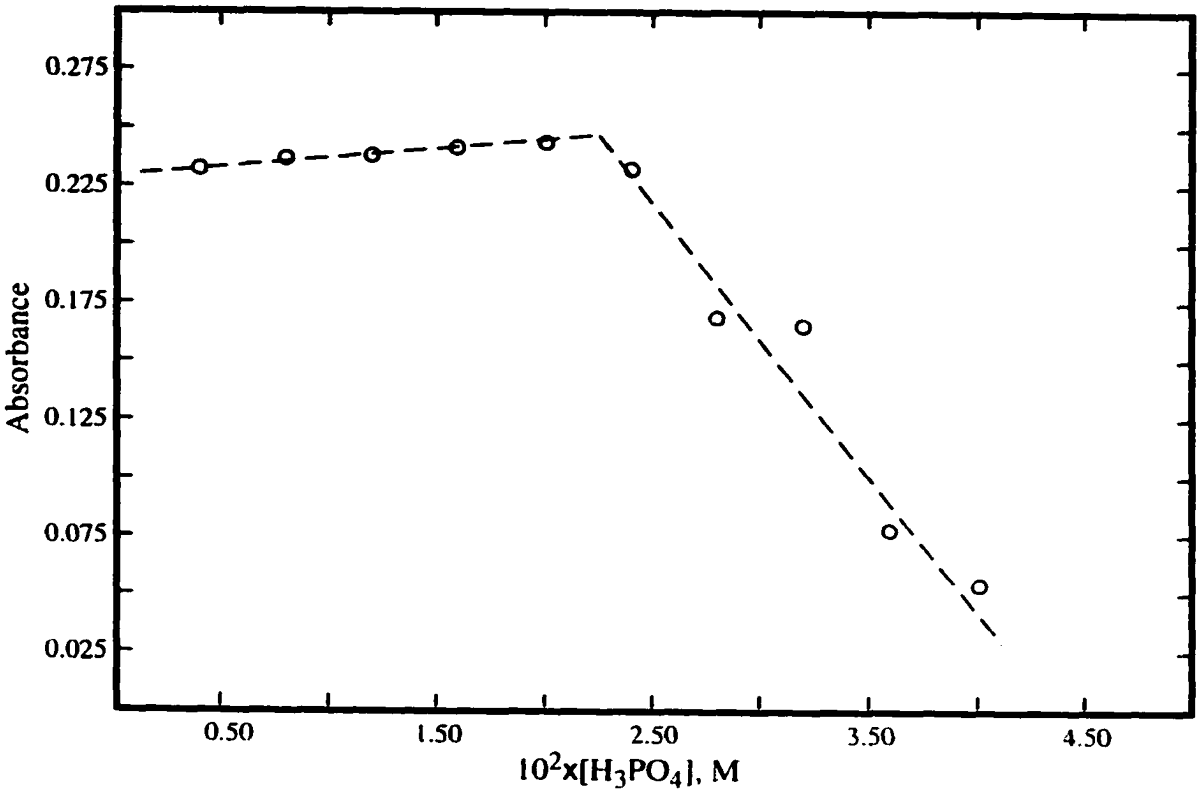


Figure 4.2. Dependence of cobalt(III)-nitroso-R complex absorbances on phosphoric acid concentration: 1.36 × 10^{-5} M cobalt(II), 1.43 × 10^{-5} M copper(II), 3.18 × 10^{-4} nitroso-R, 7.32 × 10^{-1} M sodium acetate and 1.86 M hydrochloric acid, monitored at 525 nm.

Hydrochloric acid was substituted[26] for the generally used nitric acid in the final step of decomposing the complexes of interfering metals. In the present case this interference would primarily be from copper(II). While nitric acid destroys about half the color of the excess NRS reagent, it is a source of color instability.[29]

Experiments also were done to determine an appropriate working concentration for the hydrochloric acid. The effect of the amount of hydrochloric acid concentration on the observed absorbances, is shown in Figure 4.3. A value of 1.86 M hydrochloric acid in the horizontal region in Figure 4.3 was chosen as the working concentration since it would produce consistent results and shows that most of the copper(II)-nitroso-R complex is destroyed. In this concentration range, hydrochloric acid had no effect on the absorbance of standard cobalt(II) as determined by complexation with nitroso-R. The stabilizing effect of the hydrochloric acid on the absorbances was explored and the results are given in Table 4.2 below. Solutions with hydrochloric acid added show no change in absorbances with time. For those solutions with no hydrochloric acid added, the absorbances increased with time and reached a maximum in less than 6 hours.

Copper(II) is always present under our reaction conditions. In order to ascertain that copper(II)-nitroso-R complexes were destroyed as discussed above, the following tests were carried out. Absorbances were recorded for solutions containing known amounts of cobalt(II) and compared to the same cobalt(II) concentrations with a known copper(II) concentration. The results from these experiments are presented in Table 4.3. The absorbance values in Table 4.3 indicate that there is no effect by copper(II) on cobalt(II) determination.

The linearity of the relationship between cobalt(II) concentration and absorbance was checked by making a stock solution of cobalt(II). Aliquots of 1, 2, 3, 4, and 5 mL were analyzed for cobalt and the results are given in Figure 4.4. The cell blank with 2.30×10^{-2} M phosphoric acid, 7.32×10^{-1} M sodium acetate, 1.86 M hydrochloric acid, and no cobalt(II) was measured to be 0.035 absorbance units. This value is reasonable based

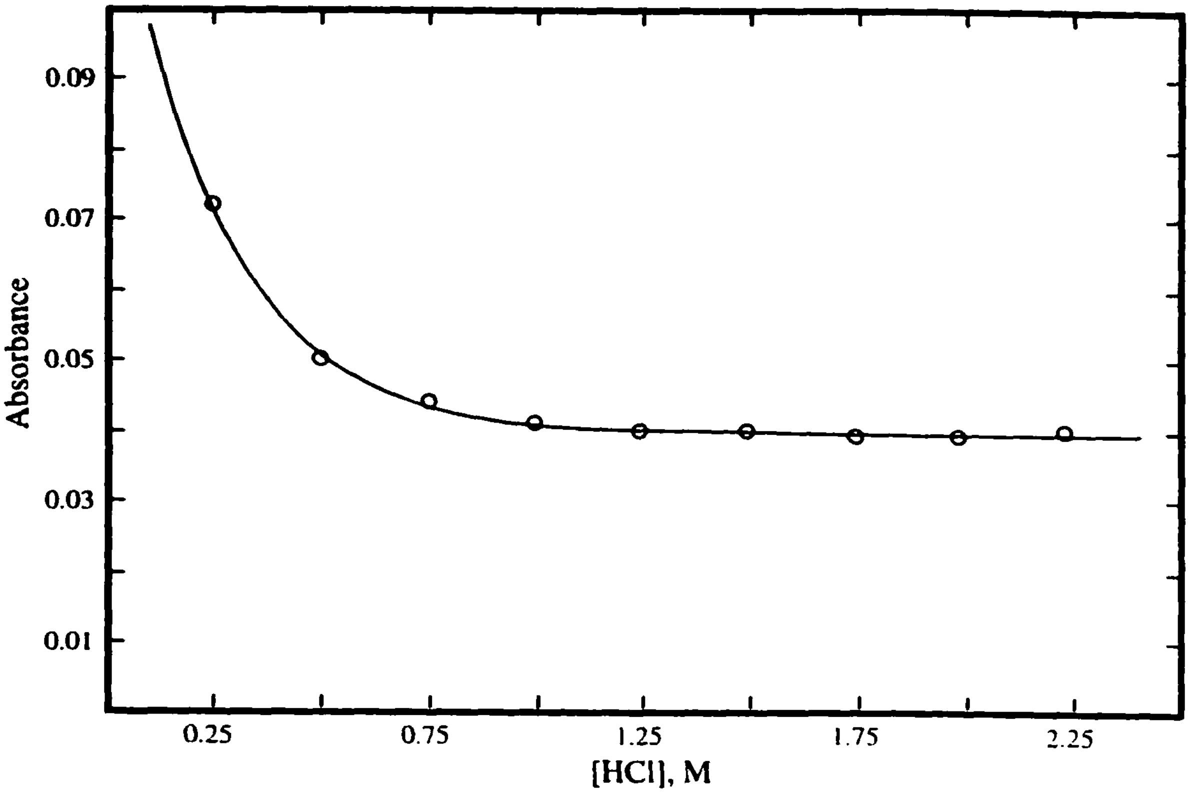


Figure 4.3. Effect of hydrochloric acid concentration on copper(II)-nitroso-R complex absorbances: 1.43 × 10^{-5} M copper(II), 3.18 × 10^{-4} M nitroso-R, 2.30 × 10^{-2} M phosphoric acid, 7.32 × 10^{-1} M sodium acetate, at 525 nm.

Table 4.2. Effect of Adding Hydrochloric Acid in the Analysis of Cobalt(III)-nitroso-R Complex: 7.32 × 10^{-1} M Sodium Acetate, 3.19 × 10^{-4} M Nitroso-R and 2.3 × 10^{-2} M Phosphoric Acid.

$10^6[Co^{2+}]$ M	Absorbance[a] ($\lambda = 525$ nm) immediately	after 6 hours	after 24 hours
6.8	0.151 (0.134)	0.166 (0.134)	0.166 (0.135)
13.6	0.258 (0.236)	0.282 (0.235)	0.283 (0.236)
20.4	0.373 (0.343)	0.399 (0.342)	0.402 (0.340)
27.2	0.483 (0.438)	0.518 (0.439)	0.522 (0.435)
34.0	0.589 (0.540)	0.632 (0.541)	0.632 (0.541)

[a] Values in brackets obtained with solutions containing 1.86 M hydrochloric acid whereas the rest of the values contain no hydrochloric acid.

Table 4.3. Absorbances for Solutions of Cobalt(II) and Cobalt(II) in the Presence of Copper(II) Determined via the NRS Method. 7.32 × 10^{-1} M Sodium Acetate, 3.19 × 10^{-4} M Nitroso-R and 2.3 × 10^{-2} M Phosphoric Acid, Monitored at 525 nm.

10^6[Co(II)], M	Absorbance (λ = 525 nm)	
7.90	0.148[a]	0.152[b]
11.7	0.203[a]	0.206[b]
15.6	0.259[a]	0.261[b]
19.6	0.316[a]	0.316[b]

[a]Absorbance values with no copper(II) added. [b]Absorbance values with solutions containing 8.64 × 10^{-6} M copper(II).

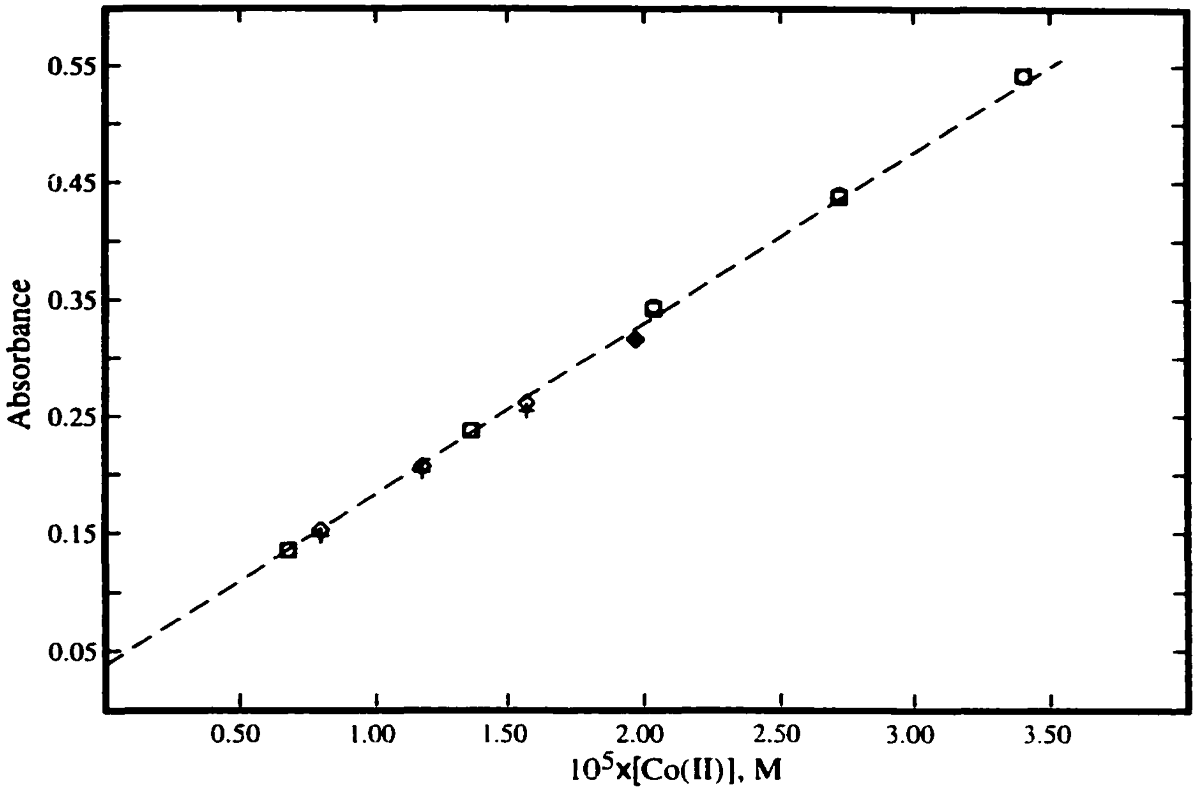


Figure 4.4. Dependence of absorbance at 525 nm on cobalt(II) concentration for optimized conditions: samples analyzed after ≤6 hours (O, +); samples analyzed after 24 hours (□); samples containing copper(II) (◊).

on the y-intercept value of 0.034 from Figure 4.4. An average ε value of 1.48 × 10^4 M^{-1} cm^{-1} is obtained from the cobalt(II) standardization curve. The color stability of these cobalt(III)-nitroso-R solutions also was investigated as a function of time. Over a period of a day, there was no appreciable change in the observed absorbances.

Under anaerobic conditions, Lalor[22] reported that cobalt(II) catalyzes the reaction of cobalt(III) amine complexes with nitroso-R. This is a potential problem in our analytical procedure if the cobalt(II) produced in the reaction between cobalt(III) and copper(I) had the same catalytic effect under our reaction conditions. Aerobically, Lalor[22] found out that oxidation of tris(nitroso-R)cobalt(II) complex is effected by dioxygen, eq. 4.16, and that some complexes were unreactive in the presence of dioxygen. NRS tests were carried out aerobically with 0.170 × 10^{-3} M cobalt(II) both without and in the presence 0.168 × 10^{-3} M cobalt(III) complexes. At 525 nm the absorbance recorded for the cobalt(II) solution alone was 0.224. The pentaammineazidocobalt(III) complexes used in this study (absorbances for the chloride and nitrate salts are 0.222 and 0.226, respectively) shows no reactivity with nitroso-R in the presence of cobalt(II) under aerobic conditions. Complexes such as $[(NH_3)_5CoCl](ClO_4)_2$ (absorbance 0.241) and $[(NH_3)_5CoBr]^{2+}$ (absorbances for the perchlorate and bromide salts are 0.331 and 0.493, respectively) though show significant reactivity with nitroso-R in the presence of cobalt(II) under aerobic conditions and are unsuitable for use in the present study for the analysis for cobalt(II).

Another potential pitfall was the possibility of the cobalt(III) complex oxidizing the catechol. Tests to establish that $[(NH_3)_5CoN_3]^{2+}$ did not oxidize catechol in the time required for a kinetic run under our reaction conditions were performed. A 0.336 × 10^{-3} M solution of the cobalt(III) complex was mixed with 2.18 × 10^{-3} M catechol, and the electronic spectra were taken every 30 minutes. There was no observable change in the spectra over a period of 20 hours. The longest kinetic run with the azido complex took about ~6 hours. The kinetic run time frames are therefore within safe limits to assume that there is no reaction between the cobalt(III) complex and catechol. For the rest of the discussion cobalt(III) will represent $[(NH_3)_5CoN_3]^{2+}$.

If copper(I) is complexed significantly by catechol under our reaction conditions, then some copper would be tied-up in this form, and it would have to be taken into account in calculating the copper(II) species present. Qualitative tests for this complexation were done by allowing 4.48×10^{-3} M copper(II) and 5.45×10^{-3} M catechol, in water, to react over copper foil under argon atmosphere. Visual inspection indicated no decrease in the color of copper(II) in the solution. Therefore, any complexation of copper(I) by catechol is too weak to displace the comproportionation equilibrium.

In summary, these experiments established the working concentrations as 3.18×10^{-4} M nitroso-R, 2.30×10^{-2} M phosphoric acid, 7.32×10^{-1} M sodium acetate and 1.86 M hydrochloric acid for the analytical method.

Kinetic Studies of the Oxidation of Catechol by Copper(II). The apparatus for the kinetic study is shown in Figure 4.5. Each reactant solution containing 0.025 M HEPES or PIPES, was adjusted to the desired pH with $HClO_4$ and/or NaOH, and the ionic strength was maintained at 0.125 M by adding appropriate amounts of $NaClO_4$. One solution contained appropriate volumes of the cobalt(III) and copper(II) stock solutions and was made to a total volume of 20.0 mL. The other solution contained the appropriate volume of catechol stock solution with a total volume of 30.0 mL. The solution vessels were connected by teflon tubing, as shown in Figure 4.5, and then deoxygenated with argon for ~1 hour. Then adjustment of the levels of the inlet and outlet tubes on the copper(II)/cobalt(III) solution allowed transfer of this solution to the catechol solution to start the reaction. The reaction solution was kept under argon for the entire run and protected from light with aluminum foil (or in brown bottles) to preclude photochemical reactions.

