I. THE KINETICS AND MECHANISM OF THE DECOMPOSITION OF AQUEOUS SOLUTIONS OF THE PENTACYANOCOBALTATE (II) ION

II. THE KINETICS OF THE FORMATION OF COBALT (III) PRODUCTS FROM THE REVERSIBLE OXYGEN CARRIER, μ- PEROXOTETRAKIS (HISTIDINATO) DICOBALT (III)

Thesis for the Degree of Ph. D.

MICHIGAN STATE UNIVERSITY

CHARLES S. SOKOL

1970

This is to certify that the

thesis entitled

I. THE KINETICS AND MECHANISM OF THE DECOMPOSITION OF AQUEOUS SOLUTIONS OF THE PENTACYANOCOBALTATE(II) ION

II. THE KINETICES OF THE FORMATION OF COBALT(III) PRODUCTS FROM THE REVERSIBLE OXYGEN CARRIER, μ-PEROXOTETRAKIS(HISTIDINATO)DICOBALT(III)

presented by

Charles S. Sokol

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Carl H. Brubaker, Jr.
Major professor

Date February 23, 1970

O-169

ABSTRACT

I. THE KINETICS AND MECHANISM OF THE DECOMPOSITION OF AQUEOUS SOLUTIONS OF THE PENTACYANOCOBALTATE(II) ION

II. THE KINETICS OF THE FORMATION OF COBALT(III) PRODUCTS FROM THE REVERSIBLE OXYGEN CARRIER, μ-PEROXOTETRAKIS(HISTIDINATO)DICOBALT(III)

By

Charles S. Sokol

The kinetics of the decomposition of the pentacyanocobaltate(II) ion in aqueous solutions at low ionic strength has been investigated. The reaction is second order with respect to the pentacyanocobaltate(II) ion. The activation energy is 9.84 ± 0.27 kcal/mole in the temperature region of 25-50^{0} and is more than twice that previously reported. It was found that the discrepancy in the activation energy is due to the large ionic strength dependence of the decomposition reaction. As the ionic strength increases, the $Co(CN)_5{}^{3-}$ ion forms ion pairs with the cations in solution. As the concentration of the ion pairs increases, the apparent activation energy decreases.

Limited evidence in support of the postulated monomer-dimer equilibrium of the pentacyanocobaltate(II) ion has been observed. As the concentration of this ion decreases from 0.17 M, there is a slight spectral shift.

The ki

dinato coba

-peroxotet

gated. Fro

product on

tion of sma

ion is prop

greater tha

is given fo

dicobalt(II

histidine s

anisms for

cation are

these mecha

for determi

not conclus

the bis(his

of the supe

Eviden

catalytic a

in its form

Charles S. Sokol

The kinetics of the slow formation of the bis(histidinato)cobalt(III) cation from the reversible oxygen carrier, μ-peroxotetrakis(histidinato)dicobalt(III) has been investigated. From the dependence of the rate of formation of the product on the histidine concentration, the equilibrium formation of small quantities of the tris(histidinato)cobaltate(II) ion is proposed, when the histidine to cobalt(II) ratio is greater than two. Spectrophotometric and kinetic evidence is given for the formation of μ-superoxotetrakis(histidinato)-dicobalt(III) ion in low yield when cobalt(II)-histidine solutions are oxygenated. The most likely mechanisms for the formation of the bis(histidinato)cobalt(III) cation are discussed and the mathematical equations for these mechanisms are derived. Least squares calculations for determination of rate and equilibrium constants could not conclusively confirm the mechanism for the formation of the bis(histidinato)cobalt(III) cation due to the presence of the superoxo complex.

Evidence is given which suggests the possible autocatalytic activity of the bis(histidinato)cobalt(III) cation in its formation from the peroxo oxygen carrier.

I. THE

AQUEOUS

II.

PR

in

I. THE KINETICS AND MECHANISM OF THE DECOMPOSITION OF AQUEOUS SOLUTIONS OF THE PENTACYANOCOBALTATE(II) ION

II. THE KINETICS OF THE FORMATION OF COBALT(III) PRODUCTS FROM THE REVERSIBLE OXYGEN CARRIER, μ-PEROXOTETRAKIS(HISTIDINATO)DICOBALT(III)

By

Charles S. Sokol

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1970

To my wife Myra and my parents Leona and Adolph.

The au

Myra, whose

The author

for his con

the work.

The au

Dye for the

The fi

is grateful

friends and

ACKNOWLEDGMENTS

The author expresses his deep gratitude to his wife, Myra, whose patience and understanding made this possible. The author is very grateful to Professor Carl H. Brubaker, Jr. for his continued assistance and encouragement throughout the work.

The author thanks Dr. R. S. Schwendeman and Dr. J. L. Dye for their helpful suggestions.

The financial support from the Atomic Energy Commission is gratefully acknowledged as is the moral support from friends and coworkers.

TABLE OF CONTENTS

TABLE OF C

TABLE OF CONTENTS (Cont.)

TABLE

LIST OF TABLES

LIST OF TA

TABLE

LIST OF TABLES (Cont.)

FIGURE

LIST OF FIGURES

LIST OF FIG

FIGURE

LIST OF FIGURES (Cont.)

In the
kinetics and
this time, t
determine th
systems that

A typic
concentratio
portional to
actants or p

Mechani
constant ion
stant temper
ally affect
there are re
ficantly alt
tions will b
"inert" elec
tant to keep
keep the ion

Spectro
convenient w
photometric

I. INTRODUCTION

In the last 15 years, much work has been done on the kinetics and mechanisms of inorganic reactions.[1] Prior to this time, the majority of investigations sought only to determine the stoichiometry and thermodynamics of the kinetic systems that were investigated.

A typical experiment involves the measurement of the concentration (or some property of the system that is proportional to the concentration) of one or more of the reactants or products of the reaction as the reaction proceeds.

Mechanistic investigations are usually performed at constant ionic strength and are always performed at a constant temperature since the ambient temperature will drastically affect both rates of reaction and equilibria. However, there are reactions in which ion pair formation will significantly alter the reaction rate and therefore, these reactions will be significantly affected by the presence of an "inert" electrolyte. In these cases, it is much more important to keep the ionic strength as low as possible than to keep the ionic strength as constant as possible.

Spectrophotometric methods of analysis can be very convenient where they can be applied. Generally, spectrophotometric methods of analysis do not give better than one percent

photometric

and product

spectrophot

the total a

all chemica

one percent accuracy.[2] In order to be able to use the spectrophotometric method, it is necessary to know, for all reactants and products, the molar absorptivities in the region of the spectrophotometric investigation. Then, at any wavelength, the total absorbance will be the sum of the absorbances of all chemical species present.

A. Cobalt

The f

peroxodecar

1852 by oxy

tion. Prio

diamagnetic

prepared.5–

century, We

prepared mar

bridged spec

etry about t

Interest in

possible use

as models fo

tion of hemo

synthetic co

Several

molecular ox

2C

No series c

II. HISTORICAL

A. Cobalt Synthetic Oxygen Carriers

The first synthetic oxygen carrier, diamagnetic μ-peroxodecamminedicobalt(III), was prepared by Fremy[3,4] in 1852 by oxygenating an aqueous ammoniacal cobalt(II) solution. Prior to the start of the twentieth century, several diamagnetic and paramagnetic oxygen bridged compounds were prepared.[5-10] Then, around the turn of the twentieth century, Werner, the father of modern coordination chemistry, prepared many cobalt complexes including additional oxygen bridged species. He also established the octahedral geometry about the cobalt atom in these compounds.[9,11-18] Interest in synthetic oxygen carriers was renewed by the possible use of these compounds for oxygen fixation[19] and as models for the investigation of the reversible oxygenation of hemoglobin.[20,21] Recently, extensive research on synthetic cobalt oxygen carriers has been performed.[21-26]

Several cobalt(II) complexes react with, and absorb, molecular oxygen according to the following equation:

$$2Co^{II}L_5X + O_2 \rightleftharpoons L_5CoO_2CoL_5 + X \ .$$

Two series of cobalt oxygen carriers can be formed. One series is

Werner[9] sh

oxygen car

Werner des

ions. This

O_2^{2-}. The

A detailed

in referenc

The ligand

cyanide[29] ar

ligands in t

the diamagne

oxygen carri

have one unp

1.7 B.M.[26]

Werner

ners as be

clature cont

by esr that

cyanide,[35,3

carriers. T

equal influe

dance - I =

of cobalt ox

series is diamagnetic and the other series is paramagnetic. Werner[9] showed that the diamagnetic binuclear cobalt ammonia oxygen carrier is the ion

$$[(NH_3)_5CoO_2Co(NH_3)_5]^{4+} .$$

Werner described the above ion as containing two cobalt(III) ions. This required that the oxygen bridge be peroxide, O_2^{2-}. The above ion can be oxidized[24] to a paramagnetic ion

$$[(NH_3)_5CoO_2Co(NH_3)_5]^{5+} .$$

A detailed discussion of much of Werner's work can be found in reference 27. There are other members of each series. The ligand can be ethylenediamine,[11] diethylenetriamine,[28] cyanide[29] and various amino acids.[26] There can be additional ligands in the bridge.[30-32] In the case of amines as ligand, the diamagnetic oxygen carriers are red and the paramagnetic oxygen carriers are green. The paramagnetic oxygen carriers have one unpaired electron and a magnetic susceptibility of 1.7 B.M.[26]

Werner had characterized the paramagnetic oxygen carriers as being peroxo-cobalt(III,IV) species. This nomenclature continued in general use.[30] However, it was shown by esr that cobalt atoms were equivalent in the amine,[33,34] cyanide,[35,36] histidine[37] and some dibridged[35] cobalt oxygen carriers. The fifteen line esr signal results from the equal influence of the two cobalt atoms (^{59}Co - 100% abundance - $I = 7/2$) on the unpaired electron. The two series of cobalt oxygen carriers were then called "diamagnetic peroxo" and '

Linhard and W

$Co^{III}O_2^{2-}Co^{I}$

correct and s

Linhard and W

An inves

oxygen carrie

was a <u>cis</u>-boa

had discussed

Co-O-O-Co arr

favored a str

Co-Co axis.

structure.

paramagnetic

oxygen carri

moved from t

carriers car

While Vlcek

the relative

oxygen carr

of these st

47.

Recent

diamine bi

magnetic ox

oxygen carr

Co-O-O bond

peroxo" and "paramagnetic peroxo" complexes.[24,32,38,39] Linhard and Weigel[40] stated that Werner's formulation of $Co^{III}O_2{}^{2-}Co^{IV}$ for the paramagnetic oxygen carriers was incorrect and should be $Co^{III}O_2{}^{-}Co^{III}$. As will be seen below, Linhard and Weigel were correct.

An investigation of the cobalt ammine paramagnetic oxygen carrier had incorrectly shown that the Co-O-O-Co was a <u>cis</u>-boat type configuration.[41] Dunitz and Orgel[42] had discussed the electronic structure for a linear Co-O-O-Co arrangement. Brosset and Vannerberg[43] and others[44] favored a structure with the O-O axis perpendicular to the Co-Co axis. Vlcek[45,46] also postulated the perpendicular structure. He stated that the greater stability of the paramagnetic oxygen carriers relative to the diamagnetic oxygen carriers was due to the fact that the electron removed from the diamagnetic carriers to form the paramagnetic carriers came from a $Co-O_2-Co$ antibonding molecular orbital. While Vlcek's structure was incorrect, his explanation of the relative stabilities of the paramagnetic and diamagnetic oxygen carriers probably was correct. A detailed discussion of these structures mentioned above can be found in reference 47.

Recent X-ray studies of some ammonia and ethylenediamine binuclear cobalt oxygen paramagnetic and diamagnetic oxygen carriers showed that for the diamagnetic oxygen carriers, the Co-O-O-Co bonds are "Z" shaped with Co-O-O bond angles of 110 to 113^{0} and an O-O bond distance of 1.47 to 1.

shaped for th

angles of 117

1.36 Å.[39,50-

O_2 carriers a

expected for

paramagnetic

1.35 Å which

dihedral angl

oxygen carrie

oxygen carrie

the diamagnet

peroxide.[56]

The str

magnetic ami

that they are

The equ

magnetic oxy

in the diama

the paramagn

of oxygen ca

and

Thus, a

sidered as c

peroxo or a

of 1.47 to 1.48 Å[48,49] and the Co-O-O-Co bonds are also "Z" shaped for the paramagnetic oxygen carriers with Co-O-O bond angles of 117 to 120^0 and an O-O bond distance of 1.31 to 1.36 Å.[39,50-53] The O-O bond distances for the diamagnetic O_2 carriers are within the range of 1.49 ± 0.02 Å which is expected for peroxides[54] and the O-O bond distances for the paramagnetic O_2 carriers are within the range of 1.32 to 1.35 Å which is expected for superoxides.[55] The Co-O-O-Co dihedral angle is approximately 0^0 for the paramagnetic oxygen carriers and approximately 146^0 for the diamagnetic oxygen carriers. Thus, the configuration of the oxygen in the diamagnetic oxygen carriers is similar to hydrogen peroxide.[56]

The striking similarity between the esr of the paramagnetic amine and cyanide cobalt oxygen carriers indicates that they are isostructural.[35]

The equivalence of the two cobalt atoms in the paramagnetic oxygen carriers, the presence of a peroxo group in the diamagnetic oxygen carriers and a superoxo group in the paramagnetic oxygen carriers showed that the two series of oxygen carriers should be formulated as follows:

$$L_5Co^{III}O_2{}^{2-}Co^{III}L_5 \quad \text{(diamagnetic)}$$

and $$L_5Co^{III}O_2{}^{-}Co^{III}L_5 \quad \text{(paramagnetic).}$$

Thus, all binuclear cobalt oxygen carriers are now considered as containing two cobalt(III) ions and either a peroxo or a superoxo bridge.

Earlier

tion of oxyge

amine complex-

slow. Howeve

carrier was f

B. The Penta

When cya

salt, a brown

redissolves t

cobalt ratio

evolution als

This per

only as an ox

tion catalys

investigated

cobalt speci

cyanide ion

However, it

five coordin

ation sphere

The vic

aqueous gree

addition of

paramagnetic

moment of 1.

75,76

Altho

Earlier research had incorrectly shown that the absorption of oxygen by ammoniacal cobalt(II)[57] and other cobalt(II) amine complexes[28,58], to form the oxygen carriers, was fairly slow. However, recent stopped-flow studies proved that the oxygen carrier was formed rapidly.[59,60]

B. The Pentacyanocobaltate(II) Ion

When cyanide ion is added to a solution of a cobalt(II) salt, a brown precipitate of $Co(CN)_2$ is first formed that redissolves to form a green solution[61] when the cyanide to cobalt ratio reaches five to one.[62-66] The maximum heat evolution also occurs at this ratio.[67]

This pentacyanocobaltate(II) ion is of interest not only as an oxygen carrier[29,68,69] but also as a hydrogenation catalyst. In the last ten years, this ion has been investigated extensively.[71,72] It has been shown that the cobalt species present in solutions containing excess cyanide ion is actually $Co(CN)_5^{3-}$ rather than $Co(CN)_6^{4-}$.[61,73] However, it could not be determined whether this ion was five coordinate or contained a water molecule in the coordination sphere.

The violet solid which is in equilibrium with the aqueous green $Co(CN)_5^{3-}$ solution may be precipitated by the addition of ethanol.[62] Whereas the green $Co(CN)_5^{3-}$ ion is paramagnetic with one unpaired electron and a magnetic moment of 1.72 B.M.,[62,74] the violet solid is diamagnetic.[62,75,76] Although the solid violet compound was reported to be

$K_4Co(CN)_6$ in

to be a hydr

the $Co(CN)_5^{3-}$

that the sol

would explain

determined s

complex, [Co_2

In 1942,

$Co(CN)_5^{3-}$ abs

ratio of one

the rate of

with a Co:CN

geneous abso

hydrido spec

studies whic

aqueous solu

sodium-cesiu

been synthe

solutions o

at a rate p

loss of the

and a hydri

$Co(CN)_5^{3-}$ a

the heterog

The "aging

to dimeriza

absorption

$K_4Co(CN)_6$ in the earlier literature,[77-79] it has been shown to be a hydrated[80] (probably a tetrahydrated[72]) dimer of the $Co(CN)_5{}^{3-}$ ion, $K_6[Co_2(CN)_{10}]$. It has been suggested that the solid dimer contains a metal-metal bond[81] (which would explain the diamagnetism) as in the more recently determined structure for the analogous methyl isocyanide complex, $[Co_2(MeNC)_{10}](ClO_4)_4$.[82]

In 1942, Iguchi[83] noted that aqueous solutions of $Co(CN)_5{}^{3-}$ absorbed molecular hydrogen in the approximate ratio of one atom of hydrogen per atom of cobalt and that the rate of heterogeneous hydrogen absorption was greatest with a Co:CN ratio of 1:4.5. The product of this heterogeneous absorption was later assumed to be the colorless hydrido species $Co(CN)_5H^{3-}$.[84] This was confirmed by nmr studies which showed the existence of Co-H bonds in reduced aqueous solutions of the pentacyanide.[81] The solid mixed sodium-cesium salts of the $Co(CN)_5H^{3-}$ ion have recently been synthesized.[85] Mills and coworkers found that aqueous solutions of $Co(CN)_5{}^{3-}$ "aged" and lost their paramagentism at a rate paralleling the loss of reducibility (i.e., the loss of the ability to absorb H_2 bubbled into the solution) and a hydride intermediate was proposed.[86] Both the original $Co(CN)_5{}^{3-}$ and the reduced solutions were found to catalyze the heterogeneous $D_{2(gas)}$-$H_2O_{(liquid)}$ hydrogen exchange. The "aging" of these solutions was first thought to be due to dimerization but it was shown to be due to homogeneous absorption of hydrogen from water to form the above mentioned

hydrido spe
"aged" solu
species.[87,8
homogeneous
The heteroge
reversible a
librium shif

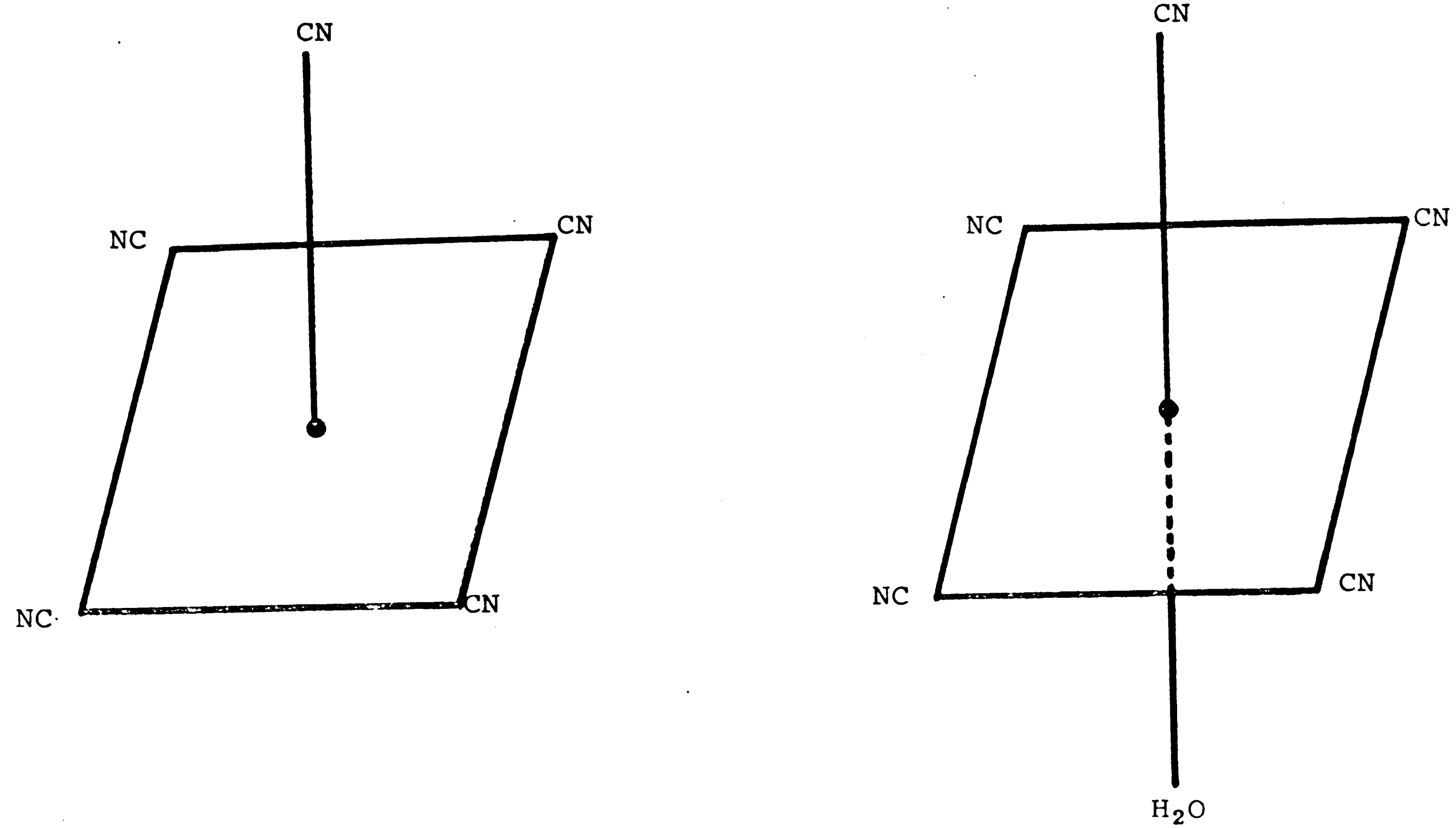
On the
the pentacya
alkyl isocya
and Williams
contain a wa
lated as Co
tors, by me
ruled out t
structure.[9
metry and c
tion site.
either of t
Figure 1.

There
under equi
certain el
the interme
25° is est
mole.[94

hydrido species.[70] In earlier literature, the reduced or "aged" solutions were thought to contain a cobalt(I) species.[87,88] Thus, $Co(CN)_5H^{3-}$ is produced by both the homogeneous and the heterogeneous absorptions of hydrogen. The heterogeneous absorption of hydrogen by $Co(CN)_5{}^{3-}$ is reversible and as the temperature is increased, the equilibrium shifts toward the evolution of H_2.[89,90]

On the basis of the similarity of solution spectra of the pentacyanocobaltate(II) ion with some corresponding alkyl isocyanates which are known to be $CoL_5H_2O^{3-}$, Pratt and Williams[91] postulated that the pentacyano ion must also contain a water molecule and therefore, it should be formulated as $Co(CN)_5H_2O^{3-}$. At the same time, other investigators, by means of analysis of esr and visible spectra, had ruled out the possibility of a trigonal bipyramidal, D_{3h} structure.[92,93] They showed that the complex had C_{4v} symmetry and could have a water molecule at a sixth coordination site. Thus, the pentacyanocobaltate(II) ion could have either of the structures of C_{4v} symmetry as shown in Figure 1.

There is no evidence for the formation of $Co(CN)_6{}^{4-}$ under equilibrium conditions ($K_{formation} << 1$).[91] However, certain electron transfer reactions appear to proceed by the intermediate $Co(CN)_6{}^{4-}$ ion whose formation constant at 25^0 is estimated to be within the range of 10^{-1} to 10^{-4} l/mole.[94]



Square Pyramidal

Tetragonal

Figure 1. Possible structures for the pentacyanocobaltate(II) ion.

C. <u>The Cobal</u>

Of the s
biological ox
carrier has p

Histidin

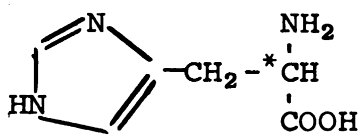
The carbon wi
the optical a
the optical i
isomer that w
anion (witho
The sites of
protonless in
late oxygen
bound to the
both in the s
state, the in
other.[95,97]
boxyl groups
meric confor

Hearon a
absorbed oxy
stoichiometr
one mole of

C. The Cobalt-histidine Oxygen Carriers

Of the synthetic oxygen carriers most closely resembling biological oxygen carriers, the cobalt l-histidine oxygen carrier has probably been the most extensively investigated.

Histidine is an amino acid with the structure



The carbon with the asterisk is asymmetric and the site of the optical activity of the compound. Since l-histidine is the optical isomer that is found biologically, this is the isomer that was used in this investigation. The histidinate anion (without the carboxyl proton) is a tridentate ligand. The sites of coordination are the amine nitrogen, the protonless imidazole nitrogen and the deprotonated carboxylate oxygen. All three of these coordination sites are bound to the cobalt in CoL_2 (L = l-histidinato anion) both in the solid state[95] and in solution.[96] In the solid state, the imidazole groups in the CoL_2 are <u>trans</u> to each other.[95,97] In the <u>trans</u> imidazole configuration, the carboxyl groups must be <u>cis</u> to each other due to the enantiomeric conformation of the l-histidine.[98]

Hearon and his coworkers found that CoL_2 reversibly absorbed oxygen and they investigated the equilibria and stoichiometry of this oxygen absorption. They found that one mole of O_2 was absorbed per two moles of CoL_2.[20,99-103]

The oxygen c
a solution c
oxygen carri
netic.[20,96,
carrier is b
ation sphere
molecules on
of a peroxo b
carboxylate
carrier, L_2C

As expe
the cobalt a
that the dia
by Ce^{IV} to a
change durin
from amber t
color change
magnetic his
hyperfine st
of the two c
bis(histidin
absorbed one
the oxygen c
a second mol
products.[20,
mers of the

The oxygen carrier was formed very rapidly upon oxygenating a solution of the cobalt(II) histidine complex.[20,59] The oxygen carrier, $L_2CoO_2CoL_2$, was amber colored and diamagnetic.[20,96,104,105] The formation of the binuclear oxygen carrier is believed to occur by dissociation from the coordination sphere of the carboxylate group of one of the histidine molecules on each of two CoL_2 molecules and the formation of a peroxo bridge at the coordination sites vacated by the carboxylate groups.[59,98] The solid trihydrate of the oxygen carrier, $L_2CoO_2CoL_2 \cdot 3H_2O$ has been isolated.[98]

As expected from the two series of oxygen carriers in the cobalt ammonia and cyano systems, it was recently shown that the diamagnetic histidine oxygen carrier can be oxidized by Ce^{IV} to a paramagnetic oxygen carrier.[37] Even the color change during this oxidation of the histidine oxygen carrier from amber to blue-green was similar to the red to green color change in the ammonia system. The esr of the paramagnetic histidine oxygen carrier contained the 15-line hyperfine structure, once again confirming the equivalence of the two cobalt ions in the oxygen carrier.[37] The bis(histidinato)cobalt(II) complex rapidly and reversibly absorbed one mole of O_2 per two moles of cobalt to form the oxygen carrier.[98] It then slowly irreversibly absorbed a second mole of O_2 per two moles of cobalt to form cobalt(III) products.[20,106] These final cobalt(III) products were isomers of the bis(l-histidinato)cobalt(III) cation.[106] There are three i

have recent

observed.[10

In str

lose a seco

This anioni

form an oxy

carrier for

are three isomers of the final cobalt(III) product and they have recently been separated and their spectra have been observed.[107]

In strongly basic solutions (pH > 12), histidine can lose a second proton and can form the complex $Co(L\text{-}H)_2^{2-}$.[96] This anionic cobalt(II) complex can also absorb oxygen to form an oxygen carrier that is different from the oxygen carrier formed by the oxygenation of the neutral CoL_2.[108]

A. Linear

In thos

reaction are

in a linear

least square

for the line

One for

where m an

of the slope

mental data

number of ex

The res

The sum

S = $\sum_{i=}$

III. THEORETICAL

A. Linear Least Squares

In those cases where the kinetics of a chemical reaction are simple enough, the rate law is usually written in a linear form. It is then possible to use the linear least squares method to calculate the optimum parameters for the linear equation. The method is as follows.[109,110]

One form of the linear equation is

$$Y = mX + b \qquad (1)$$

where m and b are respectively the least squares values of the slope and intercept of the straight line. The experimental data points are x_i and y_i and N is the total number of experimental data points.

The residual of each data point is

$$x_i m + b - y_i \ . \qquad (2)$$

The sum of the squares of the residuals, S, is

$$S = \sum_{i=1}^{N} (x_i m + b - y_i)^2 = m^2 \sum_1^N x_i^2 + 2bm \sum_1^N x_i - 2m \sum_1^N x_i y_i + nb^2 - 2b \sum_1^N y_i + \sum_1^N y_i^2 \ . \qquad (3)$$

To obta

be minimized

and b are

$\frac{\partial S}{\partial}$

$\frac{\partial S}{\partial}$

Equatio

It is a

i.e., the 5

cept, c_m a

Accordi

can be obtai

$a^2 =$

$c_m = \sqrt{}$

To obtain the optimum values for m and b, S must be minimized. The derivatives of S with respect to m and b are set equal to zero

$$\frac{\partial S}{\partial m} = 0 = 2m \sum_1^N x_i^2 + 2b \sum_1^N x_i - 2 \sum_1^N x_i y_i \qquad (4)$$

$$\frac{\partial S}{\partial b} = 0 = 2m \sum_1^N x_i + 2bn - 2 \sum_1^N y_i . \qquad (5)$$

Equations 4 and 5 can be solved for m and b

$$m = \frac{N \Sigma x_i y_i - \Sigma x_i \Sigma y_i}{N \Sigma x_i^2 - (\Sigma x_i)^2} \qquad (6)$$

$$b = \frac{\Sigma x_i^2 \Sigma y_i - \Sigma x_i \Sigma x_i y_i}{N \Sigma x_i^2 - (\Sigma x_i)^2} . \qquad (7)$$

It is also useful to determine the standard deviations (i.e., the 50% confidence limits) of the slope and incercept, σ_m and σ_b, respectively.

According to Youden,[110] the values for σ_m and σ_b can be obtained from the following equations:

$$\alpha^2 = \frac{\Sigma y_i^2 - \dfrac{(\Sigma y_i)^2}{N} - \dfrac{\left(\Sigma x_i y_i - \dfrac{\Sigma x_i \Sigma y_i}{N}\right)^2}{\Sigma x_i^2 - \dfrac{(\Sigma x_i)^2}{N}}}{N - 2} \qquad (8)$$

$$\sigma_m = \sqrt{\frac{\alpha^2}{\Sigma x_i^2 - (\Sigma x_i)^2}} \qquad (9)$$

c_b = S

The val

constants to

The com

least square

B. Non-line

In the

able to inte

rarely able

becomes nece

procedure.

The gen

where x is

species, y

parameters

to be optimi

By defi

calculated c

The su

becomes

$$\sigma_b = S \sqrt{\frac{\Sigma x_i^2}{N \Sigma x_i^2 - (\Sigma x_i)^2}} \quad . \qquad (10)$$

The values of σ_m and σ_b can be multiplied by known constants to obtain confidence limits other than 50%.

The computer program written by the author for linear least squares calculations can be found in the Appendix.

B. Non-linear Least Squares

In the case of complex kinetic systems, even if one is able to integrate the differential rate expression, he is rarely able to linearize the expression. It therefore becomes necessary to resort to a non-linear least squares procedure. Such a procedure is derived as follows.[111]

The generalized non-linear rate law can be written

$$f(x, y, a, b, c, \cdots) = 0 \qquad (11)$$

where x is the concentration of one of the chemical species, y is the time and $a, b, c, \cdots$ are the kinetic parameters (the rate and equilibrium constants) which are to be optimized.

By defining the residuals between experimental and calculated data points, one obtains

$$R_{x_i} = x_i - x_{calc} \qquad (12)$$

$$R_{y_i} = y_i - y_{calc} \quad . \qquad (13)$$

The sum of the squares of the residuals, S , now becomes

An obv

squares val

$c_{l.s.}$, ...

$f(x_{i_{ca}}$

One mu

kinetic par

a Taylor's

$(x_i, y_i, a_0$

The fo

following e

$\Delta a = a$

$\Delta b = b$

$\Delta c = c$

$F_i = f$

$F_{i_0} =$

$F_{x_i} =$

$F_{a_i} =$

$$S = \sum_{1}^{N} (R^2_{x_i} + R^2_{y_i}). \tag{14}$$

An obvious condition that must be met by the least squares values of the kinetic parameters, $a_{l.s.}$, $b_{l.s.}$, $c_{l.s.}$, $\cdots$ is

$$f(x_{i_{calc}}, y_{i_{calc}}, a_{l.s.}, b_{l.s.}, c_{l.s.}, \cdots) = 0. \tag{15}$$

One must have good enough initial estimates of the kinetic parameters, a_0, b_0, c_0, $\cdots$ to be able to truncate a Taylor's series expansion of equation 11 about the point $(x_i, y_i, a_0, b_0, c_0, \cdots)$ after the first order terms.

The following terms are defined in order to simplify following equations.

$$\Delta a = a_0 - a_{l.s.\ estimate} \tag{16}$$

$$\Delta b = b_0 - b_{l.s.\ estimate} \tag{17}$$

$$\Delta c = c_0 - c_{l.s.\ estimate}, \text{ etc.} \tag{18}$$

$$F_i = f(x_{i_{calc}}, y_{i_{calc}}, a, b, c, \cdots) \tag{19}$$

$$F_{i_0} = f(x_{i_0}, y_{i_0}, a_0, b_0, c_0, \cdots) \tag{20}$$

$$F_{x_i} = \left.\frac{\partial F_i}{\partial x}\right|_{(x_i, y_i, a_0, b_0, c_0, \cdots)} \quad \text{for each data point } i \tag{21}$$

$$F_{a_i} = \left.\frac{\partial F_i}{\partial a}\right|_{(x_i, y_i, a_0, b_0, c_0, \cdots)} \quad \text{for each data point } i. \tag{22}$$

The T

point (x_i

terms is

$F_i =$

=

Rearr

$F_{i_0} =$

In or

residuals,

$dS = -$

Since

must also s

24 must sti

F_{x_i} dR

If M

then there

differentia

of the y

kinetic par

of $2N + M$

the N equ

N of the d

$N + M$ arbi

The Taylor's series expansion of equation 11 about point $(x_i, y_i, a_0, b_0, c_0, \ldots)$ including only first order terms is

$$F_i = F_{i_0} - F_{x_i} R_{x_i} - F_{y_i} R_{y_i} - F_{a_i} \Delta a - F_{b_i} \Delta b - F_{c_i} \Delta c - \cdots = 0 \qquad i = 1, 2, \cdots, N. \qquad (23)$$

Rearranging equation 23, one obtains

$$F_{i_0} = F_{x_i} R_{x_i} + F_{y_i} R_{y_i} + F_{a_i} \Delta a + F_{b_i} \Delta b + F_{c_i} \Delta c + \ldots \qquad (24)$$

In order to minimize the sum of the squares of the residuals, S, (see equation 14), dS is set equal to zero

$$dS = \frac{\Sigma \, (R_{x_i} \, dR_{x_i} + R_{y_i} \, dR_{y_i})}{2} = 0 \qquad (25)$$

Since the change in the residuals, dR_{x_i} and dR_{y_i} must also satisfy equation 24 (the right side of equation 24 must still be equal to F_{i_0})

$$F_{x_i} \, dR_{x_i} + F_{y_i} \, dR_{y_i} + F_{a_i} \, d\Delta a + F_{b_i} \, d\Delta b + F_{c_i} \, d\Delta c + \ldots = 0 \qquad i = 1, 2, \cdots, N. \qquad (26)$$

If M is the number of kinetic parameters, a, b, c, $\cdots$, then there are N sets of equation 26 with a total of N differentials of the x residuals, dR_{x_i}, N differentials of the y residuals, dR_{y_i}, and M differentials of the kinetic parameters, $d\Delta a$, $d\Delta b$, $d\Delta c$, etc. There are a total of 2N + M differentials with only N equations. Since the N equations can be used to mathematically substitute N of the differentials, there are only 2N + M − N = N + M arbitrary differentials.

Since N

N Lagrang

plies each

$-\lambda_i F_x$

Adding equ

$\Sigma \ (R_x$

$+ \ \Sigma$

Since

for λ_i in

eliminate

N + M diffe

the differe

maining N

ents of eac

R

R

Σ

Σ

Σ

Since N of the differentials are not arbitrary, one defines N Lagrange multipliers, $-\lambda_1$, $-\lambda_2$, $-\lambda_3, \cdots, -\lambda_N$ and multiplies each of these by equations 26

$$-\lambda_i F_{x_i}\, dR_{x_i} - \lambda_i F_{y_i}\, dR_{y_i} - \lambda_i F_{a_i}\, d\Delta a - \lambda_i F_{b_i}\, d\Delta b - \lambda_i F_{c_i}\, d\Delta c - \cdots = 0 \qquad i = 1,2,\cdots, N. \tag{27}$$

Adding equations 25 and 27 and collecting terms, one obtains

$$\Sigma\,(R_{x_i} - \lambda_i F_{x_i})\, dR_{x_i} + \Sigma\,(R_{y_i} - \lambda F_{y_i})\, dR_{x_i} + \Sigma\,\lambda_i F_{a_i}\, d\Delta a + \Sigma\,\lambda_i F_{b_i}\, d\Delta b + \Sigma\,\lambda_i F_{c_i}\, d\Delta c + \cdots = 0. \tag{28}$$

Since there are N equations with N arbitrary values for λ_i in equation 28, the values of λ_i are chosen to eliminate N of the differentials. This process leaves N + M differentials. However, as stated above, N + M of the differentials are arbitrary. Therefore, since the remaining N + M differentials are arbitrary, the coefficients of each differential in equation 28 must be zero

$$R_{x_i} - \lambda_i F_{x_i} = 0 \qquad i = 1,2,3,\cdots,N \tag{29a}$$

$$R_{y_i} - \lambda_i F_{y_i} = 0 \tag{29b}$$

$$\Sigma\,\lambda_i F_{a_i} = 0 \tag{29c}$$

$$\Sigma\,\lambda_i F_{b_i} = 0 \tag{29d}$$

$$\Sigma\,\lambda_i F_{c_i} = 0 \cdots . \tag{29e}$$

(29)

By rearran

residuals

By rearrang

$F_i - F_{i_o}$

By substitu

$F_i - F_{i_o}$

and solving

$\lambda_i =$

Substituting

rearranging

the followi

$\Sigma F_{a_i} F_a$

$\Sigma F_{b_i} F_a$

$\Sigma F_{c_i} F_a$

etc.

By rearranging equations 29a and 29b, one can solve for the residuals R_{x_i} and R_{y_i}

$$R_{x_i} = \lambda_i F_{x_i} \qquad\qquad i = 1,2,3,\cdots,N. \quad (30)$$
$$R_{y_i} = \lambda_i F_{y_i}$$

By rearranging equation 23, one obtains

$$F_i - F_{i_0} = F_{x_i} R_{x_i} + F_{y_i} R_{y_i} + F_{a_i} \Delta a + F_{b_i} \Delta b + F_{c_i} \Delta c + \cdots, \quad (31)$$
$$i = 1,2,3,\cdots,N.$$

By substituting equation 30 into 31, one obtains

$$F_i - F_{i_0} = F^2_{x_i} \lambda_i + F^2_{y_i} \lambda_i + F_{a_i} \Delta a + F_{b_i} \Delta b + F_{c_i} \Delta c + \cdots, \quad (32)$$
$$i = 1,2,3,\cdots,N$$

and solving equation 32 for λ_i

$$\lambda_i = \frac{F_i - F_{i_0} - F_{a_i} \Delta a - F_{b_i} \Delta b - F_{c_i} \Delta c - \cdots}{F^2_{x_i} + F^2_{y_i}}, \quad (33)$$
$$i = 1,2,3,\cdots,N.$$

Substituting equation 33 into equations 29c, 29d, 29e, $\cdots$, rearranging and dividing by the quantity $(F^2_{x_i} + F^2_{y_i})$ yields the following set of equations

$$\Sigma F_{a_i} F_{a_i} \Delta a + \Sigma F_{a_i} F_{b_i} \Delta b + \Sigma F_{a_i} F_{c_i} \Delta c + \cdots = \Sigma F_{a_i} (F_i - F_{i_0})$$

$$\Sigma F_{b_i} F_{a_i} \Delta a + \Sigma F_{b_i} F_{b_i} \Delta b + \Sigma F_{b_i} F_{c_i} \Delta c + \cdots = \Sigma F_{b_i} (F_i - F_{i_0}) \quad (34)$$

$$\Sigma F_{c_i} F_{a_i} \Delta a + \Sigma F_{c_i} F_{b_i} \Delta b + \Sigma F_{c_i} F_{c_i} \Delta c + \cdots = \Sigma F_{c_i} (F_i - F_{i_0})$$

etc.

There

Therefore,

solved for

way to sol

the method

are as fol

$$
a = \frac{\begin{vmatrix} \Sigma F_a \\ \Sigma F_b \\ \Sigma F_c \end{vmatrix}}{\begin{vmatrix} \Sigma F_a \\ \Sigma F_b \\ \Sigma F_c \end{vmatrix}}
$$

There are M equations 34 and M unknowns (Δa, Δb, $\Delta c, \cdots$). Therefore, the M simultaneous linear equations can be solved for the M unknowns, Δa, Δb, Δc, $\cdots$. The easiest way to solve the system of M linear equations is to use the method of determinants. The determinental solutions are as follows:

$$\Delta a = \frac{\begin{vmatrix} \Sigma F_{a_i}(F_i - F_{i_0}) & \Sigma F_{a_i}F_{b_i} & \Sigma F_{a_i}F_{c_i} & \cdots \\ \Sigma F_{b_i}(F_i - F_{i_0}) & \Sigma F_{b_i}F_{b_i} & \Sigma F_{b_i}F_{c_i} & \cdots \\ \Sigma F_{c_i}(F_i - F_{i_0}) & \Sigma F_{c_i}F_{b_i} & \Sigma F_{c_i}F_{c_i} & \cdots \\ \vdots & \vdots & \vdots & \end{vmatrix}}{\begin{vmatrix} \Sigma F_{a_i}F_{a_i} & \Sigma F_{a_i}F_{b_i} & \Sigma F_{a_i}F_{c_i} & \cdots \\ \Sigma F_{b_i}F_{a_i} & \Sigma F_{b_i}F_{b_i} & \Sigma F_{b_i}F_{c_i} & \cdots \\ \Sigma F_{c_i}F_{a_i} & \Sigma F_{c_i}F_{b_i} & \Sigma F_{c_i}F_{c_i} & \cdots \\ \vdots & \vdots & \vdots & \end{vmatrix}} \quad (35a)$$

$\Sigma\, F$

$\Sigma\, F$

$\Sigma\, F$

$\Sigma b =$

$\Sigma\, F$

$\Sigma\, F$

$\Sigma\, F$

The r

If

are not c

process c

c_{new}, etc

This

The

chemical

as well a

appendix

$$\Delta b = \frac{\begin{vmatrix} \Sigma F_{a_i}F_{a_i} & \Sigma F_{a_i}(F_i - F_{i_0}) & \Sigma F_{a_i}F_{c_i} & \cdots \\ \Sigma F_{b_i}F_{a_i} & \Sigma F_{b_i}(F_i - F_{i_0}) & \Sigma F_{b_i}F_{c_i} & \cdots \\ \Sigma F_{c_i}F_{a_i} & \Sigma F_{c_i}(F_i - F_{i_0}) & \Sigma F_{c_i}F_{c_i} & \cdots \\ \vdots & \vdots & \vdots & \end{vmatrix}}{\begin{vmatrix} \Sigma F_{a_i}F_{a_i} & \Sigma F_{a_i}F_{b_i} & \Sigma F_{a_i}F_{c_i} & \cdots \\ \Sigma F_{b_i}F_{a_i} & \Sigma F_{b_i}F_{b_i} & \Sigma F_{b_i}F_{c_i} & \cdots \\ \Sigma F_{c_i}F_{a_i} & \Sigma F_{c_i}F_{b_i} & \Sigma F_{c_i}F_{c_i} & \cdots \\ \vdots & \vdots & \vdots & \end{vmatrix}} \text{, etc.} \qquad (35b)$$

The new values of a, b, c, $\cdots$ are

$$a_{new} = a_0 + \Delta a$$
$$b_{new} = b_0 + \Delta b \qquad (36)$$
$$c_{new} = c_0 + \Delta c \quad \text{, etc.}$$

If Δa, Δb, Δc, $\cdots$ are not small enough (a, b, c, $\cdots$ are not close enough to their converged values), the whole process can be repeated by using $a_0 = a_{new}$, $b_0 = b_{new}$, $c_0 = c_{new}$, etc. and calculating a new Δa, Δb, Δc, etc.