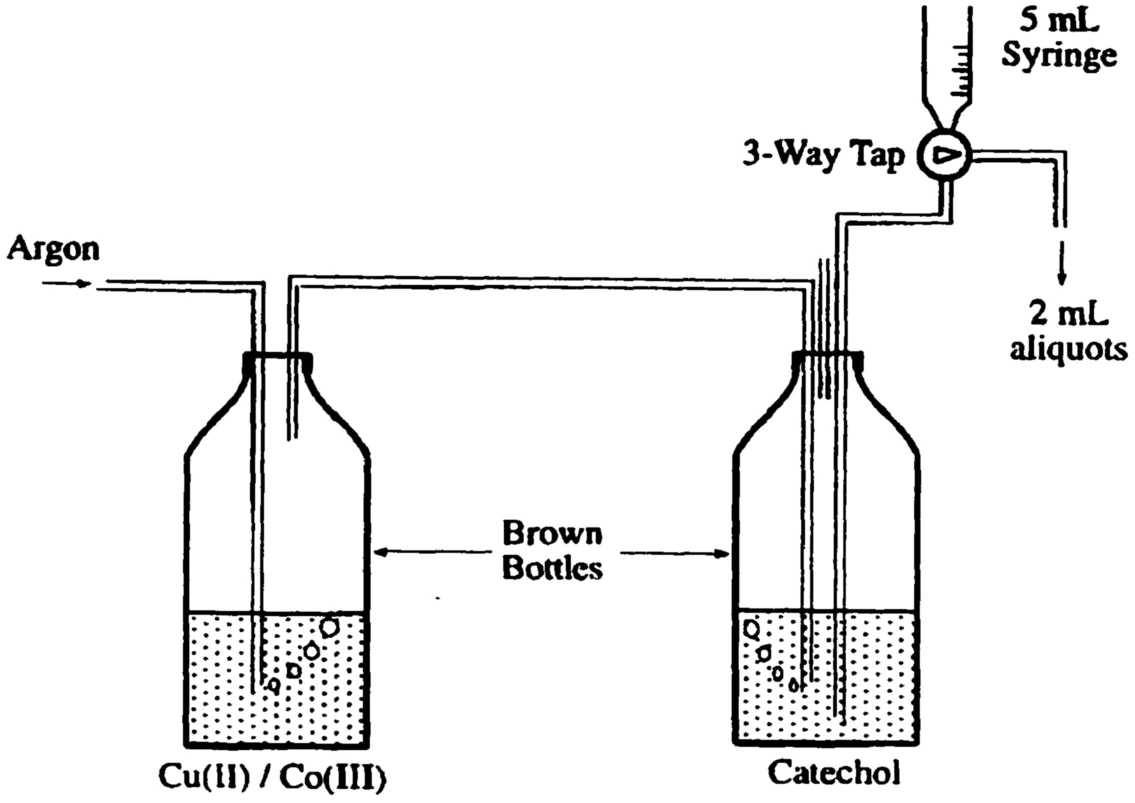


Figure 4.5. Reagent storage, transfer and sampling apparatus.

Periodically, 2.0 mL aliquots of the reaction mixture were withdrawn into the 5.0 mL syringe and transferred to 25 mL volumetric flasks containing 5.0 mL of 0.115 M phosphoric acid. The runs usually consisted of 10 - 15 samples, with time intervals ranging from a few minutes to about an hour. At the end of the run, each sample was treated with 3.0 mL of 2.65 × 10^{-3} M nitroso-R, then 5.0 mL of 3.66 M sodium acetate and finally 5.0 mL 9.30 M hydrochloric acid. The solutions were diluted to 25.0 mL with doubly distilled water. The absorbance of each solution at 525 nm was recorded in a 1 cm cuvet on a Cary 219 spectrophotometer.

A number of concentration variables were studied over the range indicated: catechol (2.00 - 144) × 10^{-4} M; copper (1.44 - 14.4) × 10^{-4} M; cobalt(III) (3.36 - 6.72) × 10^{-4} M; Tiron (1.09 - 12.1) × 10^{-3} M; chloride ion (1.25 -10.0) × 10^{-3} M and pH 6.4 - 7.8.

Results

Kinetic Data Analysis. The absorbances plotted as a function of time for a typical run are shown in Figure 4.6. The general trend of the absorbance-time plots was a linear increase of the absorbances with time for most of the reaction profile then leveling off at the end of the reaction when all the cobalt(III) is consumed. There were cases though where there was some induction period or a gradual leveling off, but for the most part the behavior in Figure 4.6 was observed. The Slopes have been determined by least-squares-fitting of the linear regions of the absorbance-time curves. In general 7 to 10 points were fitted for each run. Because of the expected curvature at the end of the reaction, some points must be rejected for the linear analysis so that there is inevitably some subjectivity in the selection of the data. In general, points with an absorbance within ~15% of the final absorbance were not used.

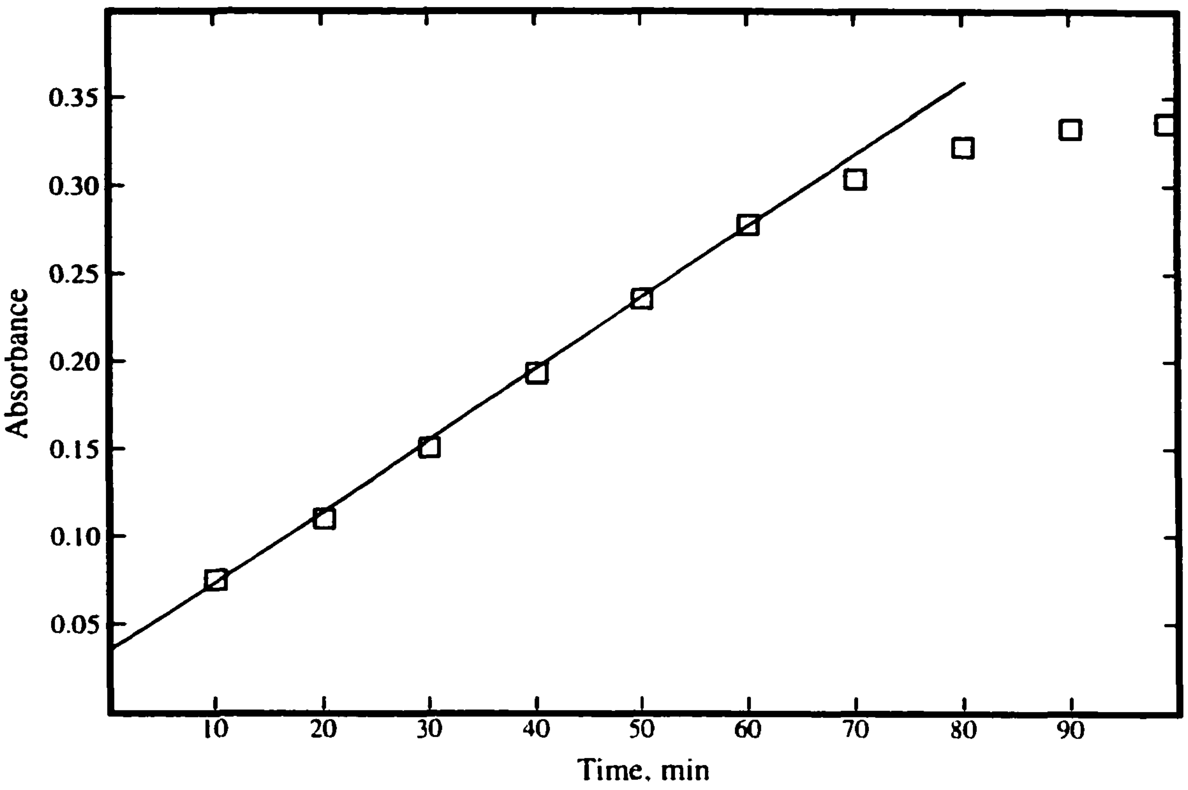


Figure 4.6. Variation with time of the absorbance of cobalt(III)-nitroso-R complex during the oxidation of catechol by copper(II) for a run with 1.64 × 10^{-3} M catechol, 0.718 × 10^{-3} M copper(II), 0.336 × 10^{-3} M cobalt(III), 0.125 M sodium perchlorate, pH 7.00 in 0.025 M HEPES, monitored at 525 nm.

The relationship between the Slope and the rate of formation of cobalt(II) in the reaction mixture is developed through the following steps. From Figure 4.6, in the linear region of the curve,

$$\text{Slope} = \frac{\text{change in absorbance}}{\text{change in time}} = \frac{\Delta\text{Abs}}{\Delta t}. \qquad (4.17)$$

Based on the 2 mL aliquots that were diluted to 25 mL, the cobalt(II) concentration in the cuvet ($[Co^{2+}]'$) is 12.5 times less concentrated than the cobalt(II) ($[Co^{2+}]$) in the reaction mixture. From Beers' law,

$$\text{Absorbance} = \varepsilon l \times [Co^{2+}]' = \frac{\varepsilon l}{12.5}[Co^{2+}] \qquad (4.18)$$

where ε is the extinction coefficient (1.48×10^4 M^{-1} cm^{-1} from this study) and l is the path length (1 cm cuvet used here).

Taking the differential with respect to time of both sides of eq. 4.18 gives an expression that can be equated to eq. 4.17 and rearrangement gives eq. 4.19.

$$\frac{d[Co^{2+}]}{dt} = \frac{12.5}{\varepsilon l}\frac{d\text{Abs}}{dt} = \frac{12.5}{\varepsilon l} \times \text{Slope} \qquad (4.19)$$

Then a consideration of the stoichiometry of the reaction in eq. 4.20,

$$2Co^{III} + H_2A \xrightarrow{Cu^{2+}} 2Co^{II} + Q + 2H^+ \qquad (4.20)$$

shows that

$$\frac{1}{2}\frac{d[Co^{2+}]}{dt} = -\frac{d[H_2A]}{dt} = \frac{12.5 \times Slope}{2\varepsilon l} = 4.22 \times 10^{-4} \times Slope. \quad (4.21)$$

Therefore, the Slope is directly related to the rate of disappearance of catechol; the higher the Slope, the faster the rate of catechol oxidation.

The linear region (constant Slope) results for the conditions of $[H_2A]_t >> [Co^{III}]_t$ and since $[Cu^{2+}]_t$ is always constant because it is regenerated. Then in general, the rate of catechol disappearance is related to the reactant concentrations and the Slope by eq. 4.22, where m, n and p are the orders of the rate with respect to the concentrations of copper(II), catechol and hydrogen ion, respectively.

$$-\frac{d[H_2A]}{dt} = k[Cu^{2+}]^m[H_2A]^n[H^+]^p = 4.22 \times 10^{-4} \times Slope \quad (4.22)$$

The above development has assumed that the rate is not controlled by the oxidation of copper(I) by the cobalt(III) complex. To test this, runs were done with two cobalt(III) concentrations, 0.335 × 10^{-3} and 0.670 × 10^{-3} M, while the concentrations of catechol (2.18 × 10^{-3} M), copper(II) (0.718 × 10^{-3} M) and pH (7.0) were kept constant. The Slope from these two runs (Appendix 4.1) were the same, the only difference being the higher final absorbance recorded for the higher concentration, as expected since more cobalt(II) is produced. The cobalt(II) produced could potentially complex with catechol. Species distribution analysis over the range of catechol concentration and pH in this study indicate insignificant amounts of cobalt(II)-catecholate species and as such they would not have an effect in analyzing the kinetic data.

In principle, the orders can be determined from the variation of the Slope as one concentration variable is changed while the others are kept constant. Before attempting to extract the kinetic order of the rate with respect to the potential reactants, one must take into account the fact that copper(II) is complexed by catechol. There have been several potentiometric studies of this system and the results are summarized in Table 4.1, where the equilibrium constants are defined by eqs. 4.23 and 4.24, and A is the catecholate dianion.

$$K_1^{*} = \frac{[\mathrm{CuA}][\mathrm{H^+}]^2}{[\mathrm{Cu^{2+}}][\mathrm{H_2A}]} \tag{4.23}$$

$$K_2^{*} = \frac{[\mathrm{CuA_2^{2-}}][\mathrm{H^+}]^2}{[\mathrm{CuA}][\mathrm{H_2A}]} \tag{4.24}$$

The above forms of the equilibrium constants, rather than the conventional successive formation constants $K_1 = [\mathrm{MA}]/[\mathrm{M}][\mathrm{A}]$ and $K_2 = [\mathrm{MA_2}]/[\mathrm{MA}][\mathrm{A}]$, have been used because they are directly determined from the potentiometric studies and are independent of the acid dissociation constants of catechol, K_{a1} and K_{a2}. The latter value is especially uncertain because $\mathrm{p}K_{a2} > 12$ and therefore is difficult to determine.

There is a reasonable level of agreement between the various studies on the values of K_1^{*} and K_2^{*}, and for the initial analysis the values of Martell et al.[18a] will be used. The known total concentrations of copper(II) and catechol are given by eqs. 4.25 - 4.28.

$$[\mathrm{Cu^{II}}]_t = [\mathrm{Cu^{2+}}] + [\mathrm{CuA}] + [\mathrm{CuA_2^{2-}}] \tag{4.25}$$

$$= [\mathrm{Cu^{2+}}] + \frac{K_1^{*}[\mathrm{H_2A}][\mathrm{Cu^{2+}}]}{[\mathrm{H^+}]^2} + \frac{K_1^{*}K_2^{*}[\mathrm{H_2A}]^2[\mathrm{Cu^{2+}}]}{[\mathrm{H^+}]^4} \tag{4.26}$$

$$[\mathrm{H_2A}]_t = [\mathrm{H_2A}] + [\mathrm{CuA}] + 2[\mathrm{CuA_2^{2-}}] \tag{4.27}$$

$$= [\mathrm{H_2A}] + \frac{K_1^{\bullet}[\mathrm{H_2A}][\mathrm{Cu^{2+}}]}{[\mathrm{H^+}]^2} + \frac{2K_1^{\bullet}K_2^{\bullet}[\mathrm{H_2A}]^2[\mathrm{Cu^{2+}}]}{[\mathrm{H^+}]^4} \tag{4.28}$$

Unfortunately the experimental conditions in this study do not permit the simplifying assumption that might be made if $[\mathrm{H_2A}]_t \gg [\mathrm{Cu^{II}}]_t$. However, rearrangement of eq. 4.26 gives an expression for $[\mathrm{Cu^{2+}}]$ (eq. 4.29) in terms of $[\mathrm{H_2A}]$, $[\mathrm{H^+}]$, $K_1^{\bullet}$ and $K_2^{\bullet}$ that can be used to substitute for $[\mathrm{Cu^{2+}}]$ in eq. 4.28.

$$[\mathrm{Cu^{2+}}] = \frac{[\mathrm{Cu^{II}}]_t[\mathrm{H^+}]^4}{[\mathrm{H^+}]^4 + K_1^{\bullet}[\mathrm{H^+}]^2[\mathrm{H_2A}] + K_1^{\bullet}K_2^{\bullet}[\mathrm{H_2A}]^2} \tag{4.29}$$

Then substitution of this expression for $[\mathrm{Cu^{2+}}]$ in eq. 4.28 and rearrangement gives the following cubic equation in $[\mathrm{H_2A}]$.

$$\begin{aligned} &K_1^{\bullet}K_2^{\bullet}[\mathrm{H_2A}]^3 + \left(K_1^{\bullet}[\mathrm{H^+}]^2 + 2K_1^{\bullet}K_2^{\bullet}[\mathrm{Cu^{II}}]_t - 2K_1^{\bullet}K_2^{\bullet}[\mathrm{H_2A}]_t\right)[\mathrm{H_2A}]^2 \\ &+ \left([\mathrm{H^+}]^4 + K_1^{\bullet}[\mathrm{H^+}]^2[\mathrm{Cu^{II}}]_t - K_1^{\bullet}[\mathrm{H^+}]^2[\mathrm{H_2A}]_t\right)[\mathrm{H_2A}] - [\mathrm{H^+}]^4[\mathrm{H_2A}]_t = 0 \end{aligned} \tag{4.30}$$

This equation (eq. 4.30) was solved by Newton's iterative method for the various experimental conditions of $[\mathrm{H_2A}]_t$, $[\mathrm{Cu^{II}}]_t$ and $[\mathrm{H^+}]$ to obtain $[\mathrm{H_2A}]_f$ (free catechol) and then $[\mathrm{Cu^{2+}}]_f$ (free copper(II)) from eq. 4.29. Then the values of [CuA] and $[\mathrm{CuA_2^{2-}}]$ were obtained from eq. 4.23 and 4.24. The results are given in Appendices 4.2 - 4.5.

The variation of the Slope with $[Cu^{II}]_t$ is illustrated by the data in Tables 4.4 and 4.5 for pH 7.0 and 6.4, respectively. Simple inspection shows that the Slope increases as the $[Cu^{II}]_t$ increases. In fact, the value of Slope/$[Cu^{II}]_t$ has a reasonably constant value of ~5, implying that the rate is first order in $[Cu^{II}]_t$. However, as noted above, the $[Cu^{II}]_t$ is only indirectly related to the concentrations of the species present, namely $[Cu^{2+}]_f$, [CuA] and $[CuA_2^{2-}]$. It seems probable that if Cu^{2+} is the reactive species, then it must be reacting with H_2A. Therefore Tables 4.4 and 4.5 also give the values of Slope divided by $[Cu^{2+}]_f[H_2A]_f$, [CuA] and $[CuA_2^{2-}]$, respectively. The first two quantities are directly related because $[\mathrm{CuA}] = K_1^{\bullet}[\mathrm{Cu}^{2+}][\mathrm{H_2A}][\mathrm{H}^+]^{-2}$, but both values are given here for future discussion of their magnitude under other conditions. These values are reasonably constant and do not show any systematic trend with $[Cu^{II}]_t$. However, the values of Slope/$[CuA_2^{2-}]$ show a systematic increase with increasing $[Cu^{II}]_t$ with about a factor of 2 variation over the range of $[Cu^{II}]_t$. These observations establish that the reaction is first-order in some copper(II) species, thereby eliminating pathways such as Cu^{2+} + CuA that involve two copper(II) species. The results also suggest that CuA_2^{2-} is not the reactive species and that the dominant pathway involves either Cu^{2+} + H_2A or CuA. In fact, the latter is suggested by the much greater consistency of its ratio between the two pH values.