This derivation is essentially that of Wentworth.[111]

The derivatives necessary to use this method for the chemical system which has been investigated by the author, as well as the computer subroutine, will be found in the appendix.

C. Mathem

cyanoc

As wi

cyanocobal

type

This

and linear

By pl

line of sl

The a

from the A

By pl

tures, T)

E_a R.

The c

points can

cedure pre

the author

found in t

C. Mathematical Equations for the Decomposition of Pentacyanocobaltate(II)

As will be shown later, the decomposition of pentacyanocobaltate(II) is a simple second order reaction of the type

$$2A \xrightarrow{k} \text{products} \qquad (37)$$

$$\frac{dA}{dt} = -kA^2. \qquad (38)$$

This differential equation can easily be integrated and linearized[112-114]

$$\frac{1}{A} = kt + \frac{1}{A_0}. \qquad (39)$$

By plotting $1/A$ *versus* t, one obtains a straight line of slope k and intercept of $1/A_0$.

The activation energy of the reaction can be obtained from the Arrhenius equation[112-114]

$$\ln k = \frac{-E_a}{RT} + \text{constant}. \qquad (40)$$

By plotting the value of ln k (at various temperatures, T) *versus* $1/T$, one obtains a straight line of slope E_a/R.

The optimum straight line from the experimental data points can be obtained from the linear least squares procedure previously described. A computer program written by the author for the linear least squares procedure will be found in the Appendix.

D. Mathem

tion o

As wi

for this r

fusion, fr

dinato ion

Or

D. Mathematical Equations for the Formation and Decomposition of μ-Dioxygentetrakis(l-histidinato)dicobalt

As will be seen, the following mechanism is proposed for this reaction (L = l-histidinato ion -- to avoid confusion, free histidine is shown as HL and free l-histidinato ion is shown as L^-)

$$Co^{2+} + L^- \overset{K_1}{\rightleftharpoons} CoL^+ \quad (41)$$

$$CoL^+ + L^- \overset{K_2}{\rightleftharpoons} CoL_2 \quad (42)$$

$$CoL_2 + L^- \overset{K_3}{\rightleftharpoons} CoL_3^- \quad (43)$$

$$CoL_2 + O_2 \overset{K_{4a}}{\rightleftharpoons} CoL_2O_2 \quad (44)$$

$$CoL_2O_2 + CoL_2 \overset{K_{4b}}{\rightleftharpoons} (CoL_2)_2O_2 \quad (45)$$

$$H^+ + L^- \overset{K_{1H}}{\rightleftharpoons} HL \quad (46)$$

$$HL + H^+ \overset{K_{2H}}{\rightleftharpoons} H_2L^+ \quad (47)$$

$$H_2L^+ + H^+ \overset{K_{3H}}{\rightleftharpoons} H_3L^{2+} \quad (48)$$

$$(CoL_2)_2O_2 \xrightarrow{k_{5a}} CoL_2^+ + CoL_2 + O_2^- \quad (49)$$

or

$$CoL_2O_2 + CoL_2 \xrightarrow{k'_{5a}} CoL_2^+ + CoL_2 + O_2^- \quad (50)$$

$$CoL_2O_2 + CoL_2^+ \xrightarrow{k_{5b}} 2CoL_2^+ + O_2^- . \quad (51)$$

The e

as follows

The r

first and

derived.

From

rate expre

d[CoL
dt

Substituti

d[CoL
dt

Since

equal to t

present

The equilibrium expressions for equations 41 to 48 are as follows:

$$\left.\begin{aligned} K_1 &= [CoL^+]/[Co^{2+}][L^-] \\ K_2 &= [CoL_2]/[CoL^+][L^-] \\ K_3 &= [CoL_3^-]/[CoL_2][L^-] \end{aligned}\right\} \quad (52)$$

$$\left.\begin{aligned} K_{4a} &= [CoL_2O_2]/[CoL_2][O_2] \\ K_{4b} &= [(CoL_2)_2O_2]/[CoL_2O_2][CoL_2] \end{aligned}\right\} \quad (53)$$

$$\left.\begin{aligned} K_{1H} &= [HL]/[H^+][L^-] \\ K_{2H} &= [H_2L^+]/[HL][H^+] \\ K_{3H} &= [H_3L^{2+}]/[H_2L^+][H^+] \ . \end{aligned}\right\} \quad (54)$$

The rate law including reaction 49 will be derived first and then the rate law including equation 50 will be derived.

From equations 49 and 51, one obtains the following rate expression

$$\frac{d[CoL_2^+]}{dt} = k_{5a}[(CoL_2)_2O_2] + k_{5b}[CoL_2O_2][CoL_2^+] \ . \quad (55)$$

Substituting equations 53 into 55

$$\frac{d[CoL_2^+]}{dt} = k_{5a}K_{4a}K_{4b}[CoL_2]^2[O_2]$$

$$+ \ k_{5b}K_{4a}[CoL_2][O_2][CoL_2^+] \ . \quad (56)$$

Since the total cobalt ion concentration, Co_t, is equal to the sum of the concentrations of all cobalt species present

Co_t =

By substit

rearranging

$[CoL_2$

+ 1 +

For t

B_1 is de

B_1 =

Equation

[Co

Equation

[Co

Si

equatio

must be

[C

F

ligand

ally v

oxyger

expre

by si

$$Co_t = [Co^{2+}] + [CoL^+] + [CoL_2] + [CoL_3^-] + [CoL_2O_2] + 2[(CoL_2)_2O_2] + [CoL_2^+]. \quad (57)$$

By substituting equations 52 and 53 into equation 57 and rearranging, one obtains

$$[CoL_2]^2(2K_{4a}[O_2]K_{4b}) + [CoL_2]\left(\frac{1}{K_1K_2[L^-]^2} + \frac{1}{K_2[L^-]} + 1 + K_3[L^-] + K_{4a}[O_2]\right) + [CoL_2^+] - Co_t = 0. \quad (58)$$

For the purpose of simplifying equation 58, the quantity B_1 is defined

$$B_1 = \frac{1}{K_1K_2[L^-]^2} + \frac{1}{K_2[L^-]} + 1 + K_3[L^-] + K_{4a}[O_2]. \quad (59)$$

Equation 58 then becomes

$$[CoL_2]^2(2K_{4a}K_{4b}[O_2]) + [CoL_2]B_1 + [CoL_2^+] - Co_t = 0. \quad (60)$$

Equation 60 is then solved for $[CoL_2]$

$$[CoL_2] = \frac{-B_1 \pm \sqrt{B_1^2 - 4(2K_{4a}K_{4b}[O_2])([CoL_2^+] - Co_t)}}{4\ K_{4a}K_{4b}[O_2]}. \quad (61)$$

Since $[CoL_2]$ must be zero or positive, the real root of equation 61 must be the positive root and the negative root must be extraneous and therefore,

$$[CoL_2] = \frac{-B_1 + \sqrt{B_1^2 - 8K_{4a}K_{4b}[O_2]([CoL_2^+] - Co_t)}}{2(2K_{4a}K_{4b}[O_2])}. \quad (62)$$

For the purpose of integrating the rate expression, the ligand concentration is assumed to be constant. (It actually varies slightly as the reaction proceeds.) Constant oxygen partial pressures are maintained in the solutions.

To further simplify the writing of the mathematical expressions, some of the constant terms will be represented by single terms as shown below

B_3

B_2

and the

By

one obta

[Co

By substi

following

$\frac{dCo^{I}}{dt}$

In or

transforma

formation

$x = \sqrt{}$

$\frac{dx}{dCo^{II}}$

Sett

tuting eq

$$B_3 = 8K_{4a}K_{4b}[O_2] \tag{63}$$

$$B_2 = B_1^2 + 8K_{4a}K_{4b}[O_2]Co_t = B_1^2 + B_3Co_t \tag{64}$$

and the symbol Co^{III} will be used to represent $[CoL_2^+]$.

By substituting equations 63 and 64 into equation 62, one obtains

$$[CoL_2] = \frac{-B_1 + \sqrt{B_2 - B_3Co^{III}}}{B_3/2}$$

$$= \frac{2}{B_3}\left(-B_1 + \sqrt{B_2 - B_3Co^{III}}\right) . \tag{65}$$

By substituting equation 65 into equation 56, one obtains the following:

$$\frac{dCo^{III}}{dt} = \frac{k_{5a}}{2B_3}\left(-B_1 + \sqrt{B_2 - B_3Co^{III}}\right)^2$$

$$+ \frac{2k_{5b}K_{4a}[O_2][CoL_2^+]}{B_3}\left(-B_1 + \sqrt{B_2 - B_3Co^{III}}\right) . \tag{66}$$

In order to be able to integrate equation 66, several transformations of variables must be made. The first transformation is shown below

$$x = \sqrt{B_2 - B_3Co^{III}}$$

$$\frac{dx}{dCo^{III}} = \frac{d\sqrt{B_2 - B_3Co^{III}}}{d(B_2 - B_3Co^{III})} \cdot \frac{d(B_2 - B_3Co^{III})}{dCo^{III}}$$

$$= \frac{-B_3}{2\sqrt{B_2 - B_3Co^{III}}} = \frac{-B_3}{2x} . \tag{67}$$

Setting up the integration of equation 66 and substituting equations 67 in to the expression, one obtains

$$\int_{Co_0^{III}}^{Co^{III}} \frac{dCo}{\frac{k_{53}}{2B_3}}$$

$$\int_{Co_0^{III}}^{Co^{III}}$$

The

By su

ranging, c

$$-2\int_{Co_0^{III}}^{Co^{III}} \left[\frac{(u}{u\{}\right.$$

To s

defined

$$\int_{Co_0^{III}}^{Co^{III}} \frac{dCo^{III}}{\frac{k_{5a}}{2B_3}\left(-B_1+\sqrt{B_2-B_3Co^{III}}\right)^2+\frac{2k_{5b}K_{4a}[O_2]Co^{III}}{B_3}\left(-B_1+\sqrt{B_2-B_3Co^{III}}\right)} \tag{68}$$

$$= \int_0^t dt = t$$

$$\int_{Co_0^{III}}^{Co^{III}} \frac{-2x\,dx}{\frac{k_{5a}}{2}(x-B_1)^2 + 2k_{5b}K_{4a}[O_2]\left(\frac{B_2 - x^2}{B_3}\right)(x - B_1)} = t. \tag{69}$$

The second transformation of a variable is shown below

$$u = x - B_1$$
$$du = dx \;. \tag{70}$$

By substituting equations 70 into equation 69 and rearranging, one obtains

$$-2\int_{Co_0^{III}}^{Co^{III}} \left[\frac{(u + B_1)\,du}{u\left\{\frac{-2K_{4a}[O_2]k_{5b}u^2}{B_3} + \left(\frac{k_{5a}}{2} - \frac{4K_{4a}[O_2]k_{5b}B_1}{B_3}\right)u + \left(\frac{2K_{4a}[O_2]k_{5b}B_2}{B_3} - \frac{2K_{4a}[O_2]k_{5b}B_1^2}{B_3}\right)\right\}}\right] = t. \tag{71}$$

To simplify equation 71, the following constants are defined

By

obtains

$$-2 \int_{Co_0^{III}}^{Co^{II}} \frac{(u}{u(c}$$

Both

be readil

these two

X =

q = 4

$$\int \frac{du}{X} = \int$$

=

$$\int \frac{du}{uX} = \int$$

$$\int \frac{du}{uX} = \frac{1}{2}$$

$$a = \frac{2K_{4a}[O_2]k_{5b}B_2}{B_3} - \frac{2K_{4a}[O_2]k_{5b}B_1{}^2}{B_3}$$

$$b = \frac{k_{5a}}{2} - \frac{4K_{4a}[O_2]k_{5b}B_1}{B_3} \qquad (72)$$

$$c = \frac{-2K_{4a}[O_2]k_{5b}}{B_3} \quad .$$

By substituting equations 72 into equation 71, one obtains

$$-2\int_{Co_0^{III}}^{Co^{III}} \frac{(u + B_1)du}{u(cu^2+bu+a)} = t = -2\int_{Co_0^{III}}^{Co^{III}} \frac{du}{cu^2+bu+a} -2\int_{Co_0^{III}}^{Co^{III}} \frac{B_1\ du}{u(cu^2+bu+a)} . \qquad (73)$$

Both terms of equation 73 are standard forms and can be readily integrated. The standard integrations[115] of these two terms is found below in equations 74

$$X = a + bu + cu^2$$

$$q = 4ac - b^2$$

$$\int\frac{du}{X} = \int\frac{du}{cu^2+bu+a} = \frac{1}{\sqrt{-q}} \log\left(\frac{2cu+b-\sqrt{-q}}{2cu+b+\sqrt{-q}}\right)$$

$$= \frac{1}{\sqrt{b^2-4ac}} \log\left(\frac{2cu+b - \sqrt{b^2-4ac}}{2cu+b+\sqrt{b^2-4ac}}\right) \qquad (74)$$

$$\int\frac{du}{uX} = \int\frac{du}{u(cu^2+bu+a)} = \frac{1}{2a}\log\left(\frac{u^2}{X}\right) - \frac{b}{2a}\int\frac{du}{X}$$

$$\int\frac{du}{uX} = \frac{1}{2a}\log\left(\frac{u^2}{cu^2+bu+a}\right) - \frac{b}{2a\sqrt{b^2-4ac}}\log\left(\frac{2cu+b-\sqrt{b^2-4ac}}{2cu+b+\sqrt{b^2-4ac}}\right).$$

By u

rearrangi

t = [(b / a

- B / a

Then by s

equation

t = [(b / a

- $\frac{B_1}{a}$ I

t = [(b / a .

-

By introdu

one obtain

By using equations 74 to integrate equation 73 and rearranging, one obtains

$$t = \left[\left(\frac{bB_1}{a\sqrt{b^2-4ac}} - \frac{2}{\sqrt{b^2-4ac}}\right)\log\left(\frac{2cu+b-\sqrt{b^2-4ac}}{2cu+b+\sqrt{b^2-4ac}}\right) - \frac{B_1}{a}\log\left(\frac{u^2}{cu^2+bu+a}\right)\right]\Bigg|_{Co_0^{III}}^{Co^{III}} . \quad (75)$$

Then by successively substituting equations 70 and 67 into equation 75, one obtains the following

$$t = \left[\left(\frac{bB_1}{a\sqrt{b^2-4ac}} - \frac{2}{\sqrt{b^2-4ac}}\right)\log\left(\frac{2c\{x-B_1\}+b-\sqrt{b^2-4ac}}{2c\{x-B_1\}+b+\sqrt{b^2-4ac}}\right) - \frac{B_1}{a}\log\left(\frac{\{x-B_1\}^2}{c\{x-B_1\}^2+b\{x-B_1\}+a}\right)\right]\Bigg|_{Co_0^{III}}^{Co^{III}} \quad (76)$$

$$t = \left[\left(\frac{bB_1}{a\sqrt{b^2-4ac}} - \frac{2}{\sqrt{b^2-4ac}}\right)\log\left(\frac{2c\{\sqrt{B_2-B_3Co^{III}}-B_1\}+b-\sqrt{b^2-4ac}}{2c\{\sqrt{B_2-B_3Co^{III}}-B_1\}+b+\sqrt{b^2-4ac}}\right) - \frac{B_1}{a}\log\left(\frac{\{\sqrt{B_2-B_3Co^{III}}-B_1\}^2}{c\{\sqrt{B_2-B_3Co^{III}}-B_1\}^2+b\{\sqrt{B_2-B_3Co^{III}}-B_1\}+a}\right)\right]\Bigg|_{Co_0^{III}}^{Co^{III}} . \quad (77)$$

By introducing the limits of integration and rearranging, one obtains

$$t = \Big(\ldots$$

$$+ \frac{B_1}{a} \ldots$$

If c...

equation b...

the bulk c...

below.

The d...

$$\frac{dCo^{II}}{dt} \ldots$$

$$\frac{dCo^{II}}{dt} \ldots$$

Equations ...

By su...

$$\frac{dCo^{III}}{dt} = \frac{k}{2} \ldots$$

$$+ \frac{2}{\ldots} \ldots$$

$$t = \left(\frac{2}{\sqrt{b^2-4ac}} - \frac{bB_1}{a\sqrt{b^2-4ac}}\right)\log\left[\frac{\dfrac{2c(\sqrt{B_2-B_3Co_0^{III}}-B_1)+b-\sqrt{b^2-4ac}}{2c(\sqrt{B_2-B_3Co_0^{III}}-B_1)+b+\sqrt{b^2-4ac}}}{\dfrac{2c(\sqrt{B_2-B_3Co^{III}}-B_1)+b-\sqrt{b^2-4ac}}{2c(\sqrt{B_2-B_3Co^{III}}-B_1)+b+\sqrt{b^2-4ac}}}\right]$$

$$+\frac{B_1}{a}\log\left[\frac{\dfrac{(\sqrt{B_2-B_3Co_0^{III}}-B_1)^2}{c(\sqrt{B_2-B_3Co_0^{III}}-B_1)^2+b(\sqrt{B_2-B_3Co_0^{III}}-B_1)+a}}{\dfrac{(\sqrt{B_2-B_3Co^{III}}-B_1)^2}{c(\sqrt{B_2-B_3Co^{III}}-B_2)^2+b(\sqrt{B_2-B_3Co^{III}}-B_1)+a}}\right]. \quad (78)$$

If one repeats the derivation and integration of the rate equation but includes reaction 50 and deletes reaction 49, the bulk of the derivation remains the same except as stated below.

The differential rate law now becomes

$$\frac{dCo^{III}}{dt} = k'_{5a}[CoL_2O_2][CoL_2] + k_{5b}[CoL_2O_2][CoL_2^+] \quad (55a)$$

$$\frac{dCo^{III}}{dt} = k'_{5a}K_{4a}[O_2][CoL_2]^2 + k_{5b}K_{4a}[O_2][CoL_2][CoL_2^+]. \quad (56a)$$

Equations 57 to 65 obviously remain the same.

By substituting equation 65 into equation 56a, one obtains

$$\frac{dCo^{III}}{dt} = \frac{k'_{5a}}{2B_3K_{4b}}(-B_1+\sqrt{B_2-B_3Co^{III}})^2$$

$$+\frac{2k_{5b}K_{4a}[O_2][Co^{III}]}{B_3}(-B_1+\sqrt{B_2-B_3Co^{III}}). \quad (66a)$$

Sett

equation

tion 70 i

Co

-2

+

In c

only diff

Therefore

was with e

represente

Setting up the integration of equation 66a, substituting equation 67 into the expression and then substituting equation 70 into the expression, one obtains

$$\int_{Co_0^{III}}^{Co^{III}} \frac{dCo^{III}}{\frac{k'_{5a}}{2B_3K_{4b}}\left(-B_1+\sqrt{B_2-B_3Co^{III}}\right)^2+\frac{2k_{5b}K_{4a}[O_2]Co^{III}}{B_3}\left(-B_1+\sqrt{B_2-B_3Co^{III}}\right)} = t \qquad (68a)$$

$$\int_{Co_0^{III}}^{Co^{III}} \frac{-2xdx}{\frac{k'_{5a}}{2K_{4b}}(x-B_1)^2+2k_{5b}K_{4a}[O_2]\left(\frac{B_2-x^2}{B_3}\right)(x-B_1)} = t \quad (69a)$$

$$-2\int_{Co_0^{III}}^{Co^{III}} \left[\frac{(u+B_1)du}{u\left\{\frac{-2k_{5b}K_{4a}[O_2]u^2}{B_3}+\left(\frac{k'_{5a}}{2K_{4b}}-\frac{4k_{5b}K_{4a}[O_2]B_1}{B_3}\right)u+\frac{2k_{5b}K_{4a}[O_2]B_2}{B_3}-\frac{2k_{5b}K_{4a}[O_2]B_1^2}{B_3}\right\}}\right] = t\,. \qquad (71a)$$

In comparing equations 71 and 71a, one sees that the only difference is the "b" term

$$b = \frac{k'_{5a}}{2K_{4b}} - \frac{4k_{5b}K_{4a}[O_2]B_1}{B_3}\,. \qquad (72a)$$

Therefore, the integrated rate equation is the same as it was with equation 49. The only difference is in the term represented by "b".

By

the equa

sary to

describe

B. Calc

tion

dina

The

is the sa

equation

ligand pr

product w

$[CoL_{2_0}^{+}]$,

$L_t =$

$+$

Then

cluding th

which was

By substi

obtains

By inspecting equation 78, one can readily see that the equation cannot be solved algebraically. It is necessary to use a method of numerical solution which will be described later in this section.

E. Calculation of Ligand Concentration During the Formation and Decomposition of μ-Dioxygentetrakis(l-histidinato)dicobalt

The equation for calculating the ligand concentration is the same for either mechanism, based on inclusion of equation 49 or equation 50. By defining L_t as the total ligand present excluding the ligand from the cobalt(III) product which was present at the start of the reaction, $[CoL_{2\,0}^{+}]$,

$$L_t = [L^-]+[HL]+[H_2L^+]+[H_3L^{2+}]+[CoL^+]+2[CoL_2]+3[CoL_3^-] +2[CoL_2O_2]+4[(CoL_2)_2O_2]+2[CoL_2^+]-2[CoL_{2\,0}^{+}]. \quad (79)$$

Then defining $\bar{n}$ as the ligand-to-metal ratio (excluding the ligand and cobalt from the cobalt(III) product which was present at the start of the reaction, $CoL_{2\,0}^{+}$)

$$\bar{n}\,Co_t - 2[CoL_{2\,0}^{+}] = L_t. \quad (80)$$

By substituting equations 52 to 54 into equation 79, one obtains

$L_t =$

$+$

$+4$

Then subs

collectin

$[CoL_2]^2($2

$+[CoL_2]\left[\right.$

$+(E-2)[Co$

The quanti

equations

$A_H =$

$E =$

By s

tains the

$[CoL$

and then

$[CoL_2] =$

$$L_t = [L^-] + K_{1H}[H^+][L^-] + K_{1H}K_{2H}[H^+]^2[L^-] + K_{1H}K_{2H}K_{3H}[H^+]^3[L^-]$$

$$+ \frac{[CoL_2]}{K_2[L^-]} + 2[CoL_2] + 3K_3[CoL_2][L^-] + 2K_{4a}[CoL_2][O_2]$$

$$+4K_{4a}K_{4b}[CoL_2]^2[O_2] + 2[CoL_2^{\ +}] - 2[CoL_2^{\ +}]_0 . \qquad (81)$$

Then substituting equations 58 and 81 into equation 80, collecting terms and rearranging, one obtains the following:

$$[CoL_2]^2(2\bar{n}-4)K_{4a}K_{4b}[O_2]$$

$$+[CoL_2]\left[\frac{\bar{n}}{K_1K_2[L^-]^2} + \frac{\bar{n}-1}{K_2[L^-]} + (\bar{n}-2) + (\bar{n}-3)K_3[L^-] + (\bar{n}-2)K_{4a}[O_2]\right] \qquad (82)$$

$$+(\bar{n}-2)[CoL_2^{\ +}] - [L^-](1+K_{1H}[H^+] + K_{1H}K_{2H}[H^+]^2 + K_{1H}K_{2H}K_{3H}[H^+]^3) = 0.$$

The quantities A_H and E are defined to simplify the equations

$$A_H = (1+K_{1H}[H^+] + K_{1H}K_{2H}[H^+]^2 + K_{1H}K_{2H}K_{3H}[H^+]^3)$$

$$E = \frac{\bar{n}}{K_1K_2[L^-]^2} + \frac{\bar{n}-1}{K_2[L^-]} + \bar{n}-2 + (\bar{n}-3)K_3[L^-] + (\bar{n}-2)K_{4a}[O_2]. \qquad (83)$$

By substituting equations 83 into equation 82 one obtains the simplified equation

$$[CoL_2]^2(2\bar{n}-4)K_{4a}K_{4b}[O_2] + [CoL_2]E + (\bar{n}-2)[CoL_2^{\ +}] - [L^-]A_H = 0 \qquad (84)$$

and then solving equation 84 for $[CoL_2]$, one obtains

$$[CoL_2] = \frac{-E \pm \sqrt{E^2 - 4(2\bar{n}-4)K_{4a}K_{4b}[O_2]\{(\bar{n}-2)[CoL_2^{\ +}] - [L^-]A_H\}}}{2\{(2\bar{n}-4)K_{4a}K_{4b}[O_2]\}} . \qquad (85)$$

Aga

$[CoL_2]$ r

85 is th

as follo

$[CoL_2] =$

Then by

-E

A ca

within th

tions 59,

present:

$[CoL_2^+]$,

The

are known

fixed at

fore, by

possible

to use a

numerical

Again using the symbol Co^{III} for $[CoL_2^+]$ and since $[CoL_2]$ must be zero or positive, the real root of equation 85 is the positive root. Therefore equation 85 is written as follows:

$$[CoL_2] = \frac{-E + \sqrt{E^2 - 4(2\bar{n}-4)K_{4a}K_{4b}[O_2]\{(\bar{n}-2)Co^{III} - [L^-]A_H\}}}{2\{(2\bar{n}-4)K_{4a}K_{4b}[O_2]\}} \quad (86)$$

Then by substituting equation 86 into equation 65 one obtains

$$\frac{-E + \sqrt{E^2 - 4(2\bar{n}-4)K_{4a}K_{4b}[O_2]\{(\bar{n}-2)Co^{III} - [L^-]A_H\}}}{(4\bar{n}-8)K_{4a}K_{4b}[O_2]}$$

$$= \frac{2}{B_3}\left(-B_1 + \sqrt{B_2 - B_3 Co^{III}}\right). \quad (87)$$

A careful examination of equation 87 and the variables within the equation, A_H, E (equations 83), B_1, B_2, B_3 (equations 59, 63, 64), reveals that the following variables are present: K_1, K_2, K_3, $K_{4a} \cdot K_{4b}$, K_{1H}, K_{2H}, K_{3H}, $[H^+]$, $[O_2]$, $[CoL_2^+]$, and $[L^-]$.

The values of K_1, K_2, K_3, $K_{4a} \cdot K_{4b}$, K_{1H}, K_{2H}, and K_{3H} are known (see Discussion section). The $[H^+]$ and $[O_2]$ are fixed at known values by the experimental conditions. Therefore, by using the experimental value for $[CoL_2^+]$, it is possible to solve equation 87 for $[L^-]$. It is necessary to use a numerical method to solve this equation. The numerical method used is described next.

F. Numer

Metho

Sinc

does not

estimate

any time

If c

an equati

necessary

to use.11

the equati

figures wi

Since

tion is av

tion 87 nu

The N

(see Figur

Let u

he wishes

ferent va

Obviously

estimate

then the e

Referring

the equat

constructe

F. Numerical Method Used to Solve Equation 87, the Newton Method

Since it has been found that the ligand concentration does not change very much as the reaction proceeds, a good estimate can be obtained for the ligand concentration at any time during the reaction.

If one has a good initial estimate for the solution of an equation and a numerical solution of the equation is necessary, the Newton method is the best numerical technique to use.[116] The Newton method converges on the solution to the equation very rapidly (usually to four significant figures within six iterations).

Since a good initial estimate of the ligand concentration is available, the Newton method is used to solve equation 87 numerically.

The Newton method can be best described graphically (see Figure 2).

Let us assume that one has an equation $f(x) = 0$ and he wishes to find a root of the equation. He can try different values of x and plot the equation $f(x) = y$. Obviously, y is the residual when one substitutes his estimate of x into the expression $f(x)$. If y is zero, then the estimate of x is a root of the equation $f(x) = 0$. Referring to Figure 2, the initial estimate of a root to the equation $f(x) = 0$ is the quantity a_1. Line A_1P_1 is constructed perpendicular to the x axis and then the

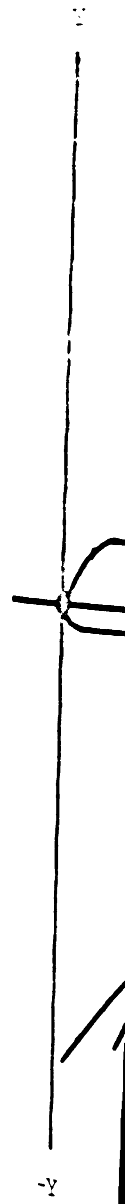


Figure 2

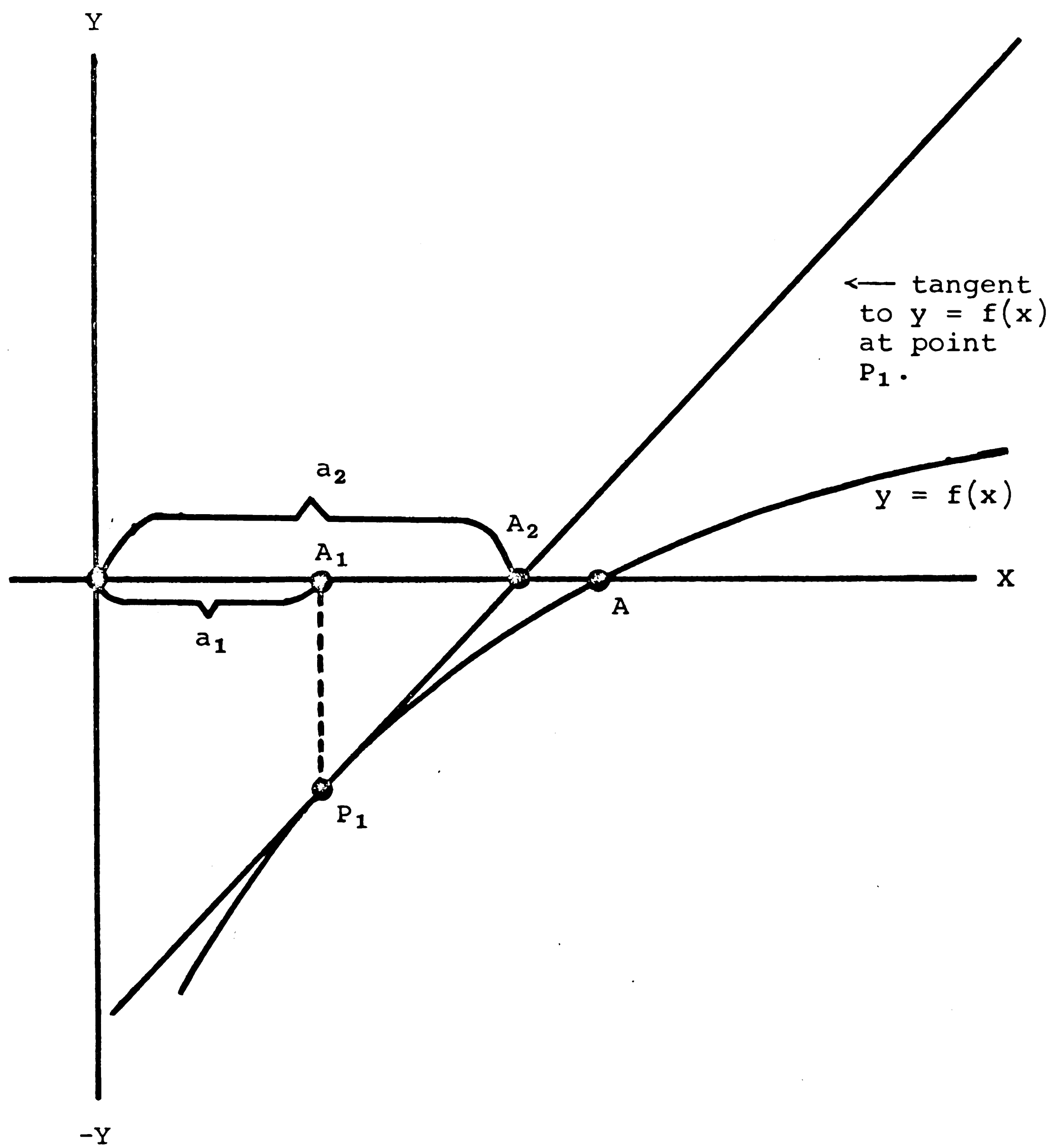


Figure 2. Geometric representation of the Newton method for numerical solution of equations.

tangent

structe

the x

is the

structi

and ther

a_i to c

repeated

accurate

y (the r

the previ

must be c

points or

$y = f(x)$

the point

or a chang

The m

described

above, the

$f(x) = 0$

the equati

P_1, $f(a_1)$

$x = a_1$).

Now

P_1 must b

must be th

point P_1.

tangent to the equation $f(x) = y$ at point P_1 is constructed. The value of x where this tangent intersects the x axis, $(x = a_2)$, is a better estimate of the root than is the original estimate, $x = a_1$. This process of constructing a line perpendicular to the x axis at point a_i and then constructing the tangent to $f(x) = y$ at point a_i to obtain a new estimate of the root, a_{i+1}, can be repeated until the estimate of the root is sufficiently accurate. The accuracy can be determined by the value of y (the residual), and the closeness of an estimate a_i to the previous estimate. The initial estimate of the root must be close enough to the real root to avoid inflection points or changes in the sign of the slope of the equation $y = f(x)$ between the point on the equation $x = a_1$ and the point where $y = 0$. If there is an inflection point or a change in slope, the Newton method will fail.

The mathematical equivalent of the geometric procedure described above and in Figure 2 is as follows. As stated above, the initial estimate of the root to the equation $f(x) = 0$ is the quantity a_1. Point P_1 is the point on the equation $f(x) = y$ where $x = a_1$. Therefore, at point P_1, $f(a_1) = y$ ($f[a_1]$ is the value of $f(x)$ evaluated with $x = a_1$). The coordinates of point P_1 are $(x, f[a_1])$.

Now the equation of the tangent to $f(x) = y$ at point P_1 must be obtained. The slope of the tangent at point P_1 must be the same as the slope of the equation $y = f(x)$ at point P_1. The slope of the equation $y = f(x)$ at point

P_1 is f

$x = a_1$.

m and co

Therefore

Rearrangi

The

where x

By substi

To us

necessary

respect t

The deriva

pendix.

values of

is found

the Newto

based upo

be found

P_1 is $f'(a_1)$, (the derivative of $f(x)$ evaluated with $x = a_1$). The general equation for a straight line of slope m and containing point (x_1, y_1) is as follows:

$$\frac{y - y_1}{x - x_1} = m. \tag{88}$$

Therefore, the equation of the tangent is

$$\frac{y - f(a_1)}{x - a_1} = f'(a_1). \tag{89}$$

Rearranging equation 89, one obtains

$$x = \frac{y - f(a_1)}{f'(a_1)} + a_1 . \tag{90}$$

The point on this tangent where $y = 0$ is the point where $x = a_2$, the new estimate of a root of $f(x) = 0$. By substituting $y = 0$ into equation 90, one obtains a_2

$$x = a_2 = a_1 - \frac{f(a_1)}{f'(a_1)} . \tag{91}$$

To use the Newton method to solve equation 87, it is necessary to obtain the derivative of equation 87 with respect to the unknown, $[L^-]$, and a good estimate of $[L^-]$. The derivative of this equation can be found in the Appendix. The estimate of $[L^-]$ can be obtained by using trial values of $[L^-]$ in the Newton method until a trial value is found that is sufficiently close to the true $[L^-]$ for the Newton method to work properly. The computer subroutine based upon the Newton method and written by the author will be found in the Appendix.

G. Num

Upo

the equa

equation

$[CoL_2^+]$

equation

(see Dis

either

estimate

tion 87

in some

k'_{5a}, and

method t

becomes

program

initial

is based

If

tries tw

to get

and signs

between

closer to

different

the signs

the small

G. Numerical Method Used to Solve Equation 78

Upon examining equation 78 and the variables within the equation, it can be seen that all the variables from equation 87 are present as are K_{4a}, K_{4b}, k_{5a}, k_{5b} and $[CoL_2^+]$. By using the value of $[L^-]$ as calculated from equation 87, choosing appropriate values for K_{4a} and K_{4b} (see Discussion section) and using the current estimates (either initial estimates of these variables or least squares estimates) for k_{5a} (or k'_{5a}) and k_{5b}, one can solve equation 87 for $[CoL_2^+]$. However, the initial estimates and in some cases the iterative computer estimates of k_{5a} (or k'_{5a}) and k_{5b} may not be accurate enough to use the Newton method to solve equation 87 numerically. Therefore, it becomes necessary to derive a numerical method and a computer program for the method which can be used even with poor initial estimates of k_{5a} (or k'_{5a}) and k_{5b}. This method is based on the method of successive approximations.

If one has a function of the form $f(x) = 0$ and he tries two estimates of roots to the equation, x_1 and x_2, to get $f(x_1)$ and $f(x_2)$, he can tell from the magnitudes and signs of $f(x_1)$ and $f(x_2)$ whether there is a root between x_1 and x_2 and if not, whether x_1 or x_2 is closer to a root. If the signs of $f(x_1)$ and $f(x_2)$ are different, there must be a root between x_1 and x_2. If the signs of $f(x_1)$ and $f(x_2)$ are the same, whichever has the smallest magnitude is based on a value of x which is closer

from x

proachi

H. Com

Th

time, w

tion en

ate(II)

6, 7, 9,

in the A

The

oxygen r

concentr

calculat

ation su

The

prelimin

squares

nitude e

reading

the estim

subrouti

and coba

gram can

the main

squares c

closer to a root. In this way, one can tell whether in going from x_1 to x_2 a root has been passed or if it is approaching or leaving a root.

H. Computer Programs

The computer program for the linear least squares routine, which is used to determine rate constants and activation energy for the decomposition of the pentacyanocobaltate(II) ion, is straightfoward. It is based upon equations 6, 7, 9, 10, 39 and 40. The computer program can be found in the Appendix.

The computer program used for the cobalt-histidine-oxygen reaction consists of a main program, "Deriv", a ligand concentration calculation subroutine, "Aligcalc", a $[CoL_2^-{}^+]$ calculation subroutine, "Co3calc", and a determinant evaluation subroutine, "Dterm".

There are two basic versions of the main program. The preliminary version, "Kintslct", does not include any least squares calculations. It is used to detemine order of magnitude estimates for k_{5a}, k'_{5a} and k_{5b}. It consists of reading in the experimental data, the known variables, and the estimates of k_{5a} or k'_{5a} and k_{5b} and then calling subroutines "Aligcalc" and "Co3calc" to calculate the ligand and cobalt(III) product concentrations. This computer program can be found in the Appendix. The regular version of the main program, "Deriv", includes the non-linear least squares calculations. There are, of course, two versions of each t

"Derivg"

equation

(paramete

of the ma

can be se

Subr

It consis

lating a

previous

checking

close eno

if not, g

mate of

Subr

approxima

seen in F

Subr

tained fr

library.

of the de

Subr

[CoL^+],

I. Esti

The

on the c

of each type of main program; one is based on equation 49, "Derivg" (and therefore, the parameter "b" is defined by equation 72); the other is based on equation 50, "Derivh" (parameter "b" is defined by equation 72a). A block diagram of the main program including the least squares calculations can be seen in Figure 3.

Subroutine "Aligcalc" is based on the Newton method. It consists of calculating the necessary derivative, calculating a new estimate of $[L^-]$ (based upon the initial or previous iterative estimate of $[L^-]$) by means of equation 91, checking to see whether the previous and new estimates are close enough to each other to terminate the calculation and if not, going back and calculating the derivative, a new estimate of $[L^-]$, etc.

Subroutine "Co3calc" is based on the method of successive approximations. A block diagram of this subroutine can be seen in Figure 4.

Subroutine "Dterm" is a standard program which was obtained from the Michigan State University computer program library. This subroutine is used to calculate the values of the determinants.

Subroutine "Cobltclc" is used to calculate $[Co^{2+}]$, $[CoL^+]$, $[CoL_2]$, $[CoL_2O_2]$, and $[(CoL_2)_2O_2]$.

I. Estimation of K_{4a} and K_{4b}

The estimation of the values of K_{4a} and K_{4b} is based on the observation that at 25^0, $K_{4a} \cdot K_{4b} = 7.2 \times 10^6$.[59]

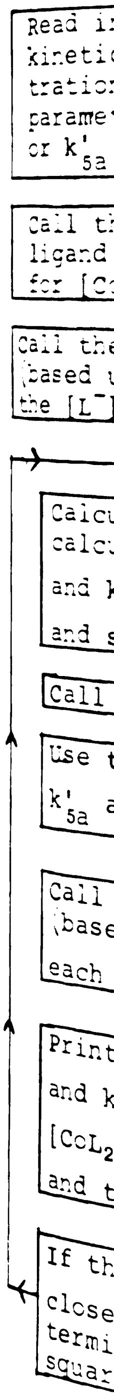

Read i
kinetic
tration
parame
or k'5a
Call t
ligand
for [C
Call the
based
the [L
Calcu
calc
and
and s
Call
Use t
k'5a a
Call
base
each
Print
and k
[CoL2
and t
If th
close
termi
squar

Figure 3

Read in the values of all constants, the experimental kinetic data, (experimental conditions, initial concentrations of reactants, $[CoL_2^+]$ and time), least squares parameters, initial estimates of the parameters (k_{5a} or k'_{5a}, k_{5b} and $[L^-]$).

↓

Call the "Aligcalc" subroutine to calculate the free ligand concentration (based on the experimental values for $[CoL_2^+]$) for each experimental data point.

↓

Call the "Co3calc" subroutine to calculate the $[CoL_2^+]$ (based upon the initial estimates of k_{5a} or k'_{5a} and k_{5b} and the $[L^-]$ calculated above) for each experimental data point.

↓

Calculate the derivatives necessary for the least squares calculation (based on the current estimates of k_{5a} or k'_{5a} and k_{5b}), the difference between $[CoL_2^+]_{exp}$ and $[CoL_2^+]_{calc}$ and set up the least squares determinants.

↓

Call the "Dterm" subroutine to evaluate the determinants.

↓

Use the determinants to calculate new values for k_{5a} or k'_{5a} and k_{5b}.

↓

Call the "Co3calc" subroutine to calculate $[CoL_2^+]$ (based on the new choices of k_{5a} or k'_{5a} and k_{5b}) for each experimental data point.

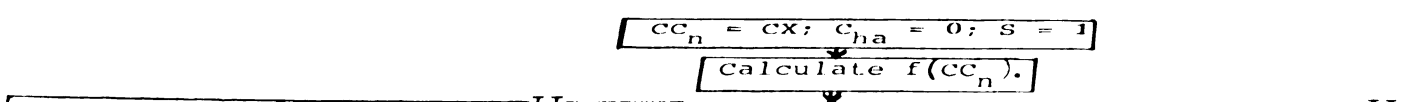
↓

Print out the previous and new estimates of k_{5a} or k'_{5a} and k_{5b}, the new and old values of $[CoL_2^+]_{calc}$, $[CoL_2^+]_{experim.}$, the quantity $([CoL_2^+]_{exp}-[CoL_2^+{}_{calc}])$, and the mean and standard deviations.

↓

If the old and new estimates of k_{5a} or k'_{5a} and k_{5b} are close enough to each other (indicating convergence), terminate the calculations. Otherwise repeat the least squares procedure up to a maximum number of iterations.

Figure 3. A block diagram of computer program "Deriv".



$CC_n = CX; C_{ha} = 0; S = 1$
Calculate $f(CC_n)$.

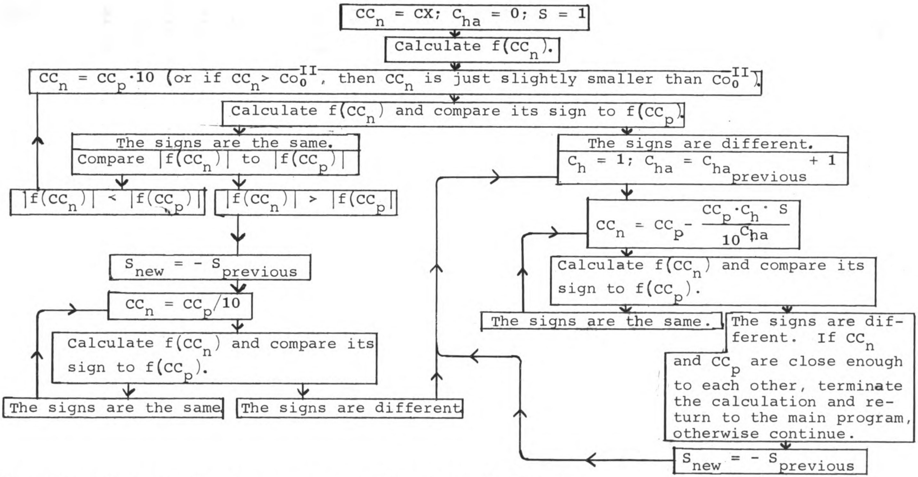


Figure 4. A block diagram of computer subroutine "Co3calc".
($CX = [CoL_2^+]_{exp}$; $CC = [CoL_2^+]_{calc}$; In any step, $CC_{previous}$ (CC_p) is the CC_{new} (CC_n) from the previous step.)