The variation of the Slope with catechol concentration at pH 7.0 is given in Table 4.6. The results are consistent with the dependence on $[Cu^{II}]_t$ in that the ratios of the Slope/$[Cu^{II}]_f[H_2A]_f$ and Slope/[CuA] are reasonably constant and of the same magnitude as those from the copper(II) dependence in Table 4.4. The values of Slope/$[CuA_2^{2-}]$ now show a much larger variations decreasing by about 75 times as the total catechol increases. This provides a very strong indication that CuA_2^{2-} is not the reactive species. These observations also establish that the reaction is first-order in some catechol species, thereby eliminating pathways such as CuA + H_2A that involve two catechol species.

Table 4.4. Dependence of the Slope on Copper(II) Concentration: 4.36 × 10^{-3} M Catechol, 0.336 × 10^{-3} M Cobalt(III), 0.125 Sodium Perchlorate and pH 7.00 in 0.025 M HEPES.[a]

$10^3[\mathrm{Cu^{II}}]_t$,	10^3Slope[b]	$\frac{\text{Slope}}{[\mathrm{Cu^{II}}]_t}$	$\frac{10^{-6}\,\text{Slope}}{[\mathrm{Cu^{2+}}]_f[\mathrm{H_2A}]_f}$	$\frac{\text{Slope}}{[\mathrm{CuA}]}$	$\frac{10^{-1}\,\text{Slope}}{[\mathrm{CuA_2^{2-}}]}$
0.144	0.622 ± 0.01	4.60	2.35	9.43	0.798
0.360	1.78 ± 0.06	4.96	2.57	10.3	0.949
0.718	2.50 ± 0.08	3.48	1.68	6.76	0.720
0.718	2.66 ± 0.06	3.72	1.78	7.17	0.763
0.861	3.47 ± 0.17	4.03	1.89	7.60	0.859
0.900	3.94 ± 0.14	4.39	2.04	8.19	0.942
1.08	5.48 ± 0.16	5.08	2.27	9.14	1.14
1.08	5.11 ± 0.21	4.74	2.12	8.52	1.07
1.44	7.52 ± 0.23	5.22	2.17	8.73	1.30
1.44	8.27 ± 0.41	5.74	2.39	9.60	1.43

[a] The subscripts t and f denote the total copper(II) concentration and the free (uncomplexed) copper(II) and catechol concentrations at equilibrium, respectively. [b] Error limits are one standard deviation.

Table 4.5. Dependence of the Slope on Copper(II) Concentration: 2.18 × 10^{-3} M Catechol, 0.336 × 10^{-3} M Cobalt(III), 0.125 Sodium Perchlorate and pH 6.4 in 0.025 M HEPES.[a]

$10^3[\mathrm{Cu^{II}}]_t$,	10^3Slope[b]	$\frac{\mathrm{Slope}}{[\mathrm{Cu^{II}}]_t}$	$\frac{10^{-4}\mathrm{Slope}}{[\mathrm{Cu^{2+}}]_f[\mathrm{H_2A}]_f}$	$\frac{\mathrm{Slope}}{[\mathrm{CuA}]}$	$\frac{10^{-2}\mathrm{Slope}}{[\mathrm{CuA_2^{2-}}]}$
0.287	1.41 ± 0.04	4.91	8.24	5.25	1.54
0.287	1.58 ± 0.03	5.51	9.23	5.88	1.72
0.574	2.83 ± 0.04	4.93	8.27	5.27	1.81
0.574	2.92 ± 0.04	5.09	8.53	5.44	1.87
0.718	2.65 ± 0.08	3.69	6.20	3.95	1.49
0.718	3.07 ± 0.07	4.28	7.18	4.57	1.72
0.718	3.10 ± 0.08	4.32	7.25	4.62	1.74
0.718	3.18 ± 0.07	4.43	7.44	4.74	1.78
0.718	4.47 ± 0.12	6.23	10.4	6.65	2.50
0.861	4.85 ± 0.05	5.63	9.48	6.04	2.50

[a] The subscripts t and f denote the total copper(II) concentration and the free (uncomplexed) copper(II) and catechol concentrations at equilibrium, respectively. [b] Error limits are one standard deviation.

Table 4.6. Dependence of the Slope on Catechol Concentration: 0.718 × 10^{-3} M Copper(II), 0.336 × 10^{-3} M Cobalt(III), 0.125 Sodium Perchlorate and pH 7.00 in 0.025 M HEPES.[a]

$10^3[H_2A]_t$,	10^3Slope[b]	$\frac{10^{-6}\text{Slope}}{[Cu^{2+}]_f[H_2A]_f}$	$\frac{\text{Slope}}{[CuA]}$	$\frac{10^{-2}\text{Slope}}{[CuA_2^{2-}]}$
0.800	2.70 ± 0.05	1.00	4.02	1.51
1.09	3.96 ± 0.10	1.52	6.09	0.665
1.64	3.98 ± 0.10	1.70	6.83	0.301
2.18	3.03 ± 0.15	1.43	5.77	0.159
2.72	3.09 ± 0.15	1.77	6.48	0.142
2.72	2.82 ± 0.13	1.47	5.91	0.117
3.27	3.51 ± 0.16	2.01	8.07	0.124
3.82	3.17 ± 0.20	1.97	7.93	0.100
4.36	2.50 ± 0.08	1.68	6.76	0.072
6.54	1.49 ± 0.02	1.31	5.27	0.034
8.72	1.74 ± 0.06	1.90	7.63	0.036
11.6	1.41 ± 0.04	1.93	7.77	0.026
14.4	1.17 ± 0.02	1.92	7.74	0.021

[a] The subscripts t and f denote the total catechol concentration and the free (uncomplexed) copper(II) and catechol concentrations at equilibrium, respectively. [b] Error limits are one standard deviation.

The variation of the Slope with pH should distinguish between whether the reacting species are Cu^{2+} + H_2A or CuA. As the pH increases, there will be more complexation and the concentration of Cu^{2+} and H_2A will decrease and the Slope, i.e. the rate, should decrease. As already noted, the results at pH 7.0 and 6.4 in Tables 4.4 and 4.5, respectively provide a preliminary indication that CuA is the reactant.

The results of a systematic study of the pH dependence are given in Table 4.7. Quantitatively, one should expect that either Slope/$[Cu^{2+}]_f[H_2A]_f$ or Slope/[CuA] will be constant with varying pH, depending on the reactants in the rate-controlling step, and assuming there is only one dominant pathway. The Slope increases moderately between pH 6.4 and 6.8, but then decreases between pH values of 6.8 to 7.4. The values of Slope/$[Cu^{2+}]_f[H_2A]_f$ and Slope/$[CuA_2{}^{2-}]$ increase and decrease, respectively, over several orders of magnitude over the one unit increase in pH, thereby eliminating these reaction pathways. The Slope/[CuA] is fairly constant over the pH range studied and this observation confirms that the reactive species in the reaction mixture is the mono copper(II)-catecholate species. An inspection of the species concentrations reveals that the CuA concentration actually decreases from pH 6.6 to 7.4 due to the formation of $CuA_2{}^{2-}$. This is why the Slope decreases in the higher pH range.

In summary, the dependence of the rate on the copper(II) and catechol concentrations and the pH are all consistent with the reactive species being the mono copper(II)-catecholate complex, CuA. Then the rate and its relationship to the Slope (from eq. 4.22) are given by eq. 4.31.

$$-\frac{d[H_2A]}{dt} = k[CuA] = 4.22 \times 10^{-4} \times \text{Slope} \tag{4.31}$$

Table 4.7. Dependence of the Slope on Hydrogen Ion Concentration: 2.18 × 10^{-3} M Catechol, 0.718 × 10^{-3} M Copper(II), 0.336 × 10^{-3} M Cobalt(III), 0.125 Sodium Perchlorate and 0.025 M HEPES.[a]

pH	10^3Slope[b]	$\frac{10^{-7}\text{Slope}}{[Cu^{2+}]_f[H_2A]_f}$	$\frac{\text{Slope}}{[CuA]}$	$\frac{10^{-2}\text{Slope}}{[CuA_2^{2-}]}$
6.4[c]	2.83 ± 0.04	0.008	5.27	1.81
6.4[c]	2.92 ± 0.04	0.009	5.44	1.87
6.4	2.65 ± 0.08	0.006	3.95	1.49
6.4	3.07 ± 0.07	0.007	4.57	1.72
6.4	3.10 ± 0.08	0.007	4.62	1.74
6.4	3.18 ± 0.07	0.007	4.74	1.78
6.4	4.47 ± 0.12	0.010	6.65	2.50
6.6	3.75 ± 0.09	0.022	5.65	0.873
6.8	3.98 ± 0.08	0.064	6.45	0.414
7.0	3.03 ± 0.15	0.144	5.77	0.159
7.2	2.74 ± 0.04	0.434	6.94	0.085
7.4	1.73 ± 0.05	1.06	6.76	0.038

[a] The subscript f denote the free (uncomplexed) copper(II) and catechol concentrations at equilibrium. [b] Error limits are one standard deviation. [c] The total copper(II) concentration in these runs is 5.74 × 10^{-4} M.

From all the kinetic runs in Tables 4.4, 4.5, 4.6 and 4.7, the average Slope/[CuA] value and standard deviation are 6.68 ± 1.65 M^{-1} min^{-1}. Therefore, the average rate constant after conversion to seconds is $k = (4.7 \pm 1.1) \times 10^{-5}$ s^{-1}.

The conclusion that CuA is the reactive species has implications that can be tested further. If a potential ligand (H_2L) that complexes copper(II) in competition with catechol is added to the system, then the rate should decrease. Tiron (disodium 4,5-dihydroxy 1,3-benzene disulfonic acid) (E^0 = 0.955 V)[5a] was chosen for this test because it closely resembles catechol, but is not oxidized by even stronger oxidants than copper(II), such as iron(III),[16b,30] and its complex formation constants with copper(II) are known.[18] The lack of reactivity of Tiron with copper(II) was demonstrated by an experiment at pH 7.0 with 11.6 × 10^{-3} M Tiron, 0.718 × 10^{-3} M copper(II) and 0.336 × 10^{-3} M cobalt(III). No formation of cobalt(II) was detected after 4.5 hours (Appendix 4.6). If the reactant solution contains a substantial excess Tiron over catechol, then the copper(II) will be complexed by Tiron and one might expect no reaction unless a contribution is made by a pathway involving CuL + H_2A. The later would be unexpected from the rate law derived since CuA + H_2A seems to make no significant contribution. Under the same conditions as before, but with 12.1 × 10^{-3} M Tiron and 2.18 × 10^{-3} M catechol no cobalt(II) was formed after 4.5 hours (Appendix 4.7). Still under the same conditions but with more catechol than Tiron, 2.18 × 10^{-3} and 1.09 × 10^{-3} M, respectively, the absorbances increased albeit very slowly with time and the reaction was complete in ~5.5 hours. This run is compared to one with catechol alone at 2.18 × 10^{-3} M (complete in ~1 hour) in Figure 4.7.

Since CuA has been shown above to be the reactive species in solution, these observations with catechol/Tiron mixtures can be explained based on the relative concentrations of the mono copper(II)-catecholate. Presented in Table 4.8 are the concentrations of the free, mono, and bis copper(II) species for catechol, Tiron and catechol/Tiron mixtures for the experiments just discussed. There is insignificant CuA

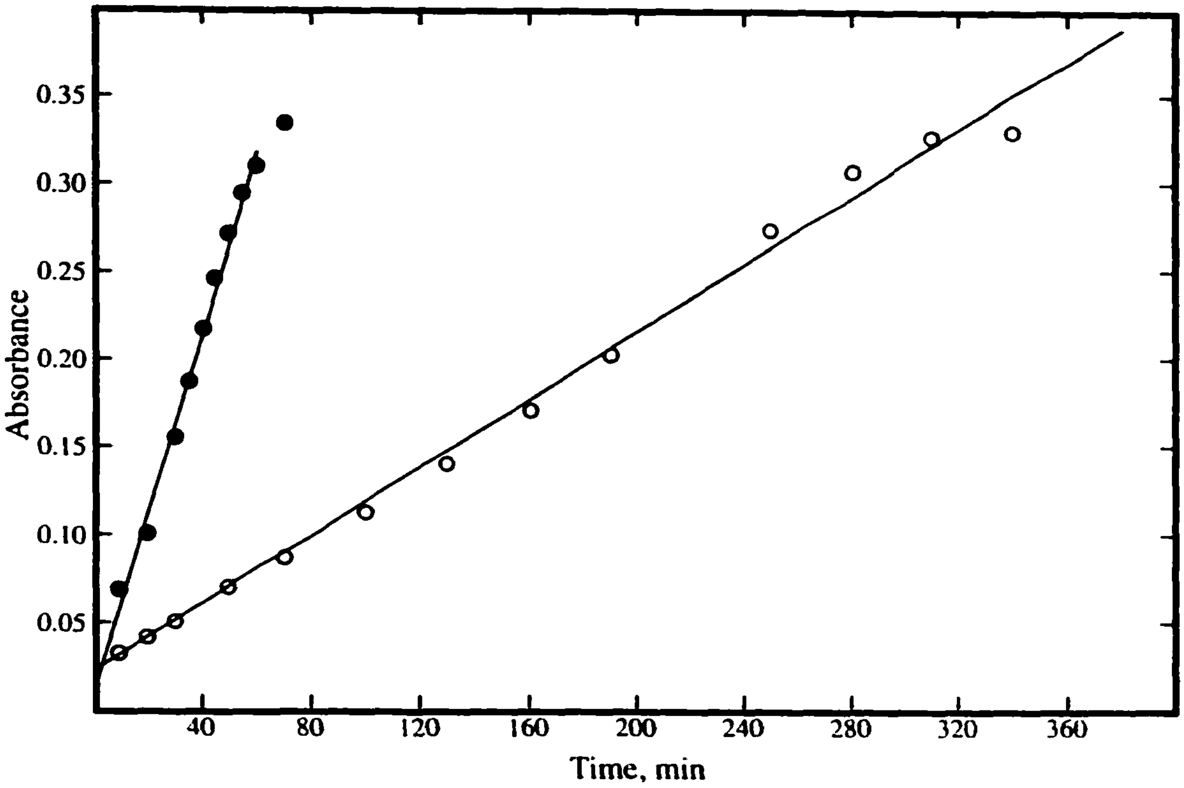


Figure 4.7. Variation with time of the absorbance of cobalt(III)-nitroso-R complex during the oxidation of catechol by copper(II) for runs with; (●) 2.18 × 10^{-3} M catechol and (O) 2.18 × 10^{-3} M catechol, 1.09 × 10^{-3} M Tiron, 0.718 × 10^{-3} M copper(II), 0.336 × 10^{-3} M pentaammineazidocobalt(III), 0.125 M sodium perchlorate, pH 7.00 in 0.025 M HEPES, monitored at 525 nm.

Table 4.8. The Calculated Concentrations of the Free Copper(II) and the Mono and Bis Complexes of Copper(II) with the Catechol and Tiron Dianions at pH 7.00. Total Copper(II) Concentration 7.18 × 10^{-4} M.[a,b]

$10^3[H_2A]_t$, M	$10^6[Cu^{2+}]_f$, M	$10^4[CuA]$, M	$10^4[CuA_2^{2-}]$, M
Catechol[c]			
1.09	8.15	6.50	5.96
2.18	1.66	5.25	1.91
11.6		1.82	5.36
14.4		1.51	5.67
Tiron[c]			
1.09		3.52	3.65
2.18		0.067	7.11
11.6		7.18	
Catechol / Tiron			
2.18 / 1.09		1.24 / 2.69	0.452 / 2.79
1.09 / 2.18		/ 0.066	/ 7.11
2.18 / 12.1			/ 7.18

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[a] The subscripts t and f denotes the total copper(II) concentration and the free (uncomplexed) copper(II) and catechol concentrations in solution, respectively. [b] Values of < 1 × 10^{-6} M are omitted. K_1^* and K_2^* values from; [c] Martell, A. E.; Smith, R. M. *NIST Critical Stability Constants of Metal Complexes Database* **1995**, U.S. Department of Commerce; $\mu = 0.1$ and 25 °C.

(1.48×10^{-10} M) for the run with catechol/Tiron of (2.18/12.1) $\times 10^{-3}$ M and therefore no cobalt(II) formation is observed. On the other hand, for the run with 2.18×10^{-3} and 1.09×10^{-3} M catechol and Tiron, respectively, the increase in absorbance can be attributed to the CuA concentration of 1.24×10^{-4} M. A solution of catechol alone at 2.18×10^{-3} M has a concentration of 5.25×10^{-4} M CuA. One then can estimate the Slope of the catechol/Tiron run based on these CuA concentrations and the average of Slope/[CuA] = 6.68 M^{-1} min^{-1} noted above. The calculated value of 8.3×10^{-4} min^{-1} is in good agreement with the value of 9.3×10^{-4} min^{-1} obtained from fitting the absorbance-time data for the catechol/Tiron run.

Previous work on the somewhat analogous copper(II)-ascorbic acid system found that chloride ion was a potent catalyst for the reaction. To test this possibility with catechol, chloride ion was added to the reaction solution at concentrations between 1.25×10^{-3} and 10.0×10^{-3} M, catechol and copper(II) concentration of 0.618×10^{-3} and 0.718×10^{-3} M, respectively. Sample absorbance-time data are given in Appendix 4.8. There seems to be no noticeable trend of the Slopes with increasing chloride ion concentration. The absence of chloride ion catalysis indicates that there is some mechanistic difference between the ascorbate and catecholate reactions with copper(II).

Discussion

The mono copper(II)-catecholate complex has been shown to be the reactive species in solution. Thus, the reaction must be proceeding through an intramolecular electron-transfer process to give either copper(I) and the catecholate anion radical directly, or a copper(I)-catecholate anion radical adduct, ($Cu^{+}A^{\bullet-}$), that may undergo rapid dissociation to Cu^{+} and $A^{\bullet-}$.

The reaction sequence in eqs. 4.32 - 4.35 is proposed for the mechanism in which the copper(II)-catecholate goes directly to copper(I) and the radical. The formation of

CuA in eq. 4.32 is a rapid equilibrium and Ox is either copper(II) or cobalt(III) and Re is copper(I) or cobalt(II), respectively.

$$\mathrm{Cu^{2+} + H_2A \rightleftarrows CuA + 2H^+} \qquad K_1^{\bullet} = 4.07 \times 10^{-9}\ \mathrm{M} \tag{4.32}$$

$$\mathrm{CuA \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cu^+ + A^{\bullet-}} \tag{4.33}$$

$$\mathrm{Ox + A^{\bullet-} \xrightarrow{k_2} Re + Q} \tag{4.34}$$

$$\mathrm{Co^{III} + Cu^+ \longrightarrow Cu^{2+} + Co^{II}} \qquad k_0 = 1.42 \times 10^3\ \mathrm{M^{-1}s^{-1}} \tag{4.35}$$

The pK_a of the semiquinone radical, HA•, is 5.0[31] so that it is in the fully deprotonated form, $A^{\bullet-}$, under the pH conditions of this study.

If copper(II) is the oxidant in eq. 4.34, then the rate of formation of cobalt(II) can be arrived at through the following steps. The rates of formation and disappearance of copper(I) are given by eqs. 4.36 and 4.37, respectively.

$$\frac{\mathrm{d}[\mathrm{Cu^+}]}{\mathrm{d}t} = k_1[\mathrm{CuA}] + k_2[\mathrm{Cu^{2+}}][\mathrm{A^{\bullet-}}] \tag{4.36}$$

$$\frac{-\mathrm{d}[\mathrm{Cu^+}]}{\mathrm{d}t} = k_0[\mathrm{Cu^+}][\mathrm{Co^{III}}] + k_{-1}[\mathrm{Cu^+}][\mathrm{A^{\bullet-}}] \tag{4.37}$$

If a steady-state is assumed for copper(I), then eq. 4.36 equals eq. 4.37, and the resultant equation can be solved to give the copper(I) concentration as eq. 4.38.

$$[\mathrm{Cu^+}] = \frac{k_1[\mathrm{CuA}] + k_2[\mathrm{Cu^{2+}}][\mathrm{A^{\bullet-}}]}{k_{-1}[\mathrm{A^{\bullet-}}] + k_0[\mathrm{Co^{III}}]} \qquad (4.38)$$

Similarly, if a steady-state is assumed for the catecholate anion radical, then its rates of formation and consumption, as given by eqs. 4.39 and 4.40, respectively are equal.

$$\frac{\mathrm{d}[\mathrm{A^{\bullet-}}]}{\mathrm{d}t} = k_1[\mathrm{CuA}] \qquad (4.39)$$

$$\frac{-\mathrm{d}[\mathrm{A^{\bullet-}}]}{\mathrm{d}t} = k_{-1}[\mathrm{Cu^+}][\mathrm{A^{\bullet-}}] + k_2[\mathrm{Cu^{2+}}][\mathrm{A^{\bullet-}}] \qquad (4.40)$$

These two expressions can be solved for the radical concentration, as given by eq. 4.41.

$$[\mathrm{A^{\bullet-}}] = \frac{k_1[\mathrm{CuA}]}{k_{-1}[\mathrm{Cu^+}] + k_2[\mathrm{Cu^{2+}}]} \qquad (4.41)$$

Substitution for the radical concentration in the second term in the numerator of eq. 4.38 gives the copper(I) concentration as eq. 4.42.

$$[\mathrm{Cu^+}] = \frac{k_1[\mathrm{CuA}]\left(1 + \dfrac{k_2[\mathrm{Cu^{2+}}]}{k_{-1}[\mathrm{Cu^+}] + \mathrm{k}_2[\mathrm{Cu^{2+}}]}\right)}{k_{-1}[\mathrm{A^{\bullet-}}] + k_0[\mathrm{Co^{III}}]} \qquad (4.42)$$

The rate of production of cobalt(II) is given by eq. 4.43,

$$\frac{d[\mathrm{Co^{II}}]}{dt} = k_0[\mathrm{Cu^+}][\mathrm{Co^{III}}] \tag{4.43}$$

and substitution for copper(I) in eq. 4.43 from eq. 4.42 gives eq. 4.44.

$$\frac{d[\mathrm{Co^{II}}]}{dt} = \frac{k_0 k_1[\mathrm{Co^{III}}][\mathrm{CuA}]\left(1 + \dfrac{k_2[\mathrm{Cu^{2+}}]}{k_{-1}[\mathrm{Cu^+}] + k_2[\mathrm{Cu^{2+}}]}\right)}{k_{-1}[\mathrm{A^{\bullet-}}] + k_0[\mathrm{Co^{III}}]} \tag{4.44}$$

This expression reduces to the experimental rate law if $k_{-1}[\mathrm{Cu^+}] << k_2[\mathrm{Cu^{2+}}]$ and $k_{-1}[\mathrm{A^{\bullet-}}] << k_0[\mathrm{Co^{III}}]$ and the predicted rate law is given by eq. 4.45.

$$\frac{d[\mathrm{Co^{II}}]}{dt} = 2k_1[\mathrm{CuA}] \tag{4.45}$$

Similarly, it can be shown that

$$\frac{d[\mathrm{Q}]}{dt} = \frac{k_1 k_2[\mathrm{Cu^{2+}}][\mathrm{CuA}]}{k_{-1}[\mathrm{Cu^+}] + k_2[\mathrm{Cu^{2+}}]}. \tag{4.46}$$

With the condition $k_{-1}[\mathrm{Cu^+}] << k_2[\mathrm{Cu^{2+}}]$, this expression reduces to eq. 4.47 as the predicted rate law.

$$\frac{d[\mathrm{Q}]}{dt} = k_1[\mathrm{CuA}] \tag{4.47}$$

The predicted rate laws in eqs. 4.45 and 4.47 satisfy the cobalt(III):catechol stoichiometric ratio of 2:1.

It should be noted that eq. 4.44 also reduces to the experimental rate law if the second condition is retained, but the first is reversed so that $k_{-1}\left[\mathrm{Cu}^{+}\right] >> k_2\left[\mathrm{Cu}^{2+}\right]$. Then $k_2\left[\mathrm{Cu}^{2+}\right]/k_{-1}\left[\mathrm{Cu}^{+}\right] << 1$ and the predicted rate law is given by eq. 4.48.

$$\frac{\mathrm{d}\left[\mathrm{Co}^{\mathrm{II}}\right]}{\mathrm{d}t} = k_1[\mathrm{CuA}] \qquad (4.48)$$

For the same limiting conditions, the rate of formation of quinone can be derived from eq. 4.46, and the steady-state concentration value of copper(I) given by eq. 4.42 with the appropriate condition applied. The result is given by eq. 4.49.

$$\frac{\mathrm{d}[\mathrm{Q}]}{\mathrm{d}t} = \frac{k_0 k_2}{k_{-1}}\left[\mathrm{Cu}^{2+}\right]\left[\mathrm{Co}^{\mathrm{III}}\right] \qquad (4.49)$$

A comparison of eq. 4.47 and 4.49 indicates that if $k_{-1}\left[\mathrm{Cu}^{+}\right] >> k_2\left[\mathrm{Cu}^{2+}\right]$, then the rate laws for production of cobalt(II) and quinone are different. The former is still controlled by k_1, but the latter depends on k_2. In other words, the rate of oxidation of the radical could be rate limiting for quinone production with the above condition.

If cobalt(III) is the oxidant in eq. 4.34, the rate of production of cobalt(II) can be worked out through similar steps to arrive at eq. 4.50.

$$\frac{\mathrm{d}\left[\mathrm{Co}^{\mathrm{II}}\right]}{\mathrm{d}t} = k_1[\mathrm{CuA}]\left[\mathrm{Co}^{\mathrm{III}}\right]\left(\frac{k_2}{k_{-1}\left[\mathrm{Cu}^{+}\right]+k_2\left[\mathrm{Co}^{\mathrm{III}}\right]}+\frac{k_0}{k_{-1}\left[\mathrm{A}^{\bullet-}\right]+k_0\left[\mathrm{Co}^{\mathrm{III}}\right]}\right) \qquad (4.50)$$

With the assumption that $k_{-1}[\mathrm{Cu}^+] << k_2[\mathrm{Co}^{\mathrm{III}}]$ and $k_{-1}[\mathrm{A}^{\bullet-}] << k_0[\mathrm{Co}^{\mathrm{III}}]$, eq. 4.50 reduces to eq. 4.45. Thus the same rate law is derived whether copper(II) or cobalt(III) act as the oxidant in eq. 4.34. In this case reversal of the first condition gives the observed rate if $[\mathrm{Co}^{\mathrm{III}}]^{-1} >> k_2/k_{-1}[\mathrm{Cu}^+]$, which is equivalent to the assumption made that $k_{-1}[\mathrm{Cu}^+] >> k_2[\mathrm{Co}^{\mathrm{III}}]$.

The assumptions made in the above derivations may be tested in various ways. As a first step in this process the equilibrium constant for eq. 4.33 will be calculated, and then k_{-1} will be obtained. One test of the mechanism is that k_{-1} should not exceed the diffusion controlled limit. If it does, then the mechanism must be abandoned.

An important factor in estimating the equilibrium constant for eq. 4.33 is the reduction potential for eq. 4.51, ($E^0(\mathrm{HA}^\bullet/\mathrm{H_2A})$).

$$\mathrm{HA}^\bullet + \mathrm{H}^+ + \mathrm{e} \rightleftharpoons \mathrm{H_2A} \qquad (4.51)$$

Mentasti et al.[32] estimated this value by first noting that, for 1,4-dihydroxybenzene systems, the difference between the overall two-electron reduction of the quinone ($E^0(\mathrm{A/H_2A})$) and the one-electron reduction of the semiquinone ($E^0(\mathrm{HA}^\bullet/\mathrm{H_2A})$) was 0.38 V. They assumed the same difference would apply to the 1,2-dihydroxybenzene systems, and this gives ($E^0(\mathrm{HA}^\bullet/\mathrm{H_2A})$) = 0.792 + 0.38 = 1.17 V, for catechol. Steenken and Neta[33] measured the equilibrium constant in the catechol-hydroquinone system at pH 13.5, and based on ($E^0(\mathrm{A}^{-\bullet}/\mathrm{A}^{2-})$) = 0.023 V for hydroquinone, obtained (($E^0(\mathrm{A}^{-\bullet}/\mathrm{A}^{2-})$) = 0.043 V for catechol. This can be combined with the acid dissociation constant of $\mathrm{HA}^\bullet$ ($\mathrm{p}K_a = 5.0$) determined by Steenken and O'Neil[31], and the first and second acid dissociation constants of catechol (Table 4.1) to obtain ($E^0(\mathrm{HA}^\bullet/\mathrm{H_2A})$) = 1.06 V. Kimura et al.[17] used oxidation kinetics in acidic solution and Marcus theory to obtain the reduction potential of the fully protonated species as ($E^0(H_2A^{\bullet+}/H_2A)$) = 1.10 V for catechol. This can be combined with the acid dissociation constant of $H_2A^{\bullet+}$ ($K_a \approx 10$)[34] to obtain ($E^0(HA^\bullet/H_2A)$) = 1.04 V.

Each of the above estimates of ($E^0(HA^\bullet/H_2A)$) is based on some approximation or approximately known equilibrium constant(s). The fact that the last two values are in good agreement and are derived from quite different approaches suggest that it is reasonable to take ($E^0(HA^\bullet/H_2A)$) = 1.05 V. As an interesting consequence, this value can be combined with two-electron reduction potential to obtain the one-electron reduction potential for the quinone ($E^0(A/HA^\bullet)$), as 0.53 V.

With ($E^0(HA^\bullet/H_2A)$) = 1.05 V, one can calculate the equilibrium constant for eq. 4.33 as 2.1×10^{-12} M by combining eq. 4.51, 4.52, 4.53 and the standard complexation reaction (eq. 4.32).

$$HA^\bullet \rightleftarrows A^{\bullet -} + H^+ \qquad pK_a = 5.0 \qquad (4.52)$$

$$Cu^{2+} + e \rightleftarrows Cu^+ \qquad E^0 = 0.153 \quad V \qquad (4.53)$$

The experimental value of $k_1 = 4.7 \times 10^{-5}$ s^{-1} can be divided by this equilibrium constant value to obtain $k_{-1} = 2.2 \times 10^7$ $M^{-1}s^{-1}$. This value is substantially below the expected diffusion controlled limit of 10^9 - 10^{10} $M^{-1}s^{-1}$. The magnitude of k_{-1} is not unexpected because one of the reactants is a radical. Meyerstein et al.[35] have measured rate constant values of (2 - 4) × 10^9 $M^{-1}s^{-1}$ for the reaction of aqueous copper(I) with the radicals $\bullet CH_3$, $\bullet CH_2COOH$, $\bullet CHMeCOOH$ and $\bullet CH_2CH_2COOH$. These are consistent with the estimate for k_{-1}.

For the assumptions that $k_{-1}[Cu^+] << k_2[Cu^{2+}]$ and $k_{-1}[A^{\bullet -}] << k_0[Co^{III}]$, the copper(I) concentration is given by eq. 4.54 for copper(II) as the oxidant in eq. 4.34.

$$\left[\mathrm{Cu}^{+}\right]=\frac{2k_1[\mathrm{CuA}]}{k_0\left[\mathrm{Co}^{\mathrm{III}}\right]} \tag{4.54}$$

One can estimate the copper(I) concentration since the values of k_1 (4.7×10^{-5} s^{-1}), k_0 (1.42×10^{3} M^{-1} s^{-1}) and the initial cobalt(III) concentration (3.36×10^{-4} M) are known and the CuA concentration is typically 10^{-4} M. This gives a copper(I) concentration of ~2×10^{-8} M.

It is possible to obtain a lower limit of k_2 from the inequality $k_{-1}\left[\mathrm{Cu}^{+}\right] << k_2\left[\mathrm{Cu}^{2+}\right]$ by using the above estimates for k_{-1} and copper(I) concentration and a typical value of 10^{-6} M for copper(II). This gives $k_2 >> 4.4 \times 10^{5}$ M^{-1} s^{-1}. Meyerstein and Cohen[36] have measured rate constants for the reaction of aqueous copper(II) with $\cdot$CH$_2$OH, $\mathrm{CH_3\dot{C}HOH}$, $\mathrm{(CH_3)_2\dot{C}OH}$ and found values in the range of $(0.45 - 1.1) \times 10^{8}$ M^{-1} s^{-1}. These are consistent with the lower limit estimate of k_2.

A similar estimate can be made if cobalt(III) (3.36×10^{-4} M) is the oxidant. From the inequality $k_{-1}\left[\mathrm{Cu}^{+}\right] << k_2\left[\mathrm{Co}^{\mathrm{III}}\right]$, one obtains $k_2 >> 1.3 \times 10^{3}$ M^{-1} s^{-1}. Meyerstein and Cohen[36] have also measured rate constants for the reaction of hexaamminecobalt(III) in aqueous solutions for the above radicals and have reported values in the range $(0.13 - 1.4) \times 10^{8}$ M^{-1} s^{-1}. These rate constants are consistent with the lower limit estimate of k_2. If the opposite assumption i.e. $k_{-1}\left[\mathrm{Cu}^{+}\right] >> k_2\left[\mathrm{Co}^{\mathrm{III}}\right]$ is tested in the same way one obtains an upper limit of $k_2 << 1.3 \times 10^{3}$ M^{-1} s^{-1}. This is $>10^{5}$ times smaller than the values of Meyerstein and Cohen,[36] and therefore it seems this alternative assumption is unreasonable.

It is also possible to test the assumption that $k_{-1}\left[\mathrm{A}^{\bullet-}\right] << k_0\left[\mathrm{Co}^{\mathrm{III}}\right]$. The value of the catecholate anion radical concentration can be estimated from eq. 4.41, after applying the condition established above that $k_{-1}\left[\mathrm{Cu}^{+}\right] << k_2\left[\mathrm{Cu}^{2+}\right]$. The results of the Meyerstein and Cohen[36] indicate that $k_2 \approx 1 \times 10^8$ M^{-1} s^{-1}, and this combined with the known values of k_1 (4.7×10^{-5} s^{-1}), copper(II)-catecholate concentration (~10^{-4} M) and copper(II) concentration (~10^{-6} M), gives $[A^{\bullet-}] \approx 5 \times 10^{-11}$ M. Then $k_{-1}\left[A^{\bullet-}\right] \approx 1.1 \times 10^{-3}$, which is much smaller than $k_0[\mathrm{Co^{III}}] \approx 5 \times 10^{-1}$, as required by the original assumption.