T

$K_{4a} \cdot K$

One

total c

after c

oxygen c

$[CoL_2]$,

absorbed

By

tially (

calculat

Before an

Co^{II}_{t}

[CoL

Sinc

be calcul

calculated

The r

sorbed per

The equations 53 can be multiplied to obtain the product $K_{4a} \cdot K_{4b}$,

$$K_{4a} \cdot K_{4b} = 7.2 \times 10^6 = \frac{[(CoL_2)_2O_2]}{[CoL_2]^2[O_2]} \quad . \qquad (92)$$

One can then assume that a specific percentage of the total cobalt(II), Co^{II}_t, is in the form $(CoL_2)_2O_2$ immediately after oxygenation (and before any decomposition of the oxygen carrier to form CoL_2^+). Then one can calculate $[CoL_2]$, $[CoL_2O_2]$, and the number of moles of oxygen initially absorbed per two moles of cobalt.

By defining F as the fraction of Co^{II}_t that is initially $(CoL_2)_2O_2$, and rearranging equation 92, one can calculate $[CoL_2]$ as follows:

$$[CoL_2] = \sqrt{\frac{[(CoL_2)_2O_2]}{K_{4a} \cdot K_{4b} \cdot [O_2]}} = \sqrt{\frac{Co^{II}_t \cdot F}{7.2 \times 10^6 \cdot [O_2]}} \ . \qquad (93)$$

Before any decomposition of the binuclear oxygen carrier

$$Co^{II}_t = [CoL_2] + [CoL_2O_2] + 2[(CoL_2)_2O_2] \qquad (94)$$

$$[CoL_2O_2] = Co^{II}_t - [CoL_2] - 2[(CoL_2O_2] \ . \qquad (95)$$

Since $[(CoL_2)_2O_2]$ is assumed, $[CoL_2]$ and $[CoL_2O_2]$ can be calculated from equations 93 and 95, K_{4a} and K_{4b} can be calculated by using equations 53.

The number of moles of oxygen that are initially absorbed per two moles of cobalt(II) is equal to the quantity

$$\frac{[(CoL_2)_2O_2] + 2[CoL_2O_2]}{2Co^{II}_t} \quad . \qquad (96)$$

J. Correct

Co^{II}_{aq}

A sim

quenched co

ance due to

Since,

the molar a

of Co^{II}_{aq},

$F_{CoL_2^+}$

where F is

tive to its

start or en

sorbances l

experimenta

tively the

the initial

final absor

Since

$F_{Co^{II}}$

The only va

J. Correction of CoL_2^+ Absorbance Due to the Presence of Co^{II}_{aq}

A simple linear correction on the absorbance of the quenched cobalt-histidine-oxygen solutions for the absorbance due to Co^{II}_{aq} has been derived by Zompa.[117]

Since, at any wavelength of the spectral observations, the molar absorptivity of CoL_2^+ is much greater than that of Co^{II}_{aq},

$$F_{Co^{II}} = \frac{A_{Co^{II}}}{A_{Co^{II}_0}} \qquad (97)$$

$$F_{CoL_2^+} = \frac{[CoL_2^+]}{[CoL_2^+]_\infty} = \frac{A_{Co^{III}}}{A_{Co^{III}_\infty}} \approx \frac{A_{total} - A_{Co^{II}_0}}{A_{Co^{III}_\infty} - A_{Co^{II}_0}} \qquad (98)$$

where F is the fraction of the subscripted species (relative to its maximum possible concentration, at either the start or end of the reaction). The A terms are all absorbances less any absorbance due to $CoL_{2\,0}^+$. A_t is the experimental absorbance; $A_{Co^{II}}$ and $A_{Co^{III}}$ are respectively the absorbances due to Co^{2+}_{aq} and CoL_2^+; $A_{Co^{II}_0}$ is the initial absorbance of the solution and $A_{Co^{III}_\infty}$ is the final absorbance of the solution.

Since the whole is equal to the sum of its parts,

$$F_{Co^{II}} + F_{CoL_2^+} = 1 \; ; \; \frac{A_t - A_{Co^{II}_0}}{A_{Co^{III}_\infty} - A_{Co^{II}_0}} + \frac{A_{Co^{II}}}{A_{Co^{II}_0}} = 1. \qquad (99)$$

The only variable in equation 99 that is not known from the experi

equati

be calc

and by

experimental procedure is $A_{Co^{II}}$ so that by rearranging this equation, the absorbance of the solution due to Co^{2+}_{aq} can be calculated

$$A_{Co^{II}} = A_{Co_0^{II}} \left(1 + \frac{A_{Co_0^{II}} - A_t}{A_{Co_0^{II}} - A_{Co_\infty^{III}}} \right) \quad (100)$$

and by difference,

$$A_{Co^{III}} = A_t - A_{Co^{II}} \; . \quad (101)$$

A. Pr

Re

histid

and was

pare th

the boi

purifie

remove

was pip

was bub

the con

A p

was pre

molar ra

lowed mi

eter cel

flask, w

shaped a

a spectr

flask wa

fied nitr

IV. EXPERIMENTAL

A. Preparation of Reagents

Reagent grade materials were used throughout. The l-histidine was obtained from Nutritional Biochemicals, Inc. and was used without purification. The water used to prepare the solutions was boiled distilled water. Throughout the boiling of the water and while cooling afterward, prepurified nitrogen gas was bubbled through the water to remove any dissolved oxygen. Thereafter, whenever water was pipetted out of the container, prepurified nitrogen was bubbled through the water to prevent air from entering the container.

A potassium pentacyanocobaltate(II) solution of 0.170$\underline{M}$ was prepared by mixing solutions of KCN and $Co(NO_3)_2$ in a molar ratio of 5.49 to 1.00, in a special flask which allowed mixing and withdrawal of samples into a spectrophotometer cell in an atmosphere of prepurified nitrogen. The flask, which is shown in Figure 5, is essentially "H"-shaped and contains a sidearm with a stopcock for connecting a spectrophotometer cell to the flask. Before use, the flask was evacuated several times and filled with prepurified nitrogen. Whenever reagents were added to the flask,

Fig

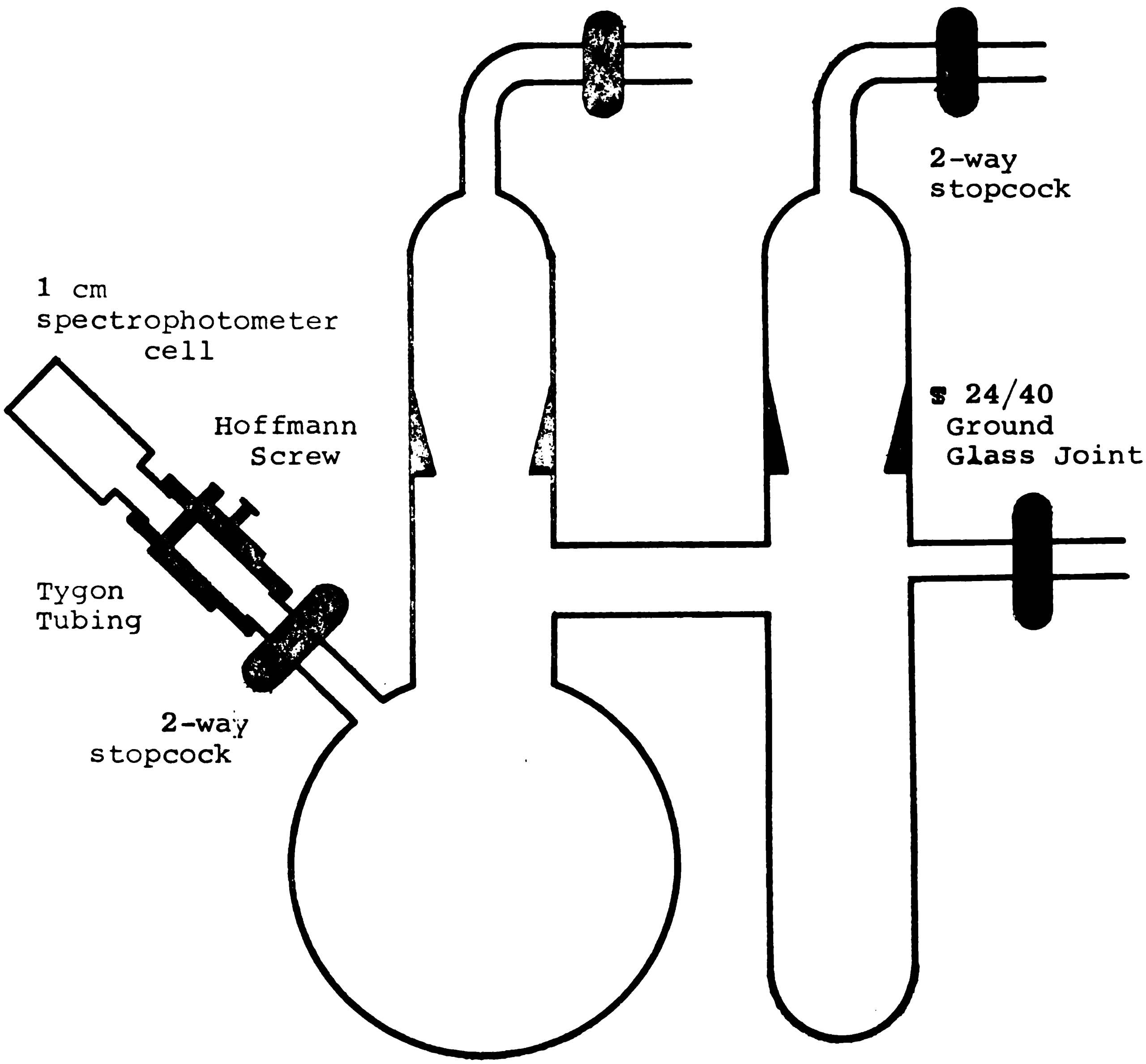


Figure 5. Special mixing cell.

nitr
trusi
one s
was p
was c
agent
soluti
photon

H
spectr
permit
shaped
flask i
is abou
is tigh
cock is
Tygon t
disconn
spectro

Bi
pH = 7
the rea
For sim
nated C
designa

nitrogen was passed through the flask to prevent the intrusion of any air. The KCN solution was pipetted into one side of the "H"-shaped flask and the $Co(NO_3)_2$ solution was pipetted into the other side of the flask. The flask was closed, tipped and shaken to thoroughly mix the reagents and then tipped at an acute angle to allow the solution to flow through the sidearm and into the spectrophotometer cell.

Hardened Tygon tubing must be used to connect the spectrophotometer cell (which must have a round top to permit the connecting of the Tygon tubing) to the "H"-shaped flask to prevent collapse of the tubing while the flask is being evacuated. When the spectrophotometer cell is about to be disconnected from the flask, a Hoffman screw is tightened about the Tygon tubing and the sidearm stopcock is closed. Then the spectrophotometer cell (with the Tygon tubing and the closed Hoffman screw attached) can be disconnected from the "H"-shaped flask and placed in the spectrophotometer.

Bis(l-histidinato)cobalt(II) solutions, buffered at pH = 7 and in a medium of 1M KNO_3, were prepared by adding the reagents shown in Table I to a 100 ml volumetric flask. For simplicity, bis(l-histidinato)cobalt(II) will be designated CoL_2 and bis(l-histidinato)cobalt(III) cation will be designated CoL_2^+.

Table I

[Co
[Co
ml 1$\underline{M}$ K
ml 1$\underline{M}$ K
g KNO_3
g 1-hi
g (CoL
ml 0.12
ml H_2O

So

mole ra

air whi

the sol

reactio

approxi

ing fin

glass f

water,

for app

line sa

was a m

Table I. Preparation of the CoL_2 solutions (2:1 histidine to cobalt ratio).

	I	II	III
$[CoL_2]$	6.08×10^{-3}	6.08×10^{-3}	12.16×10^{-3}
$[CoL_2^{+}]$	0.00	6.0×10^{-3}	0.00
ml 1M KH_2PO_4	7.00	7.00	5.00
ml 1M K_2HPO_4	25.00	25.00	25.00
g KNO_3	10.1	10.1	10.1
g l-histidine	0.1887	0.1887	0.3774
g $(CoL_2^{+})(NO_3^{-})$	0.00	0.2622	0.00
ml 0.1216M $Co(NO_3)_2$	5.00	5.00	10.00
ml H_2O	up to the 100 ml mark	up to the 100 ml mark	up to the 100 ml mark

Solid $(CoL_2)(NO_3)$ was prepared by adding a two to one mole ratio of l-histidine and $Co(NO_3)_2$ to water and bubbling air which was passed through a glass wool filter through the solution for three days. No buffer was added to the reaction flask. The resulting red solution was added to approximately four times its volume of acetone. The resulting fine precipitate was filtered through a fine fritted glass funnel, washed several times with small quantities of water, washed with acetone and ether and then dried *in vacuo* for approximately two hours. The yield of the non-crystalline salmon-red powder was approximately 50%. The powder was a mixture of the three isomers of the product.[107]

B. Analyti

The co

modificatio

volume of s

pipetted in

ml of conc.

to the beak

mately five

tating plat

to 3.5 volt

The KC

titration.[1]

small amoun

turely prec

when a drop

endpoint is

To che

tion equiva

100.5 ± 0.2

In ord

fer necessa

dine soluti

standardize

was perfor

1 M KNO_3 a

for acetic

B. Analytical

The cobalt nitrate solution was standardized by a modification of a standard electrochemical method.[118] A volume of solution containing 150 to 200 mg of cobalt was pipetted into a beaker; 0.3 g of $NaHSO_3$, 5 g of NH_4Cl, 50 ml of conc. NH_4OH and approximately 20 ml of H_2O was added to the beaker. The solution was electrolyzed for approximately five hours on a Fisher electroanalyzer using a rotating platinum anode and a platinum gauze cathode at 3.0 to 3.5 volts, 0.5 to 1.2 amperes.

The KCN solution was standardized by a silver ion titration.[119] Potassium iodide was the indicator and a small amount of NH_4OH was added to dissolve any AgCN prematurely precipitated due to a locally high Ag^+ concentration when a drop of $AgNO_3$ from the buret enters the solution. The endpoint is the first permanent clouding due to separation of AgCN.

To check the purity of the l-histidine, a neutralization equivalent titration was performed. The result was 100.5 ± 0.2% for the purity of the l-histidine.

In order to determine the quantity of phosphate buffer necessary to maintain a pH of 7 in the cobalt-histidine solutions listed in Table I, it was necessary to standardize a glass electrode for 1<u>M</u> KNO_3. A titration was performed by using standardized dilute acetic acid in 1 <u>M</u> KNO_3 and standardized NaOH in 1<u>M</u> KNO_3. Since the k_a for acetic acid in 1<u>M</u> KCl is 3.071×10^{-5} (ref.[120]), it is pcssible t

ticn poin

the same i

and experi

made. The

high.[117]

Then,

quantity c

7. The te

except tha

titrated i

with a sat

ized glass

C. Experi

Decomp

A pre

showed tha

sample of

was kept i

periodical

6 and 7.

is faster

the produc

from the p

experiment

cating eff

possible to calculate the pH of the solution at all titration points (by assuming that the k_a for acetic acid is the same in 1$\underline{M}$ KCl and KNO_3). By comparing the calculated and experimental values of pH, a calibration curve can be made. The pH meter reading was found to be 0.12 pH units high.[117]

Then, test solutions were prepared to determine the quantity of phosphate buffer necessary to maintain a pH of 7. The test solutions were the same as listed in Table I except that no KH_2PO_4 was added initially. Then KH_2PO_4 was titrated into the test solution until a Corning pH meter with a saturated calomel electrode and the 1$\underline{M}$ KNO_3 standardized glass electrode indicated pH 6.88.

C. Experimental Procedure for the Study of the $Co(CN)_5{}^{3-}$ Decomposition

A preliminary study of the decomposition of $Co(CN)_5{}^{3-}$ showed that the decomposition was affected by light. One sample of $Co(CN)_5{}^{3-}$ was kept in the light and another sample was kept in the dark. Spectra of both samples were taken periodically. Some of these spectra are shown in Figures 6 and 7. From Figure 6, one can see that the decomposition is faster in the light. From Figure 7, one can see that the products of the decomposition in the light are different from the products in the dark. Therefore, all further kinetic experiments were performed in darkness to avoid the complicating effects of the photochemical decomposition.

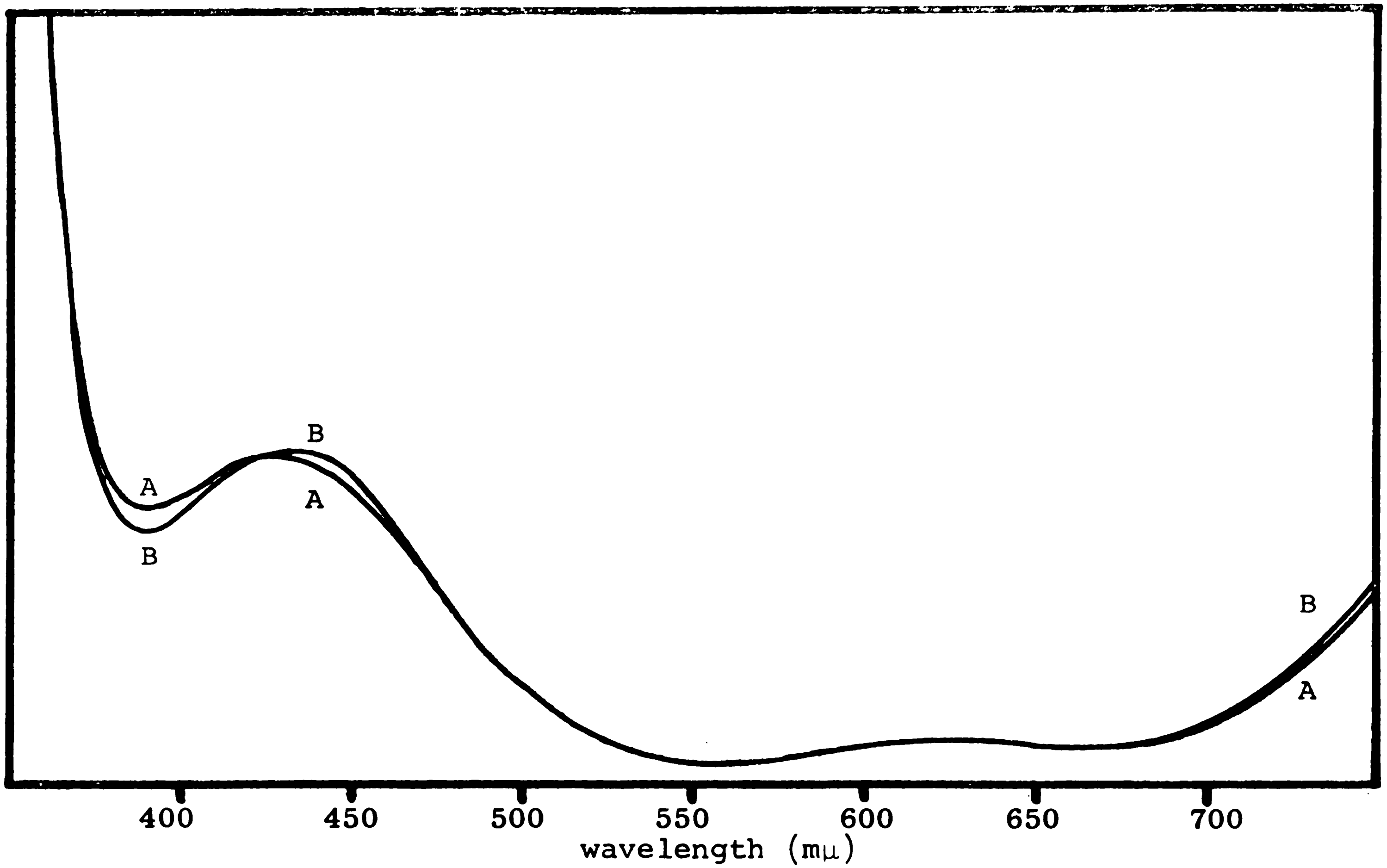


Figure 6. Comparison of visible and near uv spectra of aqueous $Co(CN)_5{}^{3-}$ kept in darkness and in daylight for 2 hours and 15 minutes after preparation.

A = spectrum of the sample kept in daylight.
B = spectrum of the sample kept in darkness.