In summary, this analysis has shown that the assumptions required to convert eq. 4.44 to 4.45 are reasonable. It also has been possible to provide an estimate of $k_{-1} \approx 2.2 \times 10^7$ M^{-1}s^{-1} and a lower limit of $k_2 >> 4.4 \times 10^5$ M^{-1} s^{-1}.

The reaction could also be proceeding through the copper(I)-catecholate anion radical complex, ($\mathrm{Cu^+A^{\bullet-}}$), as described by the following reactions; where Ox is either copper(II) or cobalt(III) and Re is copper(I) or cobalt(II), respectively. It is assumed $A^{\bullet-}$ is being oxidized in eq. 4.57.

$$\mathrm{Cu^{2+} + H_2A \rightleftarrows CuA + 2H^+} \qquad K_1^{*} = 4.07 \times 10^{-9}\ \mathrm{M} \tag{4.55}$$

$$\mathrm{CuA} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \left(\mathrm{Cu^+A^{\bullet-}}\right) \tag{4.56}$$

$$\mathrm{Ox} + \left(\mathrm{Cu^+A^{\bullet-}}\right) \xrightarrow{k_4} \mathrm{Re + Cu^+ + Q} \tag{4.57}$$

$$\mathrm{Co^{III} + Cu^+ \longrightarrow Cu^{2+} + Co^{II}} \qquad k_0 = 1.42 \times 10^3\ \mathrm{M^{-1}s^{-1}} \tag{4.58}$$

The CuA ↔ ($\mathrm{Cu^+A^{\bullet-}}$) tautomerism in eq. 4.56 has been observed in studies involving copper(II) with various ancillary ligands, (L), and catechol derivatives, (A'). The ancillary ligands strongly influence the position of the tautomeric equilibrium. Nitrogen donor ligands favor the [(L)CuA'] form, whereas typical π-acceptor ligands with soft donor atoms such as triorganophosphanes and -arsanes, carbon monoxide or isocyanides favor $[\mathrm{(L)Cu^+A'^{\bullet-}}]$.[37-39] It is expected in this study that the equilibrium will favor the copper(II)-

catecholate complex form since the H_2O ligands on copper(II) are neither soft nor π-acceptors.. Therefore, the equilibrium constant for eq. 4.56 will be expected to be < 1.

If copper(II) is the oxidant in eq. 4.57, then the rates of formation and disappearance of copper(I) are given by eqs. 4.59 and 4.60, respectively.

$$\frac{d[Cu^+]}{dt} = 2k_4[Cu^{2+}][(Cu^+A^{\bullet-})] \qquad (4.59)$$

$$\frac{-d[Cu^+]}{dt} = k_0[Cu^+][Co^{III}] \qquad (4.60)$$

If a steady-state is assumed for copper(I), then eq. 4.59 equals eq. 4.60, and the resultant equation can be solved for the copper(I) concentration, as given by eq. 4.61.

$$\left[Cu^+\right] = \frac{2k_4\left[(Cu^+A^{\bullet-})\right]\left[Cu^{2+}\right]}{k_0\left[Co^{III}\right]} \qquad (4.61)$$

Similarly, a steady-state may be assumed for the copper(I)-catecholate anion radical, where the rates of formation and consumption are given by eqs. 4.62 and 4.63, respectively.

$$\frac{d\left[(Cu^+A^{\bullet-})\right]}{dt} = k_3\left[CuA\right] \qquad (4.62)$$

$$\frac{-d\left[(Cu^+A^{\bullet-})\right]}{dt} = k_{-3}\left[(Cu^+A^{\bullet-})\right] + k_4\left[Cu^{2+}\right]\left[(Cu^+A^{\bullet-})\right] \qquad (4.63)$$

Equating these two equations and solving for the copper(I)-catecholate anion radical concentration gives eq. 4.64.

$$\left[\left(\mathrm{Cu^+A^{\bullet-}}\right)\right] = \frac{k_3[\mathrm{CuA}]}{k_{-3} + \mathrm{k}_4\left[\mathrm{Cu^{2+}}\right]} \tag{4.64}$$

Then substitution of the right-hand-side of eq. 4.64 for the $\left[\left(\mathrm{Cu^+A^{\bullet-}}\right)\right]$ term in eq. 4.61 gives the copper(I) concentration as eq. 4.65.

$$\left[\mathrm{Cu^+}\right] = \frac{2k_3k_4[\mathrm{CuA}]\left[\mathrm{Cu^{2+}}\right]}{k_0\left[\mathrm{Co^{III}}\right]\left(k_{-3} + k_4\left[\mathrm{Cu^{2+}}\right]\right)} \tag{4.65}$$

The rate of production of cobalt(II) is given by eq. 4.66,

$$\frac{\mathrm{d}\left[\mathrm{Co^{II}}\right]}{\mathrm{d}t} = k_0\left[\mathrm{Cu^+}\right]\left[\mathrm{Co^{III}}\right] \tag{4.66}$$

and substitution for copper(I) in eq. 4.66 from eq. 4.65 gives eq. 4.67.

$$\frac{\mathrm{d}\left[\mathrm{Co^{II}}\right]}{\mathrm{d}t} = \frac{2k_3k_4k_0[\mathrm{CuA}]\left[\mathrm{Cu^{2+}}\right]\left[\mathrm{Co^{III}}\right]}{k_0\left[\mathrm{Co^{III}}\right]\left(k_{-3} + k_4\left[\mathrm{Cu^{2+}}\right]\right)} \tag{4.67}$$

The rate law determined experimentally dictates that $k_{-3} << k_4\left[\mathrm{Cu^{2+}}\right]$ so that eq. 4.67 reduces to eq. 4.68.

$$\frac{d[Co^{II}]}{dt} = 2k_3[CuA] \tag{4.68}$$

Alternatively, if cobalt(III) is the oxidant in eq. 4.57, the rate of production of cobalt(II) can be worked out through similar steps to arrive at eq. 4.69.

$$\frac{d[Co^{II}]}{dt} = \frac{k_3k_4[CuA][Co^{III}]}{k_{-3} + k_4[Co^{III}]} + \frac{k_3k_0[CuA][Co^{III}]}{k_{-3} + k_0[Co^{III}]} \tag{4.69}$$

As in the previous cases, the observed rate law dictates that $k_{-3} << k_4[Co^{III}]$ and $k_{-3} << k_0[Co^{III}]$ so that eq. 4.69 reduces to eq. 4.68.

The inequality $k_{-3} << k_0[Co^{III}]$ can be combined with the known values of k_0 (1.42×10^3 $M^{-1}s^{-1}$) and cobalt(III) concentration (3.36×10^{-4} M) to obtain the upper limit of << 0.5 s^{-1}. This value can be divided into k_3 (4.7×10^{-5} s^{-1}) to give the lower limit of $K_3 >> 1 \times 10^{-4}$. This is consistent with the earlier suggestion that $K_3 < 1$ for ancillary aqua ligands on copper(II).

A question remains however as to whether it is reasonable that K_3 is much greater than 10^{-4}. The only quantitative values for such tautomeric equilibria are those reported by Kaim and co-workers[37] with the S, N-donor bidentate ancillary ligand 1-methyl-2-(methylthiomethyl)-1H-benzimidazole and derivatives of 3-tert-butyl-1,2-dihydroxybenzene. They report values of K_3 in the range of $(< 0.8 - 8.6) \times 10^{-2}$ for three catechols in THF at 300K. The values correlate qualitatively with the oxidizability of the catechol derivative in that electron-donating substituents favor the ($Cu^+A^{\bullet-}$) tautomer. The system closest to catechol is 3-tert-butyl-5-methyl-1,2-dihydroxybenzene, with a K_3 of $< 8 \times 10^{-3}$. Based on the substituent effects, one would expect a smaller value for catechol, and this puts into jeopardy the requirement of the kinetic scheme that $K_3 >> 10^{-4}$.

The preceding arguments do not take into account the ancillary ligand effect on K_3. In earlier work, Kaim and Rall[40] have shown that an N,N-donor methylimidazole chelate gives only the CuA tautomer while bi and tri-dentate S-donor ligands give only the ($Cu^+A^{\bullet-}$) tautomer. Based on these observations they projected, apparently correctly, that the S,N-donor ligands described in the previous paragraph might produce a measurable mixture of the tautomers. All of these observations are consistent with the general picture that soft donor atoms, S- in this case, favor the ($Cu^+A^{\bullet-}$) form. A consideration of the copper(II)/(I) reduction potential for simple systems also suggests that replacing N- by O-donor ligands favors the cooper(II) state. For example, the E^0 for copper(II)/(I)(py), and copper(II)/(I)$(OH_2)_n$ are 0.30 and 0.15 V, respectively. These observations lead to the expectation that K_3 with aqua ligands would be substantially smaller than the $< 8 \times 10^{-3}$ estimated above for the S, N-donor ligand system with catechol. This makes it appear even more unlikely that $K_3 >> 10^{-4}$.

On the other hand, it must be noted that Dooley and co-workers[39,41] have identified the ($Cu^+A^{\bullet-}$) tautomer from the EPR and electronic spectra of several amine oxidases under anaerobic conditions with topa (3-(2,4,5-trihydroxyphenyl)-L-alamine). They suggest that the tautomeric equilibrium constants are ~1. In these enzymes, the copper(II) is believed to have three N-donor imidazole ligands from histidine in the peptide and two water ligands in the absence of substrate. One significant difference between topa and catechol is that the reduction potential of the topa radical to the anion has been estimated to have $E^0(topaO^\bullet/topaO^-) = 0.04$ V,[42] while for catechol, the previously mentioned results for $E^0(A^{\bullet-}/A^{2-})$, the pK_a of $HA^\bullet$ and the second pK_a of catechol (~13) can be combined to obtain $E^0(A^\bullet/A^-) \approx 0.5$ V. Thus the conversion of the topa anion to the radical is much more favorable than the corresponding reaction with catechol, and this factor alone makes the ($Cu^+topaO^\bullet$) tautomer ~10^8 times more favorable than the corresponding catechol reaction. This calculation removes the apparent dichotomy between the biochemical and simple inorganic systems, and still suggests a K_3 >> 10^{-4} seems unlikely in our system.

With the above estimate of k_{-3}, it also is possible to determine if reasonable values of k_4 will satisfy the inequalities that $k_{-3} << k_4\left[\mathrm{Cu}^{2+}\right]$ or $k_{-3} << k_4\left[\mathrm{Co}^{\mathrm{III}}\right]$. For copper(II) (~$10^{-6}$ M) or cobalt(III) (3.36×10^{-4} M) the estimated limits for k_4 are > 5×10^4 and > 2×10^3, respectively. These values are consistent with those of 10^7 - 10^8 $\mathrm{M^{-1}s^{-1}}$ determined by Meyerstein and Cohen[36] for organic radical reacting with such oxidants.

There is a possible ambiguity in the k_4 step because the ($\mathrm{Cu^+A^{\bullet-}}$) complex has two centers that might be oxidized, either $\mathrm{A^{\bullet-}}$ or $\mathrm{Cu^+}$. The former is assumed to be the case in eq. 4.54 and the above discussion. In the latter case, the sequence of reactions is described by eqs. 4.55, 4.56, and 4.70 - 4.73.

$$\mathrm{Co^{III}} + \left(\mathrm{Cu^+A^{\bullet-}}\right) \xrightarrow{k'_4} \mathrm{Co^{II}} + \mathrm{Cu^{II}} + \mathrm{A^{\bullet-}} \qquad (4.70)$$

$$\mathrm{Co^{III}} + \mathrm{A^{\bullet-}} \xrightarrow{k_5} \mathrm{Co^{II}} + \mathrm{Q} \qquad (4.71)$$

$$\mathrm{Cu^{2+}} + \mathrm{A^{\bullet-}} \xrightarrow{k'_5} \mathrm{Cu^{+}} + \mathrm{Q} \qquad (4.72)$$

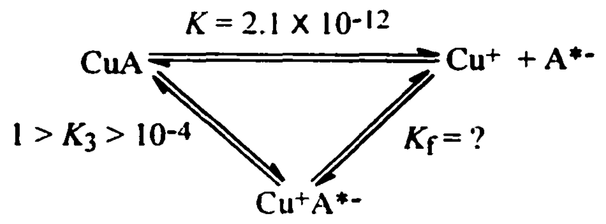
$$\mathrm{Co^{III}} + \mathrm{Cu^{+}} \longrightarrow \mathrm{Co^{II}} + \mathrm{Cu^{2+}} \qquad k_0 = 1.42 \times 10^3\ \mathrm{M^{-1}s^{-1}} \qquad (4.73)$$

If a steady-state is assumed for ($\mathrm{Cu^+A^{\bullet-}}$), $\mathrm{A^{\bullet-}}$ and $\mathrm{Cu^+}$, then it can be shown that the rate of production of cobalt(II) is given by eq. 4.74.

$$\frac{\mathrm{d}\left[\mathrm{Co^{II}}\right]}{\mathrm{d}t} = \frac{2k_3k'_4\left[\mathrm{Co^{III}}\right]\left[\mathrm{CuA}\right]}{k_{-3} + k'_4\left[\mathrm{Co^{III}}\right]} \qquad (4.74)$$

This expression reduces to the experimental rate law if $k_{-3} << k'_4\left[\mathrm{Co^{III}}\right]$. With the expectation that $K_3 < 1$ and the experimental result that $k_3 = 4.7 \times 10^{-5}$ s^{-1}, one can conclude that $k_{-3} > 5 \times 10^{-5}$ s^{-1}. Then, with a cobalt(III) concentration of 3.36×10^{-4} M, the condition will be satisfied if $k'_4 >> 0.15$ M^{-1} s^{-1}. There are no precedents for the reaction of ($\mathrm{Cu^+A^{\bullet-}}$) with a pentaamminecobalt(III) complex, but the lower limit on k'_4 has a rather modest magnitude compared, for example, to $k_0 = 1.42 \times 10^3$ M^{-1} s^{-1} for the reaction of aqueous copper(I) with azidopentaammine-cobalt(III) complex.

As a final test of the reaction pathway involving ($\mathrm{Cu^+A^{\bullet-}}$), one can estimate the formation constant of this complex from the following cycle.



From this cycle, $K_f = K_3/2 \times 10^{-12}$, and the limits on K_3 give $5 \times 10^{11} > K_f >> 5 \times 10^7$ M^{-1}. The question is whether a value of K_f of this magnitude is reasonable for this copper(I) complex. For comparison, one may look at the formation constants for various copper(I) complexes in Chapter 3. One finds that these values generally are in the range of $10^2 - 10^4$ M^{-1}. It is especially noteworthy that no detectable complexation was found with the catechol derivative Tiron with aqueous copper(I). Therefore, it appears that a value of K_f in the range of $10^8 - 10^{11}$, as required by the above cycle, would be quite anomalous. Of course, it can be argued that there is something special about the interaction of a radical anion and copper(I). However, there is no evidence for such an interaction from studies of Meyerstein et al.[35] on the reaction of aqueous copper(I) with various radicals.

The general conclusion from this analysis is that the complex ($\mathrm{Cu^+A^{\bullet-}}$) is not a significant intermediate for the oxidation of catechol by aqueous copper(II). The species is just too unstable relative to either CuA or $Cu^+ + A^{\bullet -}$. This is not to say that it could not be a viable intermediate for analogous reactions with a much more easily oxidized catechol derivative, and/or with ancillary ligands on copper(II) that would stabilize the copper(I) oxidation state.

In conclusion, the mechanism that proceeds from CuA to $Cu^+ + A^{\bullet -}$ is consistent with the experimental rate law and the relative rate constant assumptions needed to bring about this correspondence are all consistent with the known thermodynamic and kinetic results from other studies.

Using Marcus theory, one can estimate the rate constant for an outer-sphere mechanism for the reaction in eq. 4.75.

$$Cu^{2+} + H_2A \rightleftharpoons Cu^+ + H_2A^{\bullet +} \tag{4.75}$$

The redox potentials for copper(II/I) and $H_2A^{\bullet +}/H_2A$[17] are 0.153 and 1.1 V, respectively. The self-exchange rate constants for copper(II/I)[43] and $H_2A^{\bullet +}/H_2A$[16,17] are 5×10^{-7} and 3×10^7 M^{-1} s^{-1}, respectively. Using these values, one calculates that the rate constant of the reaction for eq. 4.75 to be 4×10^{-8} M^{-1} s^{-1}, whereas the experimental values range from 7×10^{-2} - 7 M^{-1} s^{-1} (Tables 4.4 - 4.6). Since the experimental rate constants are considerably larger than that calculated using the Marcus theory, the reaction is not going through this outer-sphere pathway i.e. this pathway contributes negligibly to the overall rate constant.

The study that appears most closely related to the present work is that of Jameson et al.[7] on the reaction of copper(II) and catechol in the presence of dioxygen. This is commonly referred to as the copper(II) catalyzed autoxidation of catechol. To first appearances these two studies appear to differ essentially in that different oxidizing agents are used as scavengers for copper(I). There are what might be more superficial differences in that the study of Jameson et al.[7] is at somewhat lower pH (4.6 - 5.7), and higher catechol concentration (0.02 - 0.20 M) and the copper(II) concentration was slightly greater (0.5 - 2.0 mM). In both studies the rate was determined from the disappearance of the scavenger, O_2 or $[(NH_3)_5CoN_3]^{2+}$.

Despite the apparently analogous complementary conditions, the rate law proposed by Jameson et al.[7] is entirely different from that found here. One difference is that the autoxidation is apparently half-order in dioxygen concentration while it is found to be independent of $[(NH_3)_5CoN_3]^{2+}$ here. Jameson et al.[7] also found that the rate law has terms that are both first- and second-order in the total copper(II) concentration, while a simple first-order dependence is found here. They also claim that the rate depends on the concentration of both the mono- and bis-catecholate complexes of copper(II), while only the former is found to be reactive here.

Before discussing the possible effects of the chemical and kinetic differences of the scavengers, the dependence on the copper(II) species will be analyzed. Jameson et al.[7] have tabulated the k_{obsd} values for a number of runs at varying catechol concentrations and pH values and constant total copper(II) (2.0×10^{-3} M). If these k_{obsd} are divided by the initial copper(II)-catecholate concentration one finds that this ratio has a nearly constant value of $(2.61 \pm 0.35) \times 10^{-2}$ $M^{-1/2}$ s^{-1}. The major deviations are at pH 4.60 which may indicate some systematic error. Actually the k_{obsd} values divided by the full rate law of Jameson et al.[7] do not give quotients that are more constant than those obtained from the analysis just described.

The scavengers used here ($[(NH_3)_5CoN_3]^{2+}$) and in the study of Jameson et al. (O_2) have a few similarities, but many more differences. The latter may be the source of the greatly different rate laws. Both scavengers are thought to react with aqueous copper(I) by an inner-sphere electron transfer mechanism.[10,36] They differ in that the cobalt(III) complex is a one electron oxidant yielding chemically unreactive cobalt(II), while O_2 is an overall two- or four-electron oxidant giving the very reactive superoxide radical as a one-electron reduction product and subsequently H_2O_2 and finally water. As a result, the O_2 system is potentially much more complex.

In order to assess whether the observations here and those of Jameson et al.[7] are really incompatible, a reaction scheme that combines key features of both proposed mechanisms was analyzed. The scheme has been kept as simple as possible in that it assumes only CuA as the initially reactive species and incorporates only one of a number of possibilities for the fate of the $A^{\bullet-}$ radical. It includes the (CuO_2^+) complex, but treats it as a steady-state intermediate, rather than an equilibrium species. It should be noted that combining rapid-equilibrium and steady-state assumptions, as was done by Jameson et al.,[7] is a dangerous practice, and the development here follows the steady-state procedure normally used for chain reactions.[44]

The scheme is given by the reactions in eqs. 4.76 - 4.80.

$$CuA \xrightarrow{k_1} Cu^+ + A^{\bullet-} \tag{4.76}$$

$$Cu^+ + O_2 \underset{k_{-c}}{\overset{k_c}{\rightleftarrows}} CuO_2^+ \tag{4.77}$$

$$CuO_2^+ + CuA \xrightarrow{k_2} Cu^+ + Cu^{2+} + O_2^{2-} + Q \tag{4.78}$$

$$Cu^{2+} + A^{\bullet-} \xrightarrow{k_3} Cu^+ + Q \tag{4.79}$$

$$CuO_2^+ + Cu^+ \xrightarrow{k_5} 2Cu^{2+} + O_2^{2-} \tag{4.80}$$

For the sake of simplicity, the proton equilibria that would convert $A^{\bullet-}$ to $HA^{\bullet}$ and O_2^{2-} to H_2O_2 have been omitted. The reaction of $A^{\bullet-}$ with Cu^{2+} (k_3) has been selected because Cu^{2+}, in various forms, is the dominant oxidant in solution compared to the other possibilities such as CuO_2^+ or O_2. The steady-state condition for the formation and disappearance of the radical gives eq. 4.81,

$$k_3[Cu^{2+}][A^{\bullet-}] = k_1[CuA] \tag{4.81}$$

from which $[A^{\bullet-}]$ can be determined and then used when combining the steady-state conditions for $[Cu^+]$ and $[CuO_2^+]$ to obtain eq. 4.82.

$$k_5[Cu^+][CuO_2^+] = k_1[CuA] \tag{4.82}$$

This allows one to express $[CuO_2^+]$ in terms of $[Cu^+]$, and substitution for $[CuO_2^+]$ into the steady-state equation for $[CuO_2^+]$ gives a quadratic in $[Cu^+]$ of the general form,

$$a[Cu^+]^2 - b[Cu^+] - c = 0 \tag{4.83}$$

where $a = k_e k_5[O_2]$, $b = k_1 k_5[CuA]$ and $c = k_1(k_{-e} + k_2[CuA])[CuA]$. In principle, the solution of eq. 4.83 could be used in the previous equation (eq. 4.82) to solve for $[CuO_2^+]$ in terms of known species. However, this obviously leads to a complex equation and only the simple limiting-case roots will be considered here. Positive roots of the quadratic can only be obtained if either $b^2 >> 4ac$ or $4ac >> b^2$. In the former case $[Cu^+] = b/a$, while in the latter $[Cu^+] = (c/a)^{1/2}$. Since the ultimate goal here is just to see if there is any legitimate way that the proposed scheme will lead to a half-order dependence on dioxygen concentration, the latter root will be adopted.

With the natural assumption that an insignificant amount of O_2 is tied up in the steady-state intermediate CuO_2^+, then $-d[O_2]/dt = d[O_2^{2-}]/dt$. The expression for the latter can be determined directly from the reaction scheme, and after substitution for the steady-state concentrations of [Cu^+] and [CuO_2^+], one obtains eq. 4.84.

$$\frac{-d[O_2]}{dt} = \frac{d[O_2^{2-}]}{dt} = k_2\left\{\frac{k_1 k_e}{k_5\left(k_{-e} + k_2[CuA]\right)}\right\}^{1/2}[CuA]^{3/2}[O_2]^{1/2} + k_1[CuA] \qquad (4.84)$$

The first term on the right-hand-side of eq. 4.84 does have a half-order dependence on [O_2] and one would need to assume that it is larger than the second term to be consistent with the observations of Jameson et al.[7] To obtain the first-order dependence on [CuA] suggested by the preceding analysis of Jameson's[7] data, one must further assume that k_2[CuA] >> k_{-e}. Then, with the second term still included, one obtains eq. 4.85.

$$\frac{-d[O_2]}{dt} = k_1[CuA]\left\{\left(\frac{k_2 k_e}{k_1 k_5}[O_2]\right)^{1/2} + 1\right\} \qquad (4.85)$$

This expression does predict the essence of the data of Jameson et al.[7] in that it can give the first-order dependence on [CuA] and the half-order dependence on [O_2]. Nonetheless, the full rate law is likely to be more complex, as might be guessed from the number of simplifications made to derive the above expression.

The above equation suggests that the value of k_{obsd}/[CuA] = 2.6 × 10^{-2} $M^{1/2}$ s^{-1} derived previously is equal to $k_1(k_2k_e/k_1k_5)^{1/2}$. The value of k_1 = 4.7 × 10^{-5} s^{-1} determined in the present study allows one to estimate that $(k_2k_e/k_5) \approx 14$ M^{-1} s^{-1}. Mi and Zuberbuhler[14b] have determined that $k_e \approx 6 \times 10^6$, from which one obtains $(k_2/k_5) \approx 2 \times 10^{-6}$.

The internal consistency of the procedure leading to the rate law may be assessed by determining if the assumption that 4ac >> b^2 is valid. Substitution of the appropriate expression for a, b and c and rearrangement gives the assumption as $(k_2k_e/k_1k_5)[O_2] >> 1$.

Then substitution of the above numerical values gives $3 \times 10^5\ [O_2] >> 1$ and the assumption is reasonably valid for $[O_2] > 3 \times 10^{-5}$ M. This condition appears to be satisfied for the conditions of Jameson et al.[7] because their initial $[O_2] \geq 4 \times 10^{-4}$ M. Another condition on the rate law is that, for the $[O_2]^{1/2}$ term to be dominant, $((k_2k_e/k_1k_5)[O_2])^{1/2} > 1$. This requires $[O_2] \geq 4 \times 10^{-6}$ M and is easily satisfied for the conditions of Jameson et al.[7]

Copper(II) usually is a one-electron oxidizing agent so that oxidation of catechol should produce a radical intermediate. Jameson et al.[7] claim that no radicals are formed on the basis of their failure to detect radical-initiated polymerization of acrylonitrile. However the mechanism suggested here (eq. 4.33) does produce $A^{\bullet -}$. The observations and proposal may be reconciled if other species, such as copper(II) and dioxygen are more effective radical scavengers than acrylonitrile, or if these species are effective terminators for the polymerization. Meyerstein et al.[36] have determined that copper(II) reacts with several alcohol radicals with near-diffusion controlled rate constants of $\sim 10^8$ $M^{-1}\ s^{-1}$.

It has been shown here that the copper(II)-catecholate complex undergoes an intramolecular electron transfer. In an earlier study, Rogic et al.[8c] proposed that the transfer of an electron in the copper(II) catalyzed catechol oxidation in pyridine only takes place after the formation of a copper(II)-catecholate complex. Our findings thus give support to Rogic's[8c] proposal for the necessity of complex formation to facilitate the electron transfer.

Conclusion. The analytical method used here was required because catechol oxidation generates insoluble products which prevent direct spectrophotometric analysis. The method has an advantage in that low catechol concentrations can be used because of the high molar absorptivity of the cobalt(III)-nitroso-R complex.[21] Therefore, it could be applied to catechol derivatives that have only modest solubilities in water. The method is limited to reactions with half-times of at least a few minutes because of the sampling/quenching procedure. The choice of cobalt(III) scavengers is limited to those that do not react with the cobalt(II)-nitroso-R complex.[22] Thus potentially interesting studies of more reactive cobalt(III) scavengers reacting in competition with dioxygen must be approached with caution, if the current method is to be used.

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(6) For the reaction $Q + 2H^+ + 2e^- \rightleftharpoons H_2A$, the Nernst equation is

$$E = E^0 - \frac{0.0592}{2}\log\frac{[H_2A]}{[Q][H^+]^2}$$

and therefore $\Delta E = -\frac{0.0592}{2} \times \left(\log[H_2A] - \log[Q] - 2\log[H^+]\right)$ and at 1.0 M quinone and catechol concentrations and the relation pH = -log[H$^+$] then $\Delta E = -0.0592 \times \text{pH}$. Ball, E. G.; Clark, W. M. *Proc. Natl. Acad. Sci. US* **1931**, *17*, 347, otained for quinone $\Delta E = -0.0587 \times \text{pH}$.

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Chapter 5. Conclusions

In this study we have developed kinetic methods for the determination in aqueous solutions of: (i) the formation constants for copper(I) with acetonitrile and various olefins in Chapters 2 and 3, respectively; (ii) the rate law for the oxidation of catechol by the simple aquated copper(II) ion in Chapter 4. This study was prompted in part by the observation that there were only a few reports in the chemical literature on the aforementioned two areas, and by the desire to develop kinetic methods that are simple and accurate, and which require only the use of standard laboratory equipment.

Common to these kinetic methods is the use of pentaamminecobalt(III) complexes as oxidative scavengers for aqueous copper(I), eq. 5.1.

$$\mathrm{Cu^{I}_{(aq)}} + \left[(\mathrm{NH_3})_5\mathrm{CoX}\right]^{2+}_{(aq)} \xrightarrow[5\mathrm{H^+}]{k_0} \mathrm{Cu^{II}_{(aq)}} + \mathrm{Co^{II}_{(aq)}} + 5\mathrm{NH_4^+} + \mathrm{X^-} \tag{5.1}$$

In Chapters 2 and 3, this reaction is coupled with complexation of copper(I) by various ligands, L, eq. 5.2.

$$\mathrm{Cu^{I}_{(aq)}} + n\mathrm{L_{(aq)}} \overset{\beta_n}{\rightleftharpoons} \mathrm{Cu^{I}(L)_{n(aq)}} \tag{5.2}$$

Essentially the rate of the oxidation reaction depends on the amount of aqueous copper(I) present, which in turn depends on the extent of the complexation. In Chapter 4, the amount of aqueous cobalt(II) product is used to determine the amount of aqueous copper(I) formed during the oxidation of catechol by aqueous copper(II).

The pentaamminecobalt(III) complexes, $[(\mathrm{NH_3})_5\mathrm{CoX}]^{2+}$, were chosen for several reasons. Earlier work[1] has shown that eq. 5.1 follows simple second-order kinetics with a wide range of rate constants depending on the nature of X. These complexes are easy to prepare, and well characterized in the literature.[2] They are colored, with modest intensity d-d bands in the visible region and intense charge transfer bands in the u.v. region, so that they can be monitored conveniently by spectrophotometry. The analysis is simplified by the fact that the products, aqueous copper(II) and cobalt(II) absorb much more weakly and with maxima at wavelengths different from the pentaamminecobalt(III) complexes. In this study the complex with X ≡ N_3^- has been widely used, while the more reactive complex with X ≡ Br^- also was used for the study of acetonitrile complexation.

The pentaamminecobalt(III) complexes also possesses a number of kinetic advantage as oxidative scavengers. They are kinetically inert with respect to ligand substitution because of their low-spin d^6 electronic configuration. Therefore, they are reasonably stable to hydrolysis[3,4] and do not compete with aqueous copper(I) for the added ligand, (L).

The need for a convenient probe for aqueous copper(I) stems in part from the instability of the latter towards disproportionation and oxidation by dioxygen. Although metastable solutions with moderate concentrations of aqueous copper(I) can be made,[5-7] they must be used and analyzed quickly. In addition, many copper(I) complexes do not show distinctive electronic spectra, so that spectrophotometry is often not useful. Zuberbuhler and co-workers[8] have developed a kinetic method using dioxygen as a scavenger and a Clark-type electrode to monitor the dioxygen concentration. Clearly their method requires specialized equipment, presents difficulties in controlling the dioxygen concentration, and produces oxidizing products such as superoxide radical (O_2^-) and hydrogen peroxide (H_2O_2) which may cause complications. By contrast, the cobalt(III) complexes proposed and used here are conveniently monitored by spectrophotometry, have easily controlled concentrations and produce unreactive reaction products. The absorbance change also can be used as an in-situ measure of the copper(I) concentration when $[Co^{III}] > [Cu^{I}]$. Electrochemistry[9] is an obvious alternative technique that has been used rather widely. Solubility[10] and pulse radiolysis[11] are other methods that have been used in the past. Potential errors with the former are discussed in Chapter 3 and the most obvious limitation with the latter method is the cost and availability of pulse radiolysis equipment.

The method developed here has some limitations. The pH must be low enough (<7) to prevent precipitation of the hydroxides of copper(II) and cobalt(II). There may be need for some pH control because reduction of $[(NH_3)_5CoX]^{2+}$ consumes five protons to produce NH_4^+. Although not necessarily limited to water, complications due to solubility and ion-paring would be expected in solvents of much lower polarity. This presents a further limitation in that the ligands to be studied should have a reasonable solubility in water.

For the studies described in Chapter 2 with L = CH_3CN, $[(NH_3)_5CoN_3]^{2+}$ and the more reactive $[(NH_3)_5CoBr]^{2+}$ were used as scavengers for acetonitrile concentration ranges of 0.0237 to 0.213 M and 0.568 to 2.04 M, respectively. In general, the rate of reduction decreases as the acetonitrile concentration increases, for a particular scavenger. The observed second-order rate constant for the reduction (k_{obsd}) is related to the overall formation constants (β_n) and the specific rate constants (k_n) for the oxidation of $Cu(CH_3CN)_n^+$ by eq. 5.3.

$$k_{obsd} = \frac{k_0 + k_1\beta_1[L] + k_2\beta_2[L]^2 + \ldots + k_n\beta_n[L]^n}{1 + \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n} \qquad (5.3)$$

For the lower acetonitrile concentration range with $[(NH_3)_5CoN_3]^{2+}$, the data analysis indicated that k_0 was the dominant term in the numerator of eq. 5.3, and rearrangement gives eq. 5.4.

$$\left(\frac{k_0}{k_{obsd}}-1\right)[L]^{-1}=\beta_1+\beta_2[L]^1+...+\beta_n[L]^{n-1} \quad (5.4)$$

Since k_0 is known independently, the linearity of the plot indicated by eq. 5.4 gives values of β_1 and β_2, and shows that higher complexes are not significant under these conditions. For the higher acetonitrile concentration range, this plot was not linear and a detailed analysis indicated that the β_3 term was significant and as well as either the k_1 or k_2 terms in eq. 5.3.

A least-squares analysis of all the data for the acetonitrile systems yielded values for the stepwise formation constants K_1, K_2 and K_3 of 4.3 × 10^2, 24 and 2.1 M^{-1}, respectively. These values show the commonly found trend of $K_1 > K_2 > K_3$ and do not show any abrupt changes that might be indications of changes in coordination number of copper(I).

The values of β_2 and β_3 are reasonably consistent with previous estimates.[8,9] However, the $\beta_1 = K_1$ found here is substantially smaller than the 1.89 × 10^3 M^{-1} reported by Zuberbuhler et al.[9c] and the reasons for this were advanced in Chapter 2.

In Chapter 3, the methodology developed in Chapter 2 is applied to the formation constants of copper(I) with olefins, using dicarboxylic acids and their derivatives as examples. Results for fumaric and maleic acids are compared to much earlier work,[10,11] and values for dimethyl fumarate and fumaronitrile are reported for the first time.