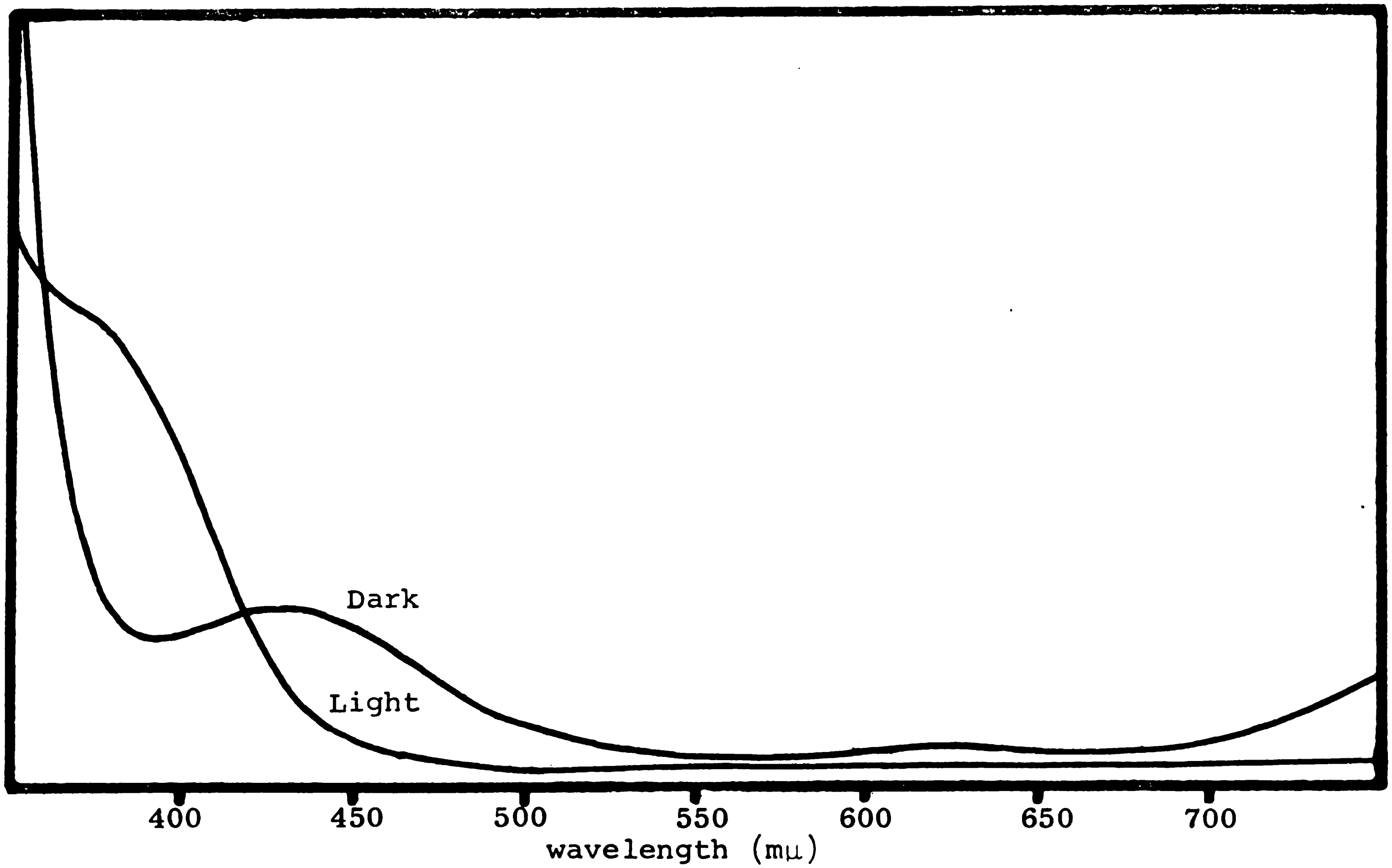


Figure 7. Comparison of visible and near uv spectra of aqueous $Co(CN)_5^{3-}$ kept in the dark and in daylight for 48 hours after preparation.

The r

ate(II io

peak of th

violet spe

oxygen gas

stated cel

of each ex

light from

photometer

tion, the

as shown b

The m

two ways.

concentrat

were prepa

were calcu

were obtai

The value

viously re

The earlie

error prob

All c

mum for de

solutions

First, fai

The rate of the decomposition of the pentacyanocobaltate(II) ion was followed by observing the decay of the 625 mμ peak of the $Co(CN)_5^{3-}$ on the Unicam SP 800 visible-ultraviolet spectrophotometer. The sample was kept in a stoppered oxygen gas-free 1-cm spectrophotometer cell in the thermostated cell compartment of the Unicam SP 800 for the duration of each experiment and thus served to prevent any stray light from reaching the sample. Since the sealed spectrophotometer cell had very little gas volume above the solution, the decomposition of one of the reaction products[71] as shown below was prevented

$$2Co(CN)_5H^{3-} \rightleftharpoons 2Co(CN)_5^{3-} + H_2\uparrow \quad .(102)$$

The molar absorptivity of $Co(CN)_5^{3-}$ was calculated in two ways. First, dilute solutions of $Co(CN)_5^{3-}$ of known concentration, in which the decomposition was very slow, were prepared and the molar absorptivities of the solutions were calculated; second, the initial molar absorptivities were obtained for the solutions used in the rate studies. The value obtained was $\epsilon_{625} = 6.15$ compared with the previously reported values[71,84,91,121] of 10, 7, 6.3 and 7. The earlier reported spectra of $Co(CN)_5^{3-}$ [76,122] were in error probably due to the presence of some oxygen.[91]

All of the previous workers had used the 970 mμ maximum for determining the concentration of $Co(CN)_5^{3-}$ in solutions. The 625 mμ peak was chosen for two reasons. First, fairly concentrated (0.170<u>M</u>) solutions of the pentacyan

molar abs

the other

this wave

$Co(CN)_5^{3-}$

be produc

has any m

$Co(CN)_5H^{3}$

tion of t

in the vis

absorbanc

measure o

for absor

D. <u>Exper</u>

<u>Histi</u>

The

Prepared

125.1, an

value of

The

carrier,

Unicam SP

ance at 5

The

temperatu

through a

pentacyano complex could be used because of the much lower molar absorptivity at the 625 mμ peak and second, none of the other species present have any measurable absorption at this wavelength. Neither $Co(CN)_5OH^{3-}$, which is one of the $Co(CN)_5{}^{3-}$ decomposition products, nor $Co(CN)_6{}^{4-}$, which can be produced by the $Co(CN)_5{}^{3-}$ catalyzed OH^- - CN^- exchange[123] has any measurable absorbance at 625 mμ. The colorless $Co(CN)_5H^{3-}$ ion, which is the other product of the decomposition of the $Co(CN)_5{}^{3-}$, has no measurable absorbance anywhere in the visible region of the spectrum.[84,85] Thus, the absorbance of the reacting solution at 625 mμ is a direct measure of the $[Co(CN)_5]^{3-}$ and no correction is necessary for absorbance due to the presence of other species.

D. Experimental Procedure for the Study of the Cobalt-Histidine-Oxygen Reaction

The molar absorptivity at 500 mμ for solutions of $CoL_2{}^+$ prepared by oxygenating aqueous CoL_2 for several days was 125.1, and agreed fairly well with the previously reported value of 115.[117]

The kinetics of the formation of $CoL_2{}^+$ from the oxygen carrier, $L_2CoO_2CoL_2$, was followed by observing, on the Unicam SP 800 spectrophotometer, the growth of the absorbance at 500 mμ due to the formation of $CoL_2{}^+$.

The reaction was performed in a thermostated constant temperature bath at 25°. Oxygen gas mixtures were passed through a series of bubblers which were immersed in the const

actin

the s

ated

evapo

the t

bubbl

gas m

throu

ture.

ionic

above

centr

oxyge

charg

tain

vation

I

reacti

$4\underline{M}$ HNO

it dic

as sho

constant temperature bath and then bubbled through the reacting solutions. The first bubbler contained 1M KOH and the second bubbler contained 1M KNO_3. Both bubblers saturated the gas mixtures with water vapor which minimized evaporation of water from the reacting vessels and brought the temperature of the gas mixtures to 25^0. The 1M KOH bubbler also removed any CO_2 from the gas mixtures. The gas mixtures used were prepurified oxygen, air (first passed through a glass wool filter) and a 5% O_2 - 95% N_2 gas mixture. Since the solubility of oxygen in water at various ionic strengths is known[124] (and in particular, for the above experimental conditions with air as gas[91]), the concentrations of O_2 dissolved in the solutions were known.

It was necessary to use an acid quench to destroy any oxygen carrier present as the oxygen carrier has a very large charge transfer absorbance that made it impossible to obtain quantitative results from the spectrophotometric observations.[117]

Every 100 minutes, a 5 ml aliquot was removed from the reacting sample and the aliquot was quenched with 1 ml of 4M HNO_3. The HNO_3 did not affect the product, CoL_2^+, but it did convert any oxygen carrier and CoL_2 to aqueous Co^{2+} as shown below

$$CoL_2 + 2H^+ \longrightarrow Co^{2+}_{aq} + 2HL$$

$$CoL_2O_2 + 2H^+ \longrightarrow Co^{2+}_{aq} + 2HL + O_2 \qquad (103)$$

$$(CoL_2)_2O_2 + 4H^+ \longrightarrow 2Co^{2+}_{aq} + 4HL + O_2 .$$

The spectrophotometric readings were taken 25 minutes after quenching for reasons that will be explained.

In the quenched solutions, the Co^{2+}_{aq} had a small but measurable absorbance at 500 mμ ($\epsilon \approx 5$).[117] Therefore, it was necessary to correct the experimentally measured absorbance for the absorbance due to the Co^{2+}_{aq}. This correction has already been described in the Theoretical section of this work (Section III, Part J).

V. RESULTS AND DISCUSSION

A. The Decomposition of $Co(CN)_5^{3-}$

The three previous investigations of the decomposition of aqueous $Co(CN)_5^{3-}$ yielded results significantly different from ours. DeVries[71] calculated an activation energy of only 4 kcal/mole but did not list rate constants. Burnett and coworkers[121] reported rate constants which varied unexplainably between 0.002 and 0.007 $M^{-1}sec.^{-1}$ Pratt and Williams[91] did not report rate constants. All three investigations showed that the decomposition was second order in $[Co(CN)_5{}^{3-}]$.

Our investigation was carried out at 5^0 intervals from 25 to 50^0C. Second order rate plots are shown in Figure 8. The very early part of each experimental second order rate plot deviated from linearity due to the lack of the attainment of thermal equilibrium. This temperature deviation is due to the high heat of reaction of 74.4 kcal/mole.[125] To minimize this temperature deviation at the start of the reaction, the $Co(NO_3)_2$ and KCN solutions for the 25^0 kinetic run were cooled to 0^0 before mixing. The solutions for the 50^0 kinetic run were not cooled. Various degrees of cooling were used for the solutions that were investigated at

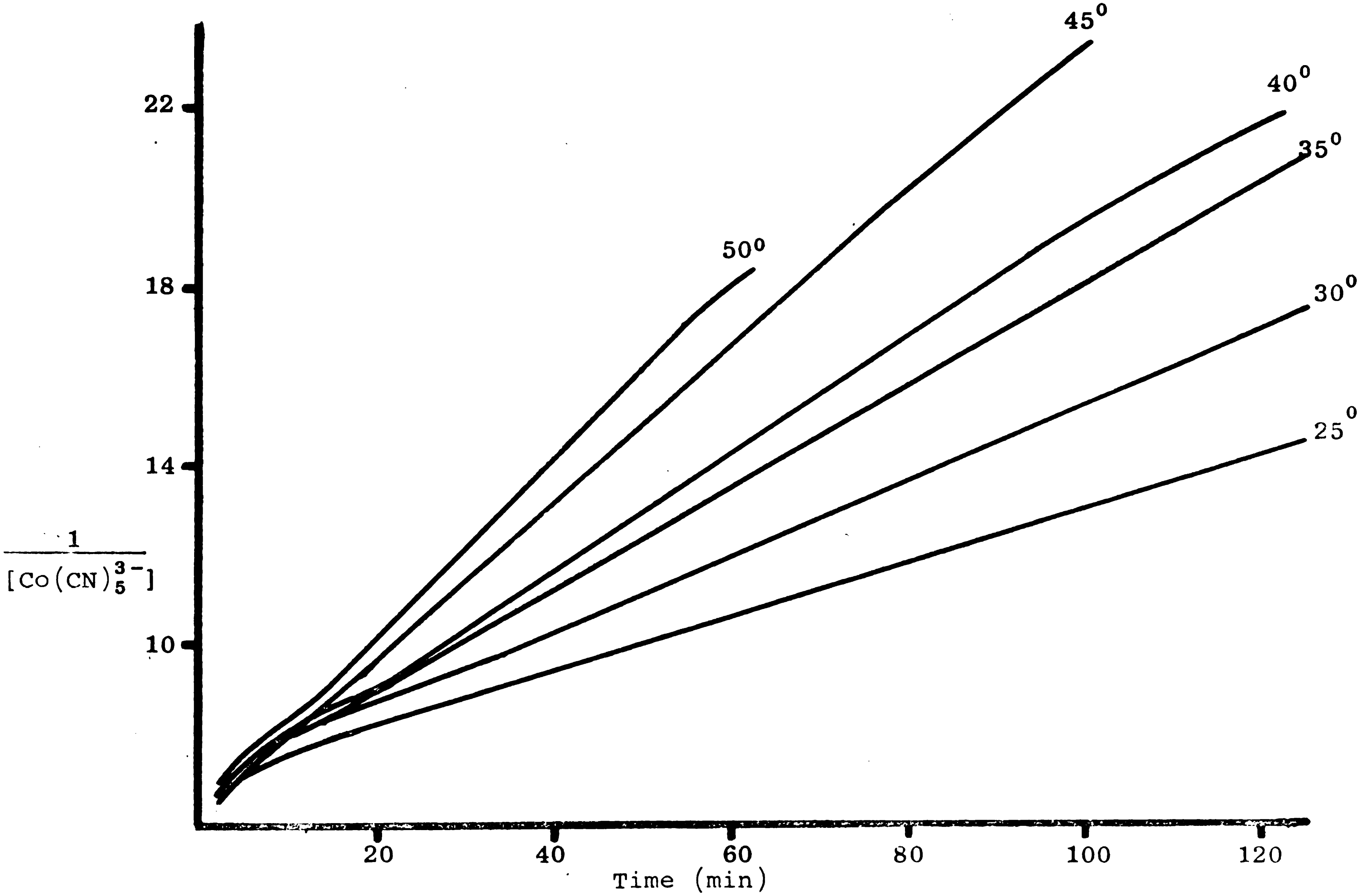


Figure 8. Second order rate plots for the decomposition of the pentacyano-cobaltate(II) ion.

interm

rate p

format

precip

is co

line

squar

versi

plot

line

was p

linea

due t

ion

tempe

ingly

and a

Table

The va
kcal/m

intermediate temperatures. Near the end of each experimental rate plot, there was a deviation from linearity due to the formation of an unidentified light brown precipitate. The precipitate was probably impure $K_3Co(CN)_5H$ which, when pure, is colorless.[85] Those points that did lie on a straight line were treated by the previously described linear least squares computer program by use of the Michigan State University Control Data Corporation 3600 computer. An Arrhenius plot of the resulting rate constants yielded the straight line shown in Figure 9. A linear least squares calculation was performed on the Arrhenius equation. The deviation from linearity of the 50^0 point on the Arrhenius plot might be due to the decomposition of one of the products (the $Co(CN)_5H^{3-}$ ion) according to equation 102. It is known that as the temperature is increased, $Co(CN)_5H^{3-}$ decomposes increasingly into $Co(CN)_5{}^{3-}$ and H_2.[71] The resulting rate constants and activation energy are shown in Table II.

Table II. Rate constants for the decomposition of $Co(CN)_5^{3-}$.

Temp. (^{0}C)	$k(M^{-1}sec^{-1}) \times 10^3$
25	1.00 ± 0.00
30	1.35 ± 0.01
35	1.72 ± 0.02
40	2.17 ± 0.02
45	2.92 ± 0.02
50	3.30 ± 0.02

The value for the Arrhenius activation energy is 9.84 ± 0.27 kcal/mole.

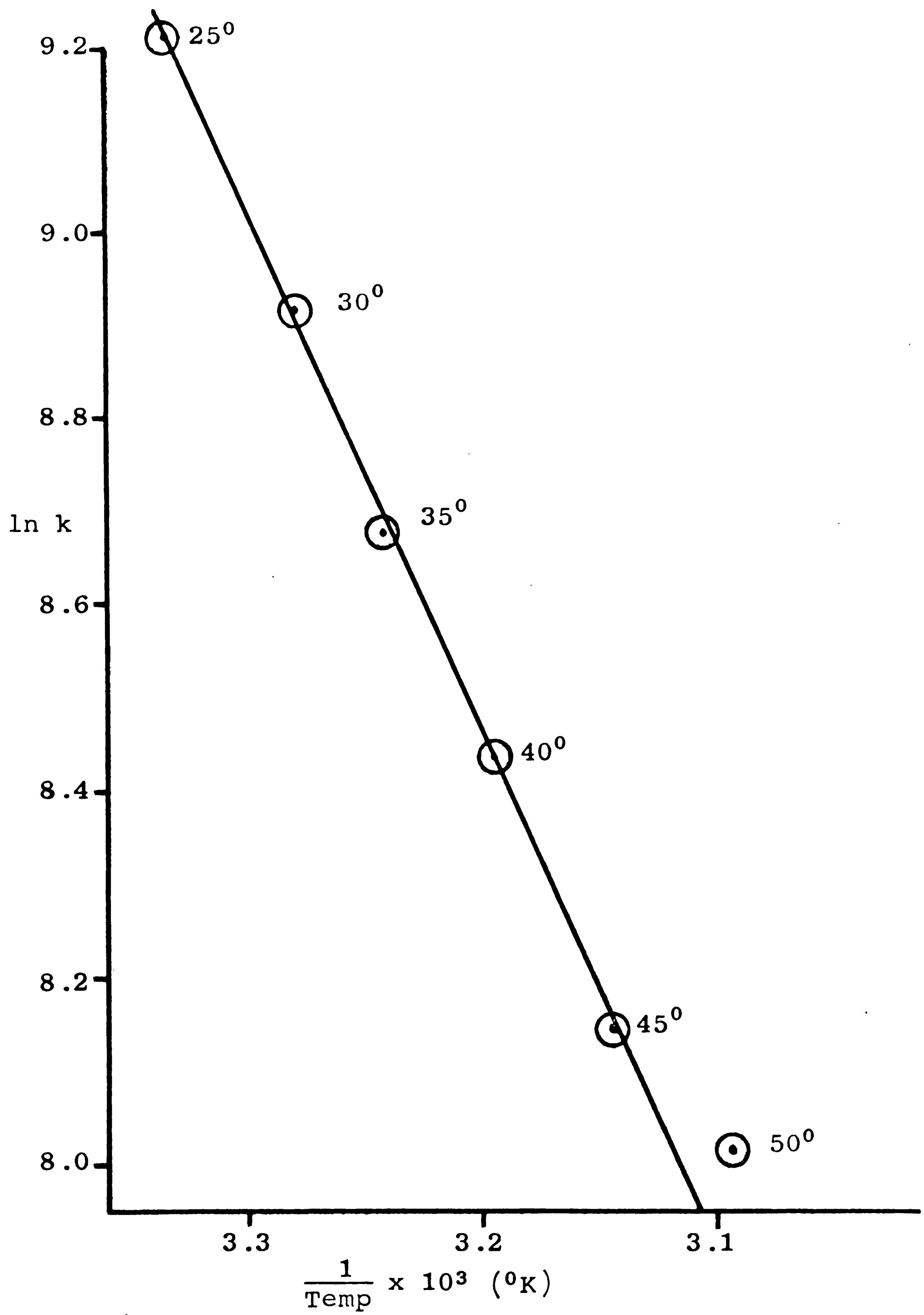


Figure 9. Arrhenius plot for the decomposition of the pentacyanocobaltate(II) ion.

That the $Co(CN)_5^{3-}$ ion is oxidized by molecular oxygen much more rapidly than $Co(NH_3)_6^{2+}$ to form the peroxo bridged species $L_5CoO_2CoL_5$ has been used as evidence to show that the cyano species is five coordinate. The rate of the uptake of oxygen by ammoniacal cobalt(II) solutions has recently been measured[60] by the stopped-flow technique whereas an attempt to measure the rate of the oxygen absorption by $Co(CN)_5^{3-}$ by this same technique has failed because the reaction is too fast to measure by the stopped-flow method.[126] The explanation being that the reaction probably proceeds by an inner sphere mechanism and the five coordinate cyano species would not have to undergo dissociation before reacting with the oxygen, whereas the six coordinate ammine species would probably have to first undergo dissociation to react with the oxygen. However, the possibility that there is a loosely bound labile water molecule in the cyano species is not ruled out (see the Historical section).[91,127]

The mechanism for the decomposition need not necessarily be as previously proposed, namely

$$2Co(CN)_5^{3-} + H_2O \longrightarrow (NC)_5CoHOHCo(CN)_5^{6-} \xrightarrow{k} \longrightarrow Co(CN)_5OH^{3-} + Co(CN)_5H^{3-} \quad (104)$$

but it might proceed as follows:

$$Co(CN)_5H_2O^{3-} \underset{fast}{\overset{fast}{\rightleftharpoons}} Co(CN)_5^{3-} + H_2O \quad (105)$$

$$Co(CN)_5H_2O^{3-} + Co(CN)_5^{3-} \longrightarrow (NC)_5CoHOHCo(CN)_5^{6-} \quad (106)$$

foll

bric

of I

invo

be p

spe

the

aqu

fin

$K_3[$C

imm

pre

sol

int

dry

$K_6[$

$K_3[$C

vio

vac

and

prob

the

no v

followed, as before, by the decomposition of the water-bridged species[128]

$$(NC)_5CoHOHCo(CN)_5^{6-} \xrightarrow{k} (NC)_5CoH^{3-} + HOCo(CN)_5^{3-}. \quad (107)$$

Therefore the decomposition or "homogeneous absorption of hydrogen" by $Co(CN)_5^{3-}$ in aqueous solutions would actually involve a disproportionation of water.

If solid mononuclear paramagnetic $K_3[Co(CN)_5]$ could be prepared, analyzed for the presence of water, and its spectra compared with those of solutions of $K_3[Co(CN)_5]$, the question of whether $Co(CN)_5^{3-}$ is five coordinate in aqueous solutions or contains water at the sixth site might finally be answered. Any attempt to prepare solid monomeric $K_3[Co(CN)_5]$ from aqueous solution failed as precipitation immediately results in dimerization.[72] Even an attempt to prepare solid $K_3[Co(CN)_5]$ by rapid freezing of very dilute solutions of $K_3[Co(CN)_5]$ sprayed from an atomizer straight into liquid nitrogen and removing the solvent by freeze drying produced a pink ice containing the dimeric diamagnetic $K_6[(NC)_5CoCo(CN)_5]$.[91] Solid monomeric paramagnetic $K_3[Co(CN)_5]$ was recently prepared by heating the solid violet diamagnetic dimer, $K_6[(NC)_5CoCo(CN)_5]$, to 230° under vacuum for 15 to 20 minutes.[129] The product was light tan and had a magnetic moment of 2.09 to 2.22 B.M. and was probably anhydrous.[129] The magnetic moment was higher than the 1.72 B.M. for aqueous solutions.[62,74] However, since no visible spectra of the solid monomer are as yet available, the

cann

that

mine

the

Tabl

Tabl

Co

ton.

coba

ever

atec

uv s

of H

that

is a

the

give

the final answer to the coordination number of $K_3[Co(CN)_5]$ cannot be answered.