For these systems, the analysis is simpler than with acetonitrile because complexation is dominated by the mono-olefin complex. The values of β_1 for fumaric and maleic acids, dimethyl fumarate and fumaronitrile are 7.3 × 10^3, 2.7 × 10^3, 6.1 × 10^3 and 8.5 × 10^2 M^{-1}, respectively. For these and a number of previously studied systems,[10,11] it is found that log β_1 decreases linearly as the Hammet sigma constant[12] increases. This implies that the bonding interaction of the olefins with aqueous copper(I) is dominated by σ-donation of the π-electrons of the olefin.

The fumaronitrile system is somewhat more complex in two ways. The data indicate formation of a weak bis complex with $K_2 = 2.4$ M^{-1}. There also is an ambiguity in the binding mode of fumaronitrile in that it could involve the π-electrons of the olefin and/or the N of the nitrile substituent. The determination of the crystal structure of bis(fumaronitrile)copper(I) nitrate shows N-coordination of the nitrile in the solid. On the other hand, the β_1 for this system fits well on the Hammet correlation with the other olefins, suggesting that the first fumaronitrile is bonding via the olefinic double bond. The rather large 350 fold difference between β_1 and K_2 suggests that the two process may involve different coordination modes, possibly the first at the double bond and the second at the nitrile substituent. This also provides a rationalization for the rather unique formation of a bis-complex in this system.

The maleic acid system also was somewhat more complicated because the apparent formation constants seemed to depend on the hydrogen ion concentration (0.033 and 0.109 M). This effect was attributed to the high K_a of maleic acid (1.78×10^{-2} M)[13] compared to that of fumaric acid (1.45×10^{-3} M)[13] which results in significant quantities of the maleate anion (HL^-) being present under the experimental conditions. The analysis gave β_1 values of 2.7×10^3 and 1.7×10^4 M^{-1} for H_2L and HL^-, respectively.

Also reported in Chapter 3 is our failure to detect any complexation between copper(I) and benzoic acid or the p-toluenesulfonate ion. Only upper limits of β_1 of $\leq 2 \times 10^2$ and ≤ 0.8 M^{-1} could be estimated for benzoic acid and the p-toluenesulfonate ion, respectively. This contrasts with an earlier report that $\beta_1 = 1 \times 10^4$ for benzoic acid,[14] (complexation proposed be to through π-bonding and not through the carboxylate) but seems consistent with the absence of detectable complexation with $[(NH_3)_5Co(benzoate)]^{2+}$ ($\beta_1 < 10^2$ M^{-1}) observed by Hurst and Lane.[7]

A somewhat different application of a cobalt(III) scavenger for copper(I) is developed in Chapter 4. The purpose is to determine the rate-controlling step and reactive species in the oxidation of catechol by aqueous copper(II). Standard spectrophotometric observation of the reaction is prevented because of the formation of insoluble organic products.[15] In our system, catechol, copper(II) and pentaammineazidocobalt(III) are allowed to react and samples are taken periodically and analyzed for the cobalt(II) produced from the reaction of copper(I) with the cobalt(III) complex.

The dependence of the rate of reaction on pH, catechol (H_2A) and copper(II) concentrations has shown that the reactive species is the monocatecholate species (CuA). The rate limiting step is the intramolecular electron transfer of this species to give copper(I) and the catecholate monoanion radical, ($A^{\bullet -}$), with $k = 4.7 \times 10^{-5}$ s^{-1}. Thermodynamic data[16] has been used to estimate the equilibrium constant for this reaction as 2.1×10^{-12} M and hence the rate constant for the reverse reaction as 2.2×10^{7} M^{-1} s^{-1}.

In general, these observations have eliminated reaction pathways involving two copper(II) or catechol species. It is hoped that this information will be of use in analyzing the kinetics of the copper(II) catalyzed oxidation of catechols by dioxygen as in the discussion section of Chapter 4, and for mechanistic studies on copper(II) oxidases for catechol and analogues such as tyrosine and dopamine.

Another pathway that seems to have been eliminated is that involving the copper(I)-catecholate monoanion radical complex, ($Cu^{+}A^{\bullet -}$), as a stable intermediate. This conclusion was reached because the estimated value for the formation constant for the reaction between copper(I) and the catecholate monoanion radical was unreasonably large.

Suggestions for Future Work

The method developed here for the determination of formation constants for copper(I) with the various ligands has a wide applicability. The copper(I) is generated in situ by the reaction of copper(II) and copper metal in the presence of the ligand. One can arrive at the equilibrium describing this reaction by combining eqs. 5.5 and 5.6 to get eq. 5.7.

$$Cu^{2+}_{(aq)} + Cu_{(s)} \rightleftarrows 2Cu^{+}_{(aq)} \qquad K_D = 7.69 \times 10^{-7}\,M \qquad (5.5)$$

$$Cu^{+}_{(aq)} + L_{(aq)} \rightleftarrows CuL^{+}_{(aq)} \qquad K_f = ? \qquad (5.6)$$

$$Cu^{2+}_{(aq)} + Cu_{(s)} + L_{(aq)} \rightleftarrows CuL^{+}_{(aq)} + Cu^{+}_{(aq)} \qquad K = K_D \times K_f \qquad (5.7)$$

The ideal conditions would have ~5 × 10^{-4} M pentaammineazidocobalt(III) in a 5 cm path-length cell, with total copper(I) of ~2.5 × 10^{-4} M. The absorbance change (~0.34 units) can be used to determine the actual total copper(I). With these constraints, a system with $K_f = 10\ M^{-1}$ would require initial copper(II) and ligand concentrations of 2 × 10^{-1} M and 1 × 10^{-1} M, respectively. At the other extreme, if $K_f = 10^5\ M^{-1}$, these concentrations would be 2 × 10^{-3} M and 1 × 10^{-3} M, respectively. Thus it can be seen that the method is applicable for a wide range of K_f values.

Values reported by Andrews et al.[10c] for the citraconic and mesaconic acids show a large deviation from the log β_1 versus $\Sigma\sigma$ correlation, (Figure 3.9). As discussed in Chapter 3, these values might be in error if the copper(I) salts have a limited solubility. Both citraconic and mesaconic acids are reasonably soluble in water, 0.345 and 0.151 M, respectively. If the K_f values are 22 M^{-1} and 410 M^{-1} for citraconic and mesaconic acids, respectively, as determined by Andrews et al.[10c], or ~10^4 M^{-1} as predicted by the correlation, these systems should be amenable to the method developed here, based on the arguments in the previous paragraph. Of course, if the copper(I) salts are really quite insoluble, neither our nor Andrew's[10c] method will work, but these points then must be removed from the Hammet correlation.

Analogous studies to those of the complexation of fumaronitrile by copper(I) should be undertaken with succinonitrile. The magnitude of the β value(s) obtained from such a study, compared to the β values of acetonitrile and fumaronitrile might shed more light on whether the latter bonds through the double bond or through the nitrogen or a combination of both.

Work in an analogous way to our method but in mixed solvents, for example water/alcohol, also would be interesting. For longer chain olefinic acids and alcohols, the ligand solubility will be improved by these other organic solvents. For a series of water/solvent ratios, it might be possible to extrapolate the β_1 values to zero solvent concentration and in effect obtain β values for the longer chain olefins in aqueous solutions. The other aspect that such kinetic studies under various water/solvent ratios might yield is useful information on solvent effects for a given system. Such studies with different water/solvent ratios can be complicated since one requires a new k_0 (for the oxidation of copper(I) by pentaamminecobalt(III) complex) value for each solvent composition.

Further attempts to form crystals of copper(I) with the various forms of fumaric and maleic acid species also should be undertaken. Crystalline material for structure determination might be made by the hydrothermal method i.e. heat the copper(I)-olefin powder in a minimum amount of solvent in a furnace and then slowly cool the solution. This method was used by Young et al.[18] to obtain crystals of $Cu_2(O_2CCH{=}CHCO_2)$. If such attempts are successful, solid state chemistry of these substances could be investigated.

The choice of the pentaamminecobalt(III) complex is crucial for the analytical procedure used to study the copper(II) catalyzed oxidation of catechol. These complexes are limited to those for which the rate of oxidation of tris(nitroso-R)cobalt(II) is faster with dioxygen than with the pentaamminecobalt(III) complex. The observations of Lalor[19] indicate that $[(NH_3)_5CoX]^{2+}$ (X = Br, Cl) are unsuitable but $[(NH_3)_6Co]^{3+}$ and $[(NH_3)_5CoNO_2]^{2+}$ are not a problem in this regard. However, liberated NO_2^- ion is likely to react with copper(I) and therefore the latter complex would not be suitable. Additionally, the rate of reaction of the complex with copper(I) should be large enough so that it is not rate-limiting. If the oxidation rate of the pentaamminecobalt(III) complex is too small, there will be increased induction periods in the absorbance versus time profiles, to the point where the whole profile might depend on the rate of cobalt(III) reduction. The isothiocyanate ligand is a strong N-donor and is isoelectronic with azide, so that one might expect $[(NH_3)_5CoNCS]^{2+}$ to be unreactive with tris(nitroso-R)cobalt(II). However, $[(NH_3)_5CoNCS]^{2+}$ has a k_0 value $\sim 10^3$ times less[1] than that of $[(NH_3)_5CoN_3]^{2+}$ and simulations indicate that its reduction rate is too slow to be applicable to the copper(II)-catechol system. The latter requires $k_0 \geq 500$ M^{-1} s^{-1}. This discussion has delineated the important factors that might be considered in future applications of this analytical method.

An obvious constraint of the analytical method used for the copper(II)/catechol system is that it is limited to reactions with half-times of ≥ 3 minutes because of the sampling/quenching procedure described in Chapter 4. This limitation might be reduced by the design of an automated sampling/quenching apparatus. This could involve the dispensing of smaller volumes. Not only would it be quicker to dispense smaller volumes, but also would save on the amount of reagents used. The rate of solution flow through the tubing is a limiting factor that can be improved by use of wider tubing. Of course, one can control the rates to some extent by the proper choice of pH and reagent concentrations.

Future work on copper(II)-catechol systems might be designed to test the generality of the mechanism proposed here. Several predictions for different ancillary ligands on copper(II) and/or various catechol derivatives can be made on the basis of this mechanism. The rate-determining step is the intramolecular electron transfer in the copper(II)-catecholate complex to give copper(I) and the monoanion catecholate radical, eq. 5.8,

$$\mathrm{CuA} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cu}^{+} + \mathrm{A}^{\bullet -} \tag{5.8}$$

and the rate of disappearance of catechol is given by eq. 5.9.

$$\frac{-\mathrm{d}[\mathrm{H_2A}]}{\mathrm{d}t} = k_1[\mathrm{CuA}] \tag{5.9}$$

Of the two contributing factors, k_1 and [CuA], to the rate of disappearance of catechol in eq. 5.9, it is easier to anticipate the effect of [CuA] for different catechol derivatives. The higher the amount of CuA present, the faster the rate of reaction is expected to be. Species distribution calculations depend on the pH and the log K^* values for the mono and bis complexes for the reaction of copper(II) with the fully protonated catechol. These values (see Table 1.1) are, catechol (log $K_1^* = -8.33$, log $K_2^* = -11.23$), 4-chlorocatechol (-7.60, -10.33), 4-carboxycatechol (-7.82, -10.80), 4-nitrocatechol (-5.89, -8.27) and Tiron (-5.87, -9.0). With initial copper(II) and catechol concentrations of 7.18×10^{-4} and 2.18×10^{-3} M, respectively, the maximum mono-complex concentrations are ~ 6.5×10^{-4} M for these catechols at pH 6.5, 6.0, 6.0, 5.0 and 5.0 for the catechol, 4-chlorocatechol, 4-carboxycatechol, 4-nitrocatechol and Tiron, respectively. These are the pH values at which rates are predicted to be maxima if CuA is the only reactive species. Studies on these catechols should be undertaken to ascertain if our mechanism correctly predicts the pH dependence of the rate.

The k_1 value can be varied by having more positive potentials for the forward reaction in eq. 5.8. Qualitatively, the equilibrium in eq. 5.8 would be shifted to the right with ancillary ligands that stabilize the copper(I) state with respect to copper(II). This can be done with soft ligands on copper(II), as has been shown by Kaim et al.[20] with mixed N, S donor ligands on copper(II). The extent that such ancillary ligands would help is hard to gauge since this might be negated by the effect of the ancillary ligands on the $K_1^\bullet$ value.

A favored forward reaction also would be predicted for electron-donating groups on the catechol, since the increased electron density on the catechol should make oxidation to the radical more favorable. The equilibrium constant for eq. 5.8 can been obtained from a combination of the following equilibria.

$$Cu^{2+} + H_2A \rightleftarrows CuA + 2H^+ \qquad K_1^\bullet \qquad (5.10)$$

$$HA^\bullet \rightleftarrows H^+ + A^{\bullet-} \qquad pK_a \approx 5 \qquad (5.11)$$

$$H_2A^{\bullet+} \rightleftarrows HA^\bullet + H^+ \qquad pK_a \approx -1 \qquad (5.12)$$

$$H_2A^{\bullet+} + e \rightleftarrows H_2A \qquad E^0 \qquad (5.13)$$

$$Cu^{2+} + e \rightleftarrows Cu^+ \qquad E^0 \qquad (5.14)$$

The pK_a values for a series of substituted catechols in eqs. 5.11[21] and 5.12[22] are fairly constant. Therefore, the equilibrium constant for eq. 5.8 will depend on the E^0 values for the $H_2A^{\bullet+}/H_2A$ couple, eq. 5.13, and the equilibrium constants for eq. 5.10.

The E^0 values[23] for the $H_2A^{\bullet+}/H_2A$ couple for catechol, 4-chlorocatechol, 4-carboxycatechol, 4-nitrocatechol and Tiron are 1.25, 1.25, 1.38, 1.46 and 1.47 V, respectively. We have chosen here to use the values of Pelizzetti and Mentasti[23] since they determined the E^0 values for a series of catechols. Since our interest is to predict the relative rates, this should be unaffected by the fact that the value for catechol of Pelizzetti and Mentasti[23] is 0.15 V higher than that used in Chapter 4 from Kimura et al.[24] The equilibrium constants calculated for eq. 5.8 from the combination of eqs. 5.10 to 5.14 (assuming that k_{-1} is the same for the different catechols) indicates that catechol has the largest k_1 and Tiron has the smallest. By taking the value for catechol to be 1, the relative k_1 values for 4-chlorocatechol, 4-carboxycatechol, 4-nitrocatechol and Tiron are 2×10^{-1}, 2×10^{-3}, 1×10^{-6} and 7×10^{-7}, respectively. In other words, the prediction with aqueous copper(II) as the oxidant is that the k_1 value for 4-chlorocatechol would be ~5 times less than that of catechol and that for 4-carboxycatechol would be ~500 times less. It is predicted that the oxidation of 4-nitrocatechol would be very slow as observed for Tiron in the present study.

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Appendix. Crystallographic and Data Tables

Complete structure and refinement of Bis(fumaronitrile)copper(I) was carried out by Dr. R. McDonald, X-Ray Crystallography Laboratory, Chemistry Department, University of Alberta. Reference file number RBJ0001.

Appendix 3.1. Crystallographic Experimental Details for Bis(fumaronitrile)copper(I) nitrate.

A. Crystal Data

formula	$C_8H_4CuN_5O_3$
formula weight	281.70
crystal dimensions (mm)	0.46 × 0.06 × 0.06
crystal system	monoclinic
space group	*C*2/*c* (No. 15)
unit cell parameters[a]	
a (Å)	5.3667 (5)
b (Å)	22.228 (2)
c (Å)	8.8952 (8)
β (deg.)	98.7072 (16)
V(Å^3)	1048.90 (17)
Z	4
ρ_{calcd} (g cm^3)	1.784
μ (mm^{-1})	2.086

B. Data Collection and Refinement Conditions

diffractometer	Bruker P4/RA/SMART I 000 CCD[b]	
radiation (A [Al)	graphite-monochromated Mo Kα (0.71073)	
temperature (°C)	-80	
scan type	ϕ rotations (0.3°) / ω scans (0.3°) (30 s exposures)	
data collection 2θ limit (deg.)	52.72	
total data collected	2808 ($-6 \leq h \leq 5$, $-23 \leq k \leq 27$, $-10 \leq l \leq 0$)	
independent reflections	1075	
No. of observed reflections (*NO*)	960 [$F_o^2 \geq -2\sigma(F_o^2)$]	
structure solution method	direct methods (*SHELXS-86*[c])	
refinement method	full-matrix least-squares on F^2 (*SHELXL-93*[d])	
absorption correction method	*SADABS*	
range of transmission factors	0.9144-0.6194	
data/restraints/parameters	1075 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 97	
goodness-of-fit (*S*)[e]	1.062 [$F_o^2 \geq -3\sigma(F_o^2)$]	
final *R* indices[f]		
	R_1 [$F_o^2 \geq -2\sigma(F_o^2)$]	0.0266
	wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0682
largest difference peak and hole	0.397 and -0.296 e Å^{-3}	

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[a] Obtained from least-squares refinement of 2852 centered reflections.

[b] programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467-473.

[d]Sheldrick, G. M. *SHELXL-93.* Program for crystal structure determination. University of Gottingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted R-factors wR_2 and all goodnesses of fit S are based on F_o^2; conventional R-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. R-factors based on F_o^2 are statistically about twice as large as those based on F_o, and R-factors based on ALL data will be even larger.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0390P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Appendix 3.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters.