In order to determine the nature of the electron transfer that occurs in reaction 107, it is first necessary to determine the oxidation state of the cobalt and the hydrogen in the $Co(CN)_5H^{3-}$ ion. The three possibilities are listed in Table III.

Table III. Possible oxidation states of Co and H in $Co(CN)_5H^{3-}$.

Co oxidation state	H oxidation state	Nature of the H
+1	+1	Proton
+2	0	Atom
+3	-1	Hydride

All three of the possibilities, cobalt(I) and a proton,[81,130] cobalt(II) and a hydrogen atom[121,131] and cobalt(III) and a hydride[84,85,132] have been proposed. However, the ability of $Co(CN)_5H^{3-}$ to hydrogenate some unsaturated organic compounds[133] along with evaluation of the near uv spectrum of $Co(CN)_5H^{3-}$ and consideration of the position of hydride in the spectrochemical series[134] strongly suggests that the hydrogen in this ion is hydride. Since $Co(CN)_5^{3-}$ is a stronger reducing agent than H_2,[135] one can consider the $Co(CN)_5^{3-}$ decomposition to be a reduction of water to give the hydride ion while itself being oxidized to Co^{III}.

Th

an

tr

ba

in

10

oc

the

thr

act

hyd

(eq

and

sio

int

Co(

and

H_2O

Thus, $Co(CN)_5H^{3-}$ should be formulated as $[Co^{III}(CN)_5H^-]^{3-}$ and should be named hydridopentacyanocobaltate(III) ion.[85]

We can now examine equation 107 to determine what electron transfers are necessary to maintain the proper charge balance. The two cobalt(II) ions in the water-bridged intermediate must be converted to cobalt(III). Equation 107 very probably occurs as follows:

$$(NC)_5Co^{II}H \; OHCo^{II}(CN)_5^{6-} \longrightarrow (NC)_5Co^{II}H\cdot^{3-} + \cdot OHCo^{II}(CN)_5^{3-} \qquad (108)$$

$$\longrightarrow (NC)_5Co^{III}H:^{3-} + :OHCo^{III}(CN)_5 .$$

In addition to the decomposition of $Co(CN)_5^{3-}$ which occurs by forming a water-bridged binuclear intermediate, there are several other reactions of $Co(CN)_5^{3-}$ which occur through similar bridged binuclear intermediates. These reactions are the reversible heterogeneous absorption of hydrogen gas bubbled into aqueous solutions of $Co(CN)_5^{3-}$ (equation 109)

$$2Co(CN)_5^{3-} + H_2 \rightleftharpoons 2\,Co(CN)_5H^{3-} \qquad (109)$$

and the $Co(CN)_5^{3-}$ catalyzed <u>ortho</u>-<u>para</u> hydrogen interconversion (equation 110) both of which presumably involve the intermediate $(NC)_5CoH_2Co(CN)_5^{6-}$ [89,128,130,131] and the $Co(CN)_5^{3-}$ catalyzed deuterium-hydrogen exchange between H_2 and H_2O[89,130,136] (equations 110-113) in which both H_2 and H_2O bridged species are probably intermediates e:

sp

ea

Ta

en

pe

Ta

Ab

De

Ca

Co

Co

$$D_2 + 2Co(CN)_5^{3-} \rightleftharpoons (NC)_5CoD_2Co(CN)_5^{6-} \rightleftharpoons 2Co(CN)_5D^{3-} \quad (110)$$

$$2Co(CN)_5^{3-} + H_2O \rightleftharpoons (NC)_5CoH_2OCo(CN)_5^{6-} \quad (111)$$

$$(NC)_5CoHOHCo(CN)_5^{6-} + Co(CN)_5D^{3-} \rightleftharpoons (NC)_5CoDOHCo(CN)_5^{6-} + Co(CN)_5H^{3-} \quad (112)$$

$$DH + 2Co(CN)_5^{3-} \rightleftharpoons (NC)_5CoDHCo(CN)_5^{6-} \rightleftharpoons Co(CN)_5H^{3-} + Co(CN)_5D^{3-} \quad (113)$$

etc. Because of the similarities of the H_2 and HOH bridged species, one would expect similar activation energies for each of the above mentioned reactions. As can be seen from Table IV, the previously reported value for the activation energy for the $Co(CN)_5^{3-}$ decomposition[71] was lower than expected and was the reason for the present investigation.

Table IV. Activation energies for reactions similar in mechanism to the decomposition of aqueous $Co(CN)_5^{3-}$.

Reaction	Activation Energy (kcal/mole)	Reference
Absorption of H_2 by $Co(CN)_5^{3-}$	11.2 ± 0.2	71
Desorption of H_2 by $Co(CN)_5^{3-}$	12 ± 1	128
Catalysis of D_2-H_2O exchange by $Co(CN)_5^{3-}$	7.3 ± 0.4	130
$Co(CN)_5^{3-}$ decomposition	4	71
$Co(CN)_5^{3-}$ decomposition	9.84 ± 0.27	137 (this work)

Co

so

KC

th

D_2

an

sh

an

Co

pe

Co

(N

ti

io

th

an

re

wi

en

wa

it

si

An interesting aspect of both the homogeneous (i.e. $Co(CN)_5^{3-}$ decomposition) and the heterogeneous hydrogen absorption was the large salt effect.[71,84,86,91] The salts KCl and KCN were about equally effective in accelerating the heterogeneous H_2 absorption and the $Co(CN)_5^{3-}$ catalyzed D_2-H_2O exchange and thus indicated that $Co(CN)_6^{4-}$ is not an intermediate in these reactions.[86] Pratt and Williams showed the same salt effect in the $Co(CN)_5^{3-}$ decomposition and calculated the association constant for the Rb^+, $Co(CN)_5^{3-}$ ion pair.[91]

The probable reason for the large ionic strength dependence is the large repulsion between the two combining $Co(CN)_5^{3-}$ ions during the formation of the intermediate, $(NC)_5CoHOHCo(CN)_5^{6-}$. As the ionic strength increases, more positive ions will surround the $Co(CN)_5^{3-}$ (forming M^+, $Co(CN)_5^{3-}$ ion pairs and M^+, $Co(CN)_5^{3-}$, M^+ ion triplets) and therefore the repulsion between adjacent $Co(CN)_5^{3-}$ ions will decrease, and it should be easier to form the water-bridged intermediate. The apparent activation energy for the reaction will then be lower. This means that as the activation energy decreases, the reaction for the formation of the water bridge species becomes

$$2[M^+, Co(CN)_5^{3-}] + H_2O \longrightarrow M^+, (NC)_5CoHOHCo(CN)_5^{6-}, M^+. \quad (114)$$

Therefore, in performing rate studies on these systems, it is necessary to work at as low an ionic strength as possible. One must also work at as low a CN:Co ratio as possible ar

ra

ch

cf

wh

th

0

th

ex

It

th

br

be

th

wh

th

mo

fo

qu

sp

de

Co

and no other salt should be added. DeVries, by using a KCN:Co ratio of approximately 400 (hence, at high ionic strength), obtained an activation energy for the decompostion reaction of 4 kcal/mole.[71] We have used a KCN:Co ratio of 5.49, which is about as low a ratio as one can have and still have the $Co(CN)_5^{3-}$ ion. Our calculated activation energy, 9.84 ± 0.27 kcal/mole, should be close to the thermodynamic activation energy.

We have made some qualitative observations of an interesting reaction originally proposed by Piringer,[130]

$$4Co(CN)_5H^{3-} + (NC)_5CoO_2Co(CN)_5^{6-} \longrightarrow 6Co(CN)_5^{3-} + 2H_2O. \qquad (115)$$

If air is admitted to a partially "aged" $Co(CN)_5^{3-}$ solution (*i.e.*, it is partially decomposed), the color changes from the green of the pentacyano ion to the orange of the O_2-bridged species. After approximately 20 min., the solution becomes green again and the visible spectrum returns to that of the pentacyano solution. This above mentioned phenomenon agrees with Piringer's postulated reaction (equation 115). Thus, there is another advantage in using moderately concentrated solutions of the pentacyano ion to follow the decomposition reaction; the presence of small quantities of oxygen, which would produce the O_2-bridged species, will not interfere with the ability to observe the decomposition reaction beyond the first few minutes. The $Co(CN)_5H^{3-}$ already present will convert any $[(NC)_5CoO_2Co(CN)_5]^{6-}$

pre

st

tha

po

in

or

At

to

di

(se

for

mi

3.

su

in

de

(th

tha

ri

B.

co

present back to $Co(CN)_5^{3-}$ by reaction 115 as long as the stoichiometric quantity of the hydrido species is greater than the amount of oxygen present.

We have observed a limited amount of evidence in support of the postulated monomer-dimer equilibrium of $Co(CN)_5^{3-}$ in aqueous solution

$$2Co(CN)_5^{3-} \rightleftharpoons (NC)_5CoCo(CN)_5^{6-} \qquad (116)$$

or

$$Co(CN)_5^{3-} + Co(CN)_5H_2O^{3-} \rightleftharpoons (NC)_5CoCo(CN)_5^{6-} + H_2O. \qquad (117)$$

At the start of each experiment, the 625 mμ maximum shifts to slightly lower wavelengths. The spectrum of the solid dimer in a mineral oil mull shows the peak shifted to 535 mμ (see Figure 10). For example, at 50^0 (shown in Figure 11), for the first experimental observation, 1.90 minutes after mixing, the peak is at 620 mμ; for the second observation, 3.50 minutes after mixing, the peak is at 622 mμ. For all subsequent observations, the peak is at 625 mμ. The shifting of this peak at the start of the reaction is most evident for the experiments at 50^0 and least evident at 25^0 (the shift is about 2 mμ). The decreasing shift indicates that the equilibrium in reactions 116 or 117 shifts to the right with increasing temperature.

B. The Formation of Cobalt(III) Products from the Oxygen Carrier, μ-Dioxygentetrakis(histidinato)dicobalt(III)

Zompa's[106] investigation of the decomposition of the cobalt-histidine oxygen carrier revealed several facts.

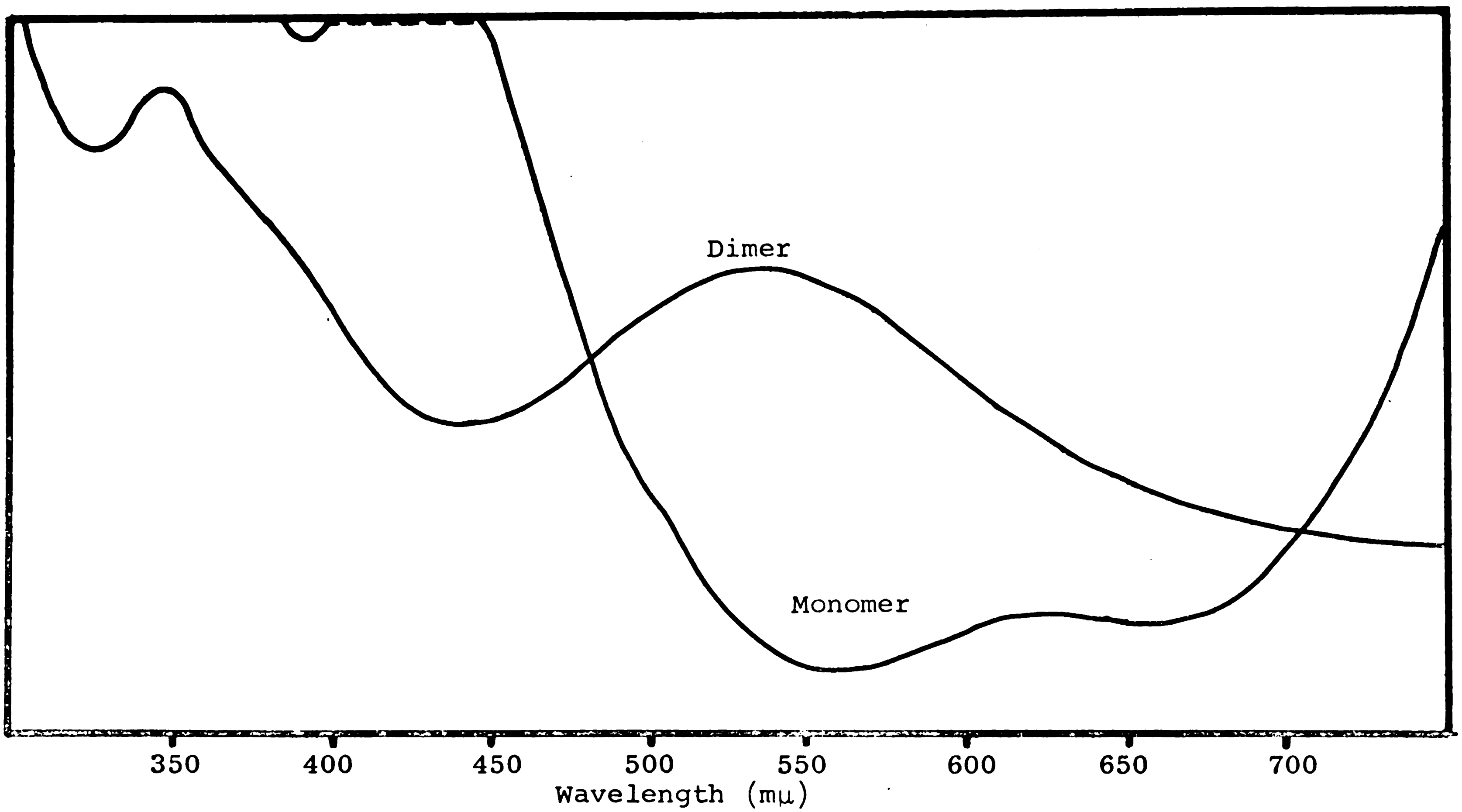


Figure 10. The visible and near uv spectra of monomeric aqueous $K_3[Co(CN)_5]$ and dimeric $K_6[(CN)_5CoCo(CN)_5]$ in a nujol mull.

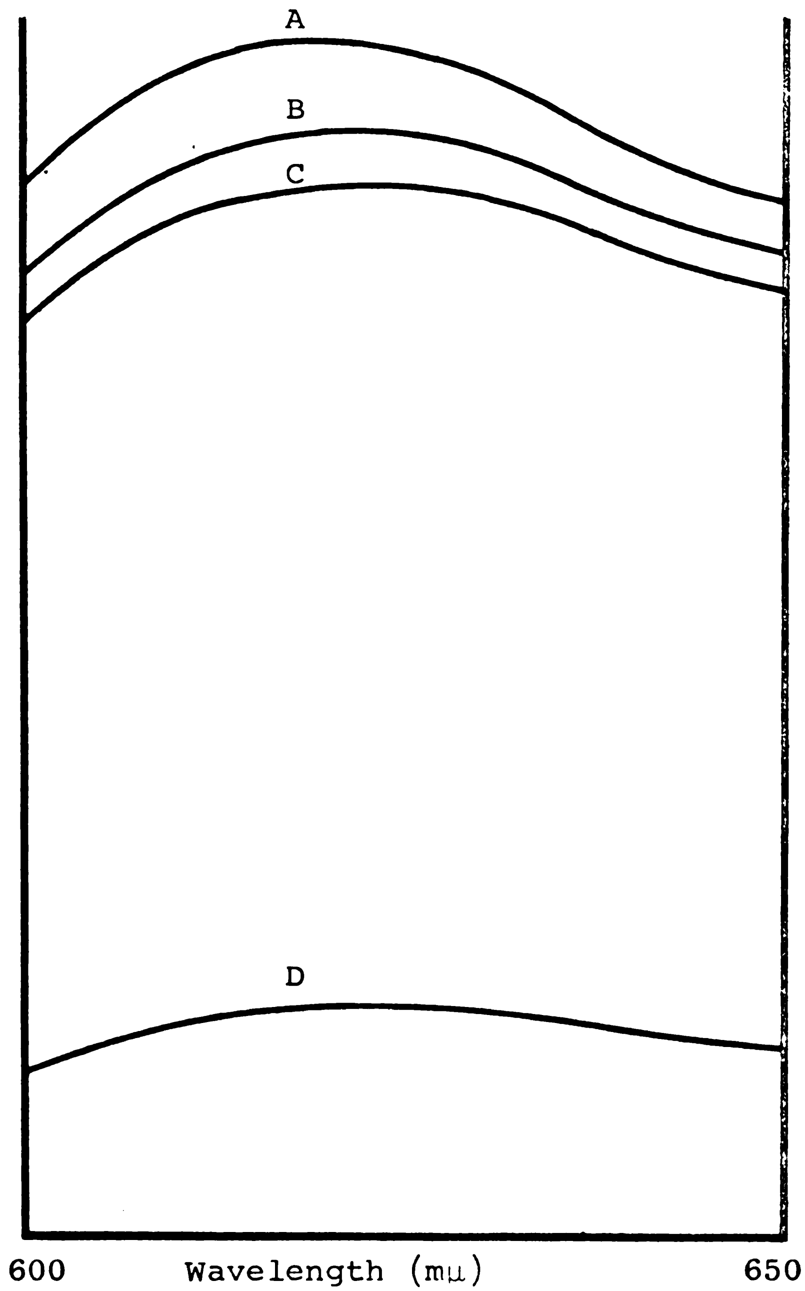


Figure 11. Enlargement of the spectra of the first three observations during the 50° kinetic experiment of the decomposition of $Co(CN)_5^{3-}$. (Time after the start of the reaction-- A = 1.90 min; B = 3.50 min; C = 5.00 min; D = 67.0 min.)

Af
tw
nu
ab
du
re
Th
of
pr

Th
th
as
1
hy
st
ra
pr
Ze
fo
It
pr

to
th
Al

After very rapid absorption of one mole of oxygen gas per two moles of CoL_2 (L = l-histidinate anion) to form the binuclear oxygen carrier, an additional mole of oxygen was absorbed per two moles of cobalt to form cobalt(III) products. This phenomenon of some of the absorbed O_2 being reversible and some irreversible had been previously observed.[20] The data could be approximately fitted for the latter part of the reaction by means of a non-linear least squares computer program which assumed the following mechanism,

$$A \xrightarrow{k_1} 2B \quad \text{and} \quad B \xrightarrow{k_2} C. \qquad (118)$$

The experimental conditions for this preliminary investigation[106,117] were as follows: temperature 25^0, pure oxygen as gas, l-histidine to cobalt ratios of 2,3,4,6,8 and 10 to 1 and $Co_0^{II} = 1.21 \times 10^{-2}\underline{M}$; the pH was maintained at 7.0 by a phosphate buffer and the ionic strength was kept constant by the presence of 1$\underline{M}$ KNO_3. As the ligand to metal ratio was increased, the rate of formation of the cobalt(III) product decreased.[106] The data from these kinetic runs of Zompa[117] are shown in Table V. The cobalt(III) product was found to be a mixture of the three isomers of $[CoL_2]NO_3$.[106,107] It was not possible to fit the early data points to the above proposed mechanism (Equation 118).

It was decided to extend Zompa's investigation[106,107,117] to determine the cobalt and oxygen dependence on the formation of $[CoL_2]NO_3$ and to improve the least squares treatment. All rate studies were performed at 25^0C, pH = 7.0,

Table V. Data of L. Zompa for the formation of CoL_2^+ from $(CoL_2)_2O_2$ (every other data point is shown). $[Co_0^{II}] = 1.2 \times 10^{-2}$ M; pure O_2 as gas; 25°C.

	$[CoL_2^+] \times 10^2$					
l-Histidine to Cobalt Ratio	2:1	3:1	4:1	6:1	8:1	10:1
Time (min)						
0	0	0	0	0	0	0
200	0.055	0.044	0.034	0.044	0.047	0.040
400	0.167	0.130	0.103	0.115	0.118	0.101
600	0.313	0.250	0.205	0.209	0.203	0.182
800	0.475	0.388	0.323	0.318	0.302	0.277
1000	0.642	0.542	0.458	0.428	0.410	0.379
1200	0.778	0.730	0.592	0.552	0.480	0.493
1400	0.896	0.871	0.715	0.668	0.641	0.605
1600	0.979	0.970	0.826	0.773	0.740	0.707
1800	1.044	1.033	0.922	0.871	0.837	0.798
2000	1.092	1.070	0.992	0.954	0.917	0.872
2200	1.123	1.094	1.040	1.016	0.978	0.934
2400	1.128	1.079	1.074	1.063	1.025	0.980
2600	1.063	---	1.100	1.093	1.060	1.010
2800	---	---	1.100	1.117	1.076	1.032
3000	---	---	1.034	1.120	1.064	1.036
3200	---	---	---	1.054	---	0.978

histidine:cobalt = 2 and in 1M KNO_3. Rate studies of type I (see Table I) were performed with pure oxygen gas, and of type III were performed with oxygen, air and 5% O_2-95% N_2. The average of the data for each type of experiment performed are shown in Table VI.

In order to obtain the best possible least squares fits between experimental and calculated concentrations of $[CoL_2]$, it was decided to include in the proposed mechanism all equilibria which occur prior to the mechanistic steps in the formation of CoL_2^+. The equilibria include the stepwise formation of the cobalt(II) histidine complex, the stepwise protonation of the histidinate anion and the stepwise formation of the binuclear cobalt-histidine oxygen carrier.

The first two stepwise formation constants for the formation of cobalt(II) histidine complex at 25° are well known[20,138,139]

$$Co^{2+} + L^- \underset{}{\overset{K_1}{\rightleftharpoons}} CoL^+ \qquad K_1 = 8.3 \times 10^6 \quad (41)$$

$$CoL^+ + L^- \overset{K_2}{\rightleftharpoons} CoL_2 \qquad K_2 = 3.3 \times 10^5. \quad (42)$$

The stepwise protonation constants for the histidinate anion at 25° are also well known[138,139]

$$L^- + H^+ \overset{K_{1H}}{\rightleftharpoons} HL \qquad K_{1H} = 1.5 \times 10^9 \quad (46)$$

$$HL + H^+ \overset{K_{2H}}{\rightleftharpoons} H_2L^+ \qquad K_{2H} = 1.2 \times 10^6 \quad (47)$$

$$H_2L^+ + H^+ \overset{K_{3H}}{\rightleftharpoons} H_3L^{2+} \qquad K_{3H} = 6.6 \times 10^1. \quad (48)$$

Ta

Ti

2

4

6

8

10

12

14

16

18

20

22

24

26

28

Table VI. Data showing the dependence of the formation of CoL_2^+ from $(CoL_2)_2O_2$ on the cobalt(II) and oxygen concentration at 2:1 l-histidine to cobalt ratio at 25^0C. (Every other data point shown.)