Atom	x	y	z	U_{eq}, Å^2
Cu	0.0000	-0.143121(16)	0.2500	0.02311(15)*
N1	0.2752(3)	-0.18805(8)	0.3711(2)	0.0267(4)*
N2	0.1751(4)	-0.08896(9)	0.1237(2)	0.0346(5)*
C1	0.4582(4)	-0.20563(10)	0.4382(3)	0.0263(5)*
C2	0.6922(4)	-0.22626(10)	0.5233(3)	0.0282(5)*
C3A[a]	0.2725(12)	-0.0455(3)	0.0884(8)	0.0263(13)*
C4A[a]	0.4128(9)	0.0044(3)	0.0424(6)	0.0324(10)*
C3B[b]	0.3173(15)	-0.0651(3)	0.0565(9)	0.0228(15)*
C4B[b]	0.4861(13)	-0.0293(3)	-0.0156(7)	0.0280(12)*
O1	0.1782(5)	0.13085(11)	0.2105(3)	0.0675(7)*
O2	0.0000	0.04688(12)	0.2500	0.0655(10)*
N3	0.0000	0.10260(14)	0.2500	0.0413(8)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$. [a]Refined with an occupancy factor of 0.55. [b]Refined with an occupancy factor of 0.45.

Appendix 3.3. Selected Interatomic Distances (A)

Atoml	Atom2	Distance	Atoml	Atom2	Distance
Cu	Nl	1.9641(19)	C3A	C4A	1.435(9)
Cu	N2	1.9788(19)	C4A	C4A*	1.303(10)
N1	C1	1.138(3)	C3B	C4B	1.429(11)
N2	C3A	1.164(7)	C4B	C4B*	1.335(12)
N2	C3B	1.165(8)	O1	N3	1.239(3)
C1	C2	1.440(3)	O2	N3	1.239(4)
C2	C2"	1.323(5)			

Appendix 3.4. Selected Interatomic Angles (deg.)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
N1	Cu	N1'	118.87(11)	N1	C1	C2	178.5(2)
N1	Cu	N2	103.80(8)	C1	C2	C2"	120.2(3)
N1	Cu	N2'	112.35(8)	N2	C3A	C4A	174.4(6)
N2	Cu	N2'	105.06(13)	C3A	C4A	C4A*	120.2(8)
Cu	N1	C1	168.38(18)	N2	C3B	C4B	172.9(6)
Cu	N2	C3A	158.3(4)	C3B	C4B	C4B*	120.5(9)
Cu	N2	C3B	166.4(4)	O1	N3	O1'	119.1(4)
C3A	N2	C3B	29.3(3)	O1	N3	O2	120.46(18)

Appendix 3.5. Torsional Angles (deg.)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
N1'	Cu	N1	C1	153.2(10)	Cu	N1	C1	C2	17(10)
N2	Cu	N1	C1	27.5(9)	Cu	N2	C3A	C4A	128(6)
N2'	Cu	N1	C1	-85.4(9)	C3B	N2	C3A	C4A	-25(6)
N1	Cu	N2	C3A	-92.8(10)	Cu	N2	C3B	C4B	-126(5)
N1	Cu	N2	C3B	18.9(17)	C3A	N2	C3B	C4B	9(5)
N1'	Cu	N2	C3A	137.6(9)	N1	C1	C2	C2"	-134(9)
N1'	Cu	N2	C3B	-110.8(17)	N2	C3A	C4A	C4A*	23(7)
N2'	Cu	N2	C3A	25.4(9)	N2	C3B	C4B	C4B*	-3(7)
N2'	Cu	N2	C3B	137.0(17)					

Primed atoms are related to unprimed ones via the twofold rotational axis (0, *y*, ¼).

Double-primed atoms are related to unprimed ones via the inversion center (¾, -¼, ½).

Starred atoms are related to unprimed ones via the inversion center (½, 0, 0).

Appendix 3.6. Anisotropic Displacement Parameters (U_{ij}, Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	0.0196(2)	0.0223(2)	0.0273(2)	0.000	0.00299(15)	0.000
N1	0.0229(10)	0.0288(10)	0.0283(10)	0.0069(8)	0.0039(8)	0.0024(8)
N2	0.0329(11)	0.0372(12)	0.0323(11)	0.0106(9)	0.0006(9)	-0.0101(9)
C1	0.0281(13)	0.0253(11)	0.0268(12)	0.0056(9)	0.0080(10)	-0.0003(9)
C2	0.0260(12)	0.0302(11)	0.0265(12)	0.0048(9)	-0.0026(10)	-0.0015(9)
C3A	0.027(3)	0.025(3)	0.026(3)	0.000(2)	0.001(2)	0.002(2)
C4A	0.030(3)	0.030(3)	0.035(3)	0.000(2)	-0.001(2)	-0.006(3)
C3B	0.028(4)	0.015(4)	0.025(4)	-0.004(3)	0.002(3)	0.000(3)
C4B	0.024(3)	0.030(4)	0.030(3)	-0.002(3)	0.004(2)	-0.007(3)
O1	0.0687(16)	0.0770(15)	0.0604(15)	-0.0252(12)	0.0216(13)	-0.031(13)
O2	0.109(3)	0.0324(15)	0.0464(18)	0.000	-0.0166(18)	0.000
N3	0.051(2)	0.0409(18)	0.0285(16)	0.000	-0.0059(15)	0.000

The form of the anisotropic displacement parameter is:

$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Appendix 3.7. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H2	0.7636	-0.2057	0.6133	0.034
H4A[a]	0.3783	0.0440	0.0738	0.039
H4B[b]	0.5793	-0.0473	-0.0864	0.034

[a]Included with an occupancy factor of 0.55. [b]Included with an occupancy factor of 0.45

Appendix 3.8. Uncomplexed Fumaric Acid Concentration as a Percentage of the Total Fumaric Acid Concentration in a Kinetic Run.[a]

10^4[Co(III)], M	$10^4[Cu(I)]_0$, M	$10^4[L]_0$, M	I[b]	%[c]
3.54	1.31	5.00	0.372	91.6
1.93	1.75	8.33	0.190	87.5
3.54	2.21	10.0	0.380	87.0
3.54	3.15	15.0	0.340	87.0
3.54	2.96	20.0	0.365	90.0
6.45	5.38	50.0	0.680	92.2

[a] For kinetic runs where $[Cu(I)]_0$ was more than 10% of $[L]_0$. [b] First absorbance point recorded on the chart paper used to calculate the k_{obsd} for the run. [c] Percentage of free ligand calculated as explained in the text, see Chapter 3.

Appendix 3.9. Uncomplexed Dimethyl Fumarate Concentration as a Percentage of the Total Dimethyl Fumarate Concentration in a Kinetic Run.[a]

10^4[Co(III)], M	$10^4[\mathrm{Cu(I)}]_0$, M	$10^4[\mathrm{L}]_0$, M	I[b]	%[c]
3.53	1.00	5.00	0.425	90.6
3.44	1.89	10.0	0.360	90.4
3.53	1.75	15.0	0.405	92.6
3.53	2.43	15.0	0.375	89.9
3.53	2.83	23.3	0.390	91.2

[a] For kinetic runs where $[\mathrm{Cu(I)}]_0$ was more than 10% of $[\mathrm{L}]_0$. [b] First absorbance point recorded on the chart paper used to calculate the k_{obsd} for the run. [c] Percentage of free ligand calculated as explained in the text, see Chapter 3.

Appendix 3.10. Calculated Percentage Difference[a] between k_{obsd} and k_{calc} for Maleic Acid.

10^2[Maleic] M	$10^2[H^+]_0$ M	$10^2[H^+]_f$ M	k_{obsd} $M^{-1}s^{-1}$	%[b]	%[c]
1.72	3.30	3.84	17.7	29.9	24.4
3.38	3.30	4.29	9.05	26.3	11.2
5.05	3.30	4.69	7.36	36.7	16.6
5.05	3.30	4.69	6.25	25.5	1.83
5.05	10.9	11.6	8.54	18.7	13.0
8.38	3.30	5.38	3.82	21.6	18.6
8.38	3.30	5.38	4.23	29.2	7.08

[a] Calculated from $(k_{obsd} - k_{calc})/k_{obsd}$. [b] Calculated using k_{calc} obtained from data fitting to eq. 3.19. [c] Calculated using k_{calc} obtained from data fitting to either eq. 3.22 or 3.27.

Appendix 4.1. Variation with time of the absorbance of cobalt(III)-nitroso-R complex during the oxidation of catechol by copper(II) for a run with: 2.18×10^{-3} M catechol, 0.718×10^{-3} copper(II), 0.125 M sodium perchlorate, pH 7.00 in 0.025 M HEPES.

0.335×10^{-3} M cobalt(III)		0.670×10^{-3} M cobalt(III)	
Time (min.)	Absorbance (λ = 525 nm)	Time (min.)	Absorbance (λ = 525 nm)
5	0.043	10	0.077
10	0.058	20	0.099
15	0.067	30	0.122
20	0.078	50	0.189
30	0.121	70	0.277
40	0.162	90	0.390
50	0.211	100	0.449
60	0.256	120	0.563
75	0.302	130	0.583
90	0.317	145	0.593

Appendix 4.2. The Calculated Concentrations of the Free Copper(II), Free Catechol and the Mono and Bis Complexes of Copper(II) with the Catechol Dianion at pH 7.00. Total Catechol(II) Concentration 4.36 × 10^{-3} M.[a,b]

$10^3[\mathrm{Cu^{II}}]_t$, M	$[\mathrm{H_2A}]_f$, M	$[\mathrm{Cu^{2+}}]_f$, M	[CuA], M	$[\mathrm{CuA_2}^{2-}]$, M
0.144	4.14 × 10^{-3}	6.41 × 10^{-8}	6.60 × 10^{-5}	7.80 × 10^{-5}
0.360	3.81 × 10^{-3}	1.82 × 10^{-7}	1.72 × 10^{-4}	1.88 × 10^{-4}
0.718	3.29 × 10^{-3}	4.53 × 10^{-7}	3.71 × 10^{-4}	3.49 × 10^{-4}
0.861	3.10 × 10^{-3}	5.93 × 10^{-7}	4.57 × 10^{-4}	4.04 × 10^{-4}
0.900	3.04 × 10^{-3}	6.36 × 10^{-7}	4.81 × 10^{-4}	4.18 × 10^{-4}
1.08	2.80 × 10^{-3}	8.60 × 10^{-6}	5.99 × 10^{-4}	4.80 × 10^{-4}
1.44	2.34 × 10^{-3}	1.48 × 10^{-6}	8.62 × 10^{-4}	5.77 × 10^{-4}

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[a] K_1^* and K_2^* values from Martell, A. E.; Smith, R. M. *NIST Critical Stability Constants of Metal Complexes Database* **1995**, U.S. Department of Commerce; μ = 0.1 and 25 °C.

[b] The subscripts t and f denote the total copper(II) and the free (uncomplexed) copper(II) and catechol concentrations at equilibrium, respectively.

Appendix 4.3. The Calculated Concentrations of the Free Copper(II), Free Catechol and the Mono and Bis Complexes of Copper(II) with the Catechol Dianion at pH 7.00. Total Catechol Concentration 2.18 × 10^{-3} M.[a,b]

$10^3[\text{Cu}^{\text{II}}]_t$, M	$[H_2A]_f$, M	$[\text{Cu}^{2+}]_f$, M	[CuA], M	$[\text{CuA}_2^{2-}]$, M
0.287	1.89×10^{-3}	9.05×10^{-6}	2.69×10^{-4}	9.17×10^{-6}
0.574	1.61×10^{-3}	2.12×10^{-6}	5.37×10^{-4}	1.56×10^{-6}
0.718	1.47×10^{-3}	2.90×10^{-5}	6.71×10^{-4}	1.78×10^{-5}
0.861	1.34×10^{-3}	3.83×10^{-5}	8.03×10^{-4}	1.94×10^{-5}

[a] $K_1^{\bullet}$ and $K_2^{\bullet}$ values from Martell, A. E.; Smith, R. M. *NIST Critical Stability Constants of Metal Complexes Database* **1995**. U.S. Department of Commerce; μ = 0.1 and 25 °C. [b] The subscripts t and f denote the total copper(II) concentration and the free (uncomplexed) copper(II) and catechol concentrations at equilibrium, respectively.

Appendix 4.4. The Calculated Concentrations of the Free Copper(II), Free Catechol and the Mono and Bis Complexes of Copper(II) with the Catechol Dianion at pH 7.00. Total Copper(II) Concentration 0.718 × 10^{-3} M.[a,b]

$10^3[H_2A]_t$, M	$[H_2A]_f$, M	$[Cu^{2+}]_f$, M	[CuA], M	$[CuA_2^{2-}]$, M
0.800	9.31×10^{-5}	2.90×10^{-5}	6.71×10^{-4}	1.79×10^{-5}
1.09	3.21×10^{-4}	8.15×10^{-6}	6.50×10^{-4}	5.96×10^{-5}
1.64	7.93×10^{-4}	2.96×10^{-6}	5.83×10^{-4}	1.32×10^{-4}
2.18	1.27×10^{-3}	1.66×10^{-6}	5.25×10^{-4}	1.91×10^{-4}
2.72	1.76×10^{-3}	1.09×10^{-6}	4.77×10^{-4}	2.40×10^{-4}
3.27	2.27×10^{-3}	7.70×10^{-7}	4.35×10^{-4}	2.82×10^{-4}
3.82	2.78×10^{-3}	5.77×10^{-7}	4.00×10^{-4}	3.18×10^{-4}
4.36	3.29×10^{-3}	4.51×10^{-7}	3.70×10^{-4}	3.48×10^{-4}
6.54	5.39×10^{-3}	2.11×10^{-7}	2.83×10^{-4}	4.35×10^{-4}
8.72	7.51×10^{-3}	1.22×10^{-7}	2.28×10^{-4}	4.90×10^{-4}
11.6	1.03×10^{-2}	7.05×10^{-8}	1.82×10^{-4}	5.36×10^{-4}
14.4	1.31×10^{-2}	4.64×10^{-8}	1.51×10^{-4}	5.67×10^{-4}

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[a] $K_1^{\bullet}$ and $K_2^{\bullet}$ values from Martell, A. E.; Smith, R. M. *NIST Critical Stability Constants of Metal Complexes Database* **1995**, U.S. Department of Commerce; μ = 0.1 and 25 °C.

[b] The subscripts t and f denote the total catechol concentration and the free (uncomplexed) copper(II) and catechol concentrations at equilibrium, respectively.

Appendix 4.5. **The Calculated Concentrations of the Free Copper(II), Free Catechol and the Mono and Bis Complexes of Copper(II) with the Catechol Dianion. Total Copper(II) and Catechol Concentrations 0.718 × 10^{-3} M and 2.18 × 10^{-3} M, respectively.**[a,b]

pH	$[H_2A]_f$, M	$[Cu^{2+}]_f$, M	[CuA], M	$[CuA_2^{2-}]$, M
6.4[c]	1.61×10^{-3}	2.12×10^{-5}	5.37×10^{-4}	1.56×10^{-5}
6.4	1.47×10^{-3}	2.90×10^{-5}	6.71×10^{-4}	1.78×10^{-5}
6.6	1.43×10^{-3}	1.18×10^{-5}	6.63×10^{-4}	4.30×10^{-5}
6.8	1.37×10^{-3}	4.55×10^{-6}	6.17×10^{-4}	9.62×10^{-5}
7.0	1.27×10^{-3}	1.66×10^{-6}	5.25×10^{-4}	1.91×10^{-4}
7.2	1.14×10^{-3}	5.54×10^{-7}	3.95×10^{-4}	3.23×10^{-4}
7.4	1.00×10^{-3}	1.63×10^{-7}	2.56×10^{-4}	4.62×10^{-4}

[a] K_1^* and K_2^* values from Martell, A. E.; Smith, R. M. *NIST Critical Stability Constants of Metal Complexes Database* **1995**, U.S. Department of Commerce; μ = 0.1 and 25 °C. [b] The subscript f denotes the free (uncomplexed) copper(II) and catechol concentrations at equilibrium. cTotal copper(II) concentration is 5.74 × 10^{-4} M.

Appendix 4.6. Variation with time of the absorbance of cobalt(III)-nitroso-R complex for a run with: 11.61 × 10^{-3} M Tiron, 0.718 × 10^{-3} copper(II), 0.336 × 10^{-3} M cobalt(III), 0.125 M sodium perchlorate, pH 7.00 in 0.025 M HEPES.

Time (min.)	Absorbance (λ = 525 nm)
10	0.023
20	0.024
36	0.026
136	0.037
156	0.032
216	0.030
276	0.031

Appendix 4.7. Variation with time of the absorbance of cobalt(III)-nitroso-R complex during the oxidation of a catechol solution by copper(II) for a run with: 12.1 × 10^{-3} M Tiron, 2.18 × 10^{-3} catechol, 0.718 × 10^{-3} copper(II), 0.336 × 10^{-3} M cobalt(III), 0.125 M sodium perchlorate, pH 7.00 in 0.025 M HEPES.

Time (min.)	Absorbance ($\lambda = 525$ nm)
10	0.017
20	0.017
30	0.018
60	0.021
90	0.023
150	0.028
155	0.026

Appendix 4.8. Variation with time of the absorbance of cobalt(III)-nitroso-R complex during the oxidation of catechol by copper(II) for a run with: 0.618 × 10^{-3} M catechol, 0.718 × 10^{-3} copper(II), 0.333 × 10^{-3} M cobalt(III), 0.125 M sodium perchlorate, pH 7.00 in 0.025 M HEPES.

	5.00 × 10^{-3} M NaCl	10.0 × 10^{-3} M NaCl
Time (min.)	Absorbance (λ = 525 nm)	
10	0.089	0.087
20	0.143	0.143
30	0.179	0.179
40	0.206	0.208
50	0.231	0.233
60	0.254	0.261
70	0.278	0.277
80	0.298	0.299
90	0.311	0.313