Co_0^{II}	$[CoL_2^+] \times 10^2$				
	6.08×10^3M		12.16×10^{-3}M		
Time (min)	O_2gas	O_2gas ($[CoL_2^+]$ shown is twice actual $[CoL_2^+]_{exp}$)	O_2gas	Air	5% O_2 gas
0	0	0	0	0	0
200	0.024	0.047	0.048	0.054	0.039
400	0.065	0.131	0.156	0.148	0.100
600	0.133	0.266	0.307	0.278	0.203
800	0.230	0.459	0.479	0.446	0.320
1000	0.309	0.618	0.640	0.590	0.488
1200	0.383	0.766	0.753	0.708	0.559
1400	0.432	0.864	0.834	0.802	0.681
1600	0.464	0.928	0.892	0.890	0.788
1800	0.482	0.963	0.932	0.937	0.885
2000	0.492	0.983	0.932	0.965	0.927
2200	0.499	0.999	0.961	0.971	0.976
2400	0.502	1.003	0.965	0.997	1.031
2600	0.510	1.020	0.969	1.008	1.077
2800	---	---	0.964	1.009	1.110

Several mononuclear cobalt peroxo complexes are known.[60,132,140-142] An investigation of the rapid reversible uptake of oxygen by bis(l-histidinato)cobalt(II) shows that the oxygen uptake is a two-step process

$$CoL_2 + O_2 \underset{}{\overset{K_{4a}}{\rightleftharpoons}} CoL_2O_2 \qquad (44)$$

$$CoL_2O_2 + CoL_2 \underset{}{\overset{K_{4b}}{\rightleftharpoons}} L_2CoO_2CoL_2 \qquad (45)$$

with an overall formation constant for the binuclear oxygen carrier, $K_{4a} \cdot K_{4b} = 7.2 \times 10^6$ at 25^0.[59] A recent investigation showed that the two-step formation of the oxygen carrier also occurs for the cobalt(II) complexes of diethylenetriamine, histamine, ethylenediamine and 2-aminomethylpyridine.[143]

The dependence of the formation of CoL_2^+ on the histidine concentration has been described earlier and can be seen from Table V. As the histidine to cobalt ratio increases, the ratio of fomration of CoL_2^+ decreases slightly. The oxygen dependence can be seen from inspection of the last three columns of Table VI. In the early stages of the reaction, the rate of formation of CoL_2^+ increases as $[O_2]$ in the solution increases. However, in the late stages of the reaction, there is a reversal of the oxygen dependence; the rate of formation of CoL_2^+ decreases as the $[O_2]$ in the solution increases. By comparing columns 2 and 3 of Table VI (O_2 as gas and $Co_0^{II} = 6.08 \times 10^{-3}$ and 12.16×10^{-3} <u>M</u> respectively) one can see the dependence of the formation of CoL_2^+ on the cobalt(II) concentration is slightly less than first order. As stated earlier, one mole of O_2 is rapidly and reversibly absorbed per two moles of CoL_2 and a second mole of O_2 is slowly and irreversibly absorbed per two moles of CoL_2^+.

Any proposed mechanism would have to include equations 41, 42 and 44-48 and would have to explain the histidine, cobalt and oxygen dependencies on the rate of formation of the CoL_2^+ as well as the stoichiometry and nature of the oxygen uptake.

Since there was some preliminary evidence for the dependence of the rate of formation of CoL_2^+ on $[CoL_2^+]$, experiments of types I and II (see Table I) were performed in which pure oxygen was used as the gas and the results are tabulated in columns 1 to 3 of Table VII. The underlined data from Table VII that are listed in Table VIII confirm the catalytic nature of CoL_2^+ on the decomposition of the cobalt-histidine oxygen carrier.

In comparing columns 1 and 2 of Table VIII, one sees that the solution containing the 6.08×10^{-3} M CoL_2^+ at "time 1" has a rate of production almost 40% greater than the solution without the CoL_2^+ initially present. Even though the solution listed in column 3 has a smaller $[Co^{II}]_{initial}$ than the solution listed in column 2, and therefore a lower concentration of oxygen carrier, this solution has a greater $[CoL_2^+]_{initial}$ and thus there is a greater production of CoL_2^+ after 500 min. for the solution in column 3. When after 500 min., 6.08×10^{-3} M CoL_2^+ is added to the solution listed in column 1 (it then becomes the solution listed in column 4) the production of CoL_2^+

Ta

1

2

3

4

5

6

7

8

9

10

11

Table VII. Experimental data in support of the catalytic nature of CoL_2^+ in the decomposition of $(CoL_2)_2O_2$. 6.08×10^{-3} M Co_0^{II}; 25°C

	$([CoL_2^+] - [CoL_2^+]_0) \times 10^2$				
Time (min.)	0.0M $CoL_2^+{}_0$, O_2 gas	6.08×10^{-3}M $CoL_2^+{}_0$, O_2 gas	*	0.0M $CoL_2^+{}_0$, 5% O_2 gas	6.08×10^{-3}M $CoL_2^+{}_0$, 5% O_2 gas
0	0	0		0	0
100	---	0.0202		0.0058	0.0163
200	0.0269	0.0422		0.0096	0.0240
300	0.0518	0.0796		0.0182	0.0384
400	0.0749	0.1055		0.0317	0.0643
500	0.1122	0.1554	0.1122	0.0394	0.0882
600	**	0.1938	0.1458	0.0682	0.1093
700		0.2226	0.1756	0.0824	0.1343
800		0.2695	0.2254	0.1055	0.1688
900		0.2983	0.2666	0.1324	0.1928
1000		0.3338	0.3098	0.1736	0.2188
1100		0.3646	0.3338		

*The solution listed in column 1 after 500 min. of reaction to which 6.08×10^{-3}M CoL_2^+ has been added.

**Immediately after the 500 min. measurement of $[CoL_2^+]$, 6.08×10^{-3}M $[CoL_2^+]$ is added to this solution and it becomes the solution listed in column 3.

Table VIII. Data in support of the catalytic nature of CoL_2^+ in the decomposition of $(CoL_2)_2O_2$.

Column Number	1	2	3	4
Column of Table VII from which the data comes	I	II	II	III
Time 1 (min.)	0	0	400	500
Time 2 (min.)	500	500	900	1000
$[Co^{II}_{total}]$ at time 1 (**M**)	6.08×10^{-3}	6.08×10^{-3}	5.02×10^{-3}	4.96×10^{-3}
$[Co^{II}_{total}]$ at time 2 (**M**)	4.96×10^{-3}	4.53×10^{-3}	2.74×10^{-3}	2.98×10^{-3}
$[CoL_2^+]$ at time 1 (**M**)	0	6.08×10^{-3}	7.14×10^{-3}	7.20×10^{-3}
$[CoL_2^+]$ at time 2 (**M**)	1.12×10^{-3}	7.64×10^{-3}	9.06×10^{-3}	9.18×10^{-3}
$\Delta [CoL_2^+]$ during the 500 min. from time 1 to time 2. (**M**)	1.12×10^{-3}	1.58×10^{-3}	1.92×10^{-3}	1.98×10^{-3}

increases to the rate of the solution which had 6.08 x 10^{-3} $\underline{M}$ CoL_2^+ added initially (compare columns 3 and 4). The above data confirm that [CoL_2^+] does indeed have a catalytic effect on the rate of formation of CoL_2^+ from the oxygen carrier.

Since the rate of formation of CoL_2^+ depends both on the concentration of cobalt(II) species present and on the [CoL_2^+], two steps are postulated; one step depends upon [CoL_2] or [$(CoL_2)_2O_2$] and the other depends upon [CoL_2^+]

$$(CoL_2)_2O_2 \xrightarrow{k_{5a}} CoL_2^+ + CoL_2 + O_2^- \qquad (49)$$

or

$$CoL_2O_2 + CoL_2 \xrightarrow{k'_{5a}} CoL_2^+ + CoL_2 + O_2^- \qquad (50)$$

and

$$CoL_2O_2 + CoL_2^+ \xrightarrow{k_{5b}} 2CoL_2^+ + O_2^- . \qquad (51)$$

It was originally thought that the CoL_2O_2 shown above and in the formation of the binuclear oxygen carrier (equations 44 and 45) might be $Co^{II}L_2O_2$ and the initial product of equations 49 to 51 might be $Co^{III}L_2O_2^-$ which then would either rapidly or at a measurable rate decompose to CoL_2^+ and O_2^-. However, a recent esr study of some stable mononuclear cobalt O_2 adducts has shown that they contain only one unpaired electron which spends most of its time on the oxygen atoms and therefore the adducts should be formulated as $(Co^{III}X_mO_2^-)$.[142] Thus, the mononuclear CoL_2O_2 is probably cobalt(III) and superoxide rather than $Co^{II}L_2O_2$ and therefore, CoL_2^+ and O_2^- would have to be formed directly by equations 49 to 51.

The most likely reason for the dependence of the rate of formation of CoL_2^+ on histidine is the following reaction:

$$CoL_2 + L^- \underset{}{\overset{K_3}{\rightleftharpoons}} CoL_3^- \quad . \qquad (43)$$

Although a species such as CoL_3^- would not be favored sterically, this author feels that this is more likely than a dissociation reaction such as

$$(CoL_2)_2O_2 \rightleftharpoons L_2CoO_2L^+ + L^- \qquad (119)$$

as the dissociation of the L^- from the oxygen carrier would involve the breakage of two strong bonds, the cobalt imidazole and cobalt amine bonds, (the cobalt carboxylate bonds having been previously broken during the formation of the oxygen carrier), whereas only one fairly weak cobalt carboxylate bond in CoL_2 would have to break to allow the formation of CoL_3^-.

Preliminary attempts to fit the experimental data of Zompa[117] (see Table V) show that the equilibrium constant for the postulated formation of CoL_3^- is equal to or less than 1.4×10^4. Considering the steric difficulty in forming CoL_3^-, a value of 1.4×10^4 for the third stepwise cobalt-histidine formation constant is a little higher than expected but it is believable. A typical set of calculated and experimental data based on $K_3 = 1.4 \times 10^4$ is shown in Table IX.

A value for K_3 of equal to or less than 1.4×10^4 will only affect the calculated data for histidine to cobalt

Table IX. A typical set of calculated and experimental data (based upon Zompa's[117] histidine dependence studies) that shows $K_3 \leq 1.4 \times 10^4$.

($Co_0^{II} = 1.211 \times 10^{-2}$, $Co_0^{III} = 0$, pure O_2 as gas, $K_3 = 1.4 \times 10^4$.)

Histidine to cobalt ratio and data set	$[CoL_2^+] \times 10^3$											
	2:1		3:1		4:1		6:1		8:1		10:1	
	Exp	Calc	Exp	Calc	Exp	Calc	Exp	Calc	Exp	Calc	Exp	Calc
Time (min)												
200	0.055	0.063	0.044	0.063	0.034	0.059	0.044	0.051	0.047	0.044	0.040	0.038
400	0.167	0.153	0.130	0.151	0.103	0.140	0.115	0.120	0.118	0.104	0.101	0.089
600	0.313	0.275	0.250	0.272	0.205	0.251	0.209	0.214	0.203	0.182	0.182	0.155
800	0.475	0.432	0.388	0.428	0.323	0.394	0.318	0.333	0.302	0.282	0.277	0.239
1000	0.642	0.619	0.542	0.615	0.458	0.567	0.428	0.479	0.410	0.405	0.379	0.342

ratios of greater than 2:1 (see Table X). This is expected since with a histidine to cobalt ratio of 2:1, there should be only a negligible concentration of CoL_3^-.

After the solutions are quenched, there is a slow attack on the solutions by the acid quench as shown in Figure 12. A quench with HCl compared to the HNO_3 yielded the same rate of acid attack. Therefore the H^+ is the species that is causing the attack and not the oxidizing ability of the nitrate. Since the rate of the acid attack decreases rapidly with time, all spectrophotometer readings were taken 25 minutes after quench when the rate of the acid attack is slow. The value used for the molar absorptivity of $(CoL_2)NO_3$ synthesized by oxygenating aqueous CoL_2, (ϵ = 125.1), includes a correction for the 25 minute acid attack before taking the spectrophotometer reading.

The initial reversible absorption of one mole of O_2 per two moles of CoL_2 results from the almost quantitative initial formation of $(CoL_2)_2O_2$ by reactions 44 and 45. The slow irreversible absorption of the additional mole of O_2 per two moles of CoL_2 results from the shifting of the equilibrium of reactions 44 and 45 toward the CoL_2O_2 as a result of the depletion of CoL_2O_2 resulting from reactions 49 to 51.

A preliminary calculation showed that if the value of $K_{4a} \cdot K_{4b}$ is kept constant at 7.2×10^6, one can change the value K_{4a} from 7.2 to 7.2×10^{-10} and by making appropriate changes in k_{5a} and k_{5b} (see Tables XI and XII) one can obtain the identical set of calculated values for

Table X. A comparison of the calculated data from Table IX and data calculated with $K_3 = 1$ to show that a value of $K_3 \leq 1.4 \times 10^4$ significantly changes $[CoL_2^+]_{calc}$ only for ligand to metal ratios of greater than 2.

($Co_0^{II} = 1.211 \times 10^{-2}$, $Co_0^{III} = 0$, pure O_2 as gas, A is $K_3 = 1.0$, B is $K_3 = 1.40 \times 10^4$)

Histidine to cobalt ratio and data set	$[CoL_2^+] \times 10^3$											
	2:1		3:1		4:1		6:1		8:1		10:1	
	A	B	A	B	A	B	A	B	A	B	A	B
Time (min)												
200	0.064	0.063	0.067	0.063	0.068	0.059	0.068	0.051	0.068	0.044	0.068	0.038
400	0.154	0.153	0.164	0.151	0.164	0.140	0.164	0.120	0.164	0.104	0.164	0.089
600	0.276	0.275	0.296	0.272	0.296	0.251	0.297	0.214	0.297	0.182	0.297	0.155
800	0.435	0.432	0.467	0.428	0.468	0.394	0.468	0.333	0.468	0.282	0.468	0.239
1000	0.623	0.619	0.670	0.615	0.671	0.567	0.671	0.479	0.672	0.405	0.672	0.342

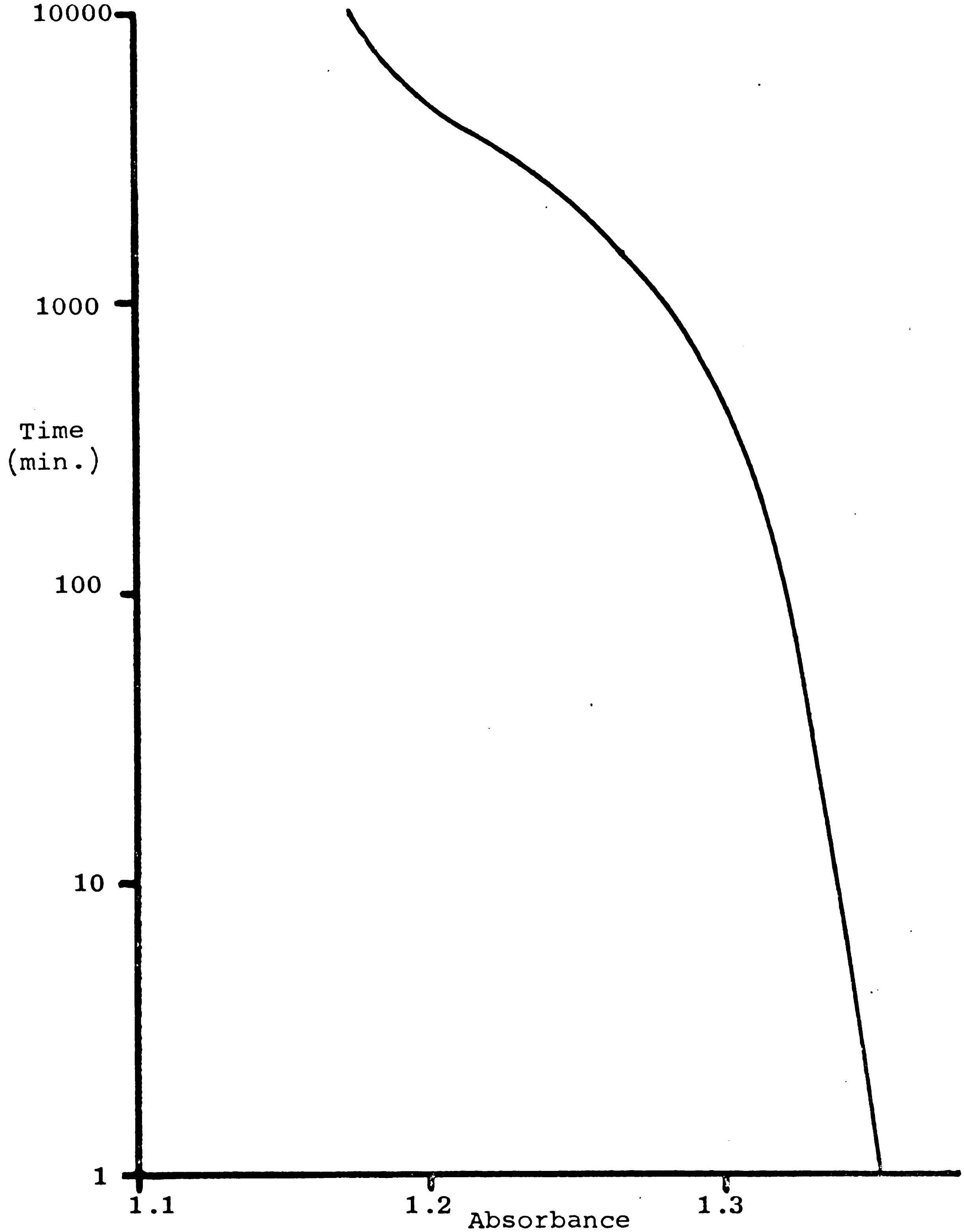


Figure 12. Plot of absorbance *versus* time of the quenched solutions which shows the acid attack on these quenched solutions.

$[CoL_2^+]$. By varying K_{4a} from 7.2×10^3 to 7.2 and making the appropriate changes in k_{5a} and k_{5b}, one can obtain similar sets of calculated values for $[CoL_2^+]$. Examples of this can be seen in Table XI for the mechanism based on reaction 49 and in Table XII for the mechanism based on equation 50.

Therefore, it may not be possible to calculate optimum values for K_{4a} and K_{4b} by the least squares procedure. In this case the values for k_{5a} or k'_{5a} and k_{5b} obtained by the least squares procedure would be related to the values of K_{4a} and K_{4b} as shown in Tables XI and XII.

The least squares values for $[CoL_2^+]$ for each of the proposed mechanisms and the experimental values for $[CoL_2^+]$ for the 5% O_2 rate study runs are shown in Figures 13 and 14.

As can be seen from Figures 13 and 14, the agreement between calculated and experimental values of $[CoL_2^+]$ is not too good.

From the results shown in Figures 12 and 13, it can be seen that either the reaction mechanism must be incorrect or there must be something additionally occurring in the reaction. Other mechanisms including the following steps were found to be far less satisfactory

$$(CoL_2)_2O_2 + O_2 \longrightarrow CoL_2^+ + CoL_2O_2 + O_2^- \qquad (120)$$

$$CoL_2O_2 + CoL_2^+ \rightleftharpoons (CoL_2)_2O_2^+ \; . \qquad (121)$$

Equations such as (120) are unsatisfactory as they predict

Table XI. Values of k_{5a} and k_{5b} which result in almost identical sets of values of $[CoL_2^+]_{calc}$ for the mechanism including equation 49.

(K_1 = 8.316 x 10^6, K_2 = 3.311 x 10^5, K_3 = 1.40 x 10^4)

K_{4a}	K_{4b}	k_{5a}	k_{5b}
7.2 x 10^3	1.0 x 10^3	1.11 x 10^{-3}	2.79 x 10^{-1}
7.2 x 10^2	1.0 x 10^4	1.11 x 10^{-3}	1.83
7.2 x 10^1	1.0 x 10^5	1.11 x 10^{-3}	1.74 x 10^1
7.2	1.0 x 10^6	1.11 x 10^{-3}	1.73 x 10^2
7.2 x 10^{-1}	1.0 x 10^7	1.11 x 10^{-3}	1.73 x 10^3
7.2 x 10^{-2}	1.0 x 10^8	1.11 x 10^{-3}	1.73 x 10^4
7.2 x 10^{-3}	1.0 x 10^9	1.11 x 10^{-3}	1.73 x 10^5
7.2 x 10^{-4}	1.0 x 10^{10}	1.11 x 10^{-3}	1.73 x 10^6
7.2 x 10^{-5}	1.0 x 10^{11}	1.11 x 10^{-3}	1.73 x 10^7
7.2 x 10^{-6}	1.0 x 10^{12}	1.11 x 10^{-3}	1.73 x 10^8
7.2 x 10^{-7}	1.0 x 10^{13}	1.11 x 10^{-3}	1.73 x 10^9
7.2 x 10^{-8}	1.0 x 10^{14}	1.11 x 10^{-3}	1.73 x 10^{10}
7.2 x 10^{-9}	1.0 x 10^{15}	1.11 x 10^{-3}	1.73 x 10^{11}
7.2 x 10^{-10}	1.0 x 10^{16}	1.11 x 10^{-3}	1.73 x 10^{12}

Table XII. Values of k'_{5a} and k_{5b} which result in almost identical sets of values of $[CoL_2^{+}]_{calc}$ for the mechanism including equation 50.

($K_1 = 8.316 \times 10^6$, $K_2 = 3.311 \times 10^5$, $K_3 = 1.40 \times 10^4$)

K_{4a}	K_{4b}	k'_{5a}	k_{5b}
7.2×10^3	1.0×10^3	1.45	1.13×10^{-1}
7.2×10^2	1.0×10^4	1.45×10^1	2.19×10^{-1}
7.2×10^1	1.0×10^5	1.45×10^2	1.30
7.2	1.0×10^6	1.45×10^3	1.21×10^1
7.2×10^{-1}	1.0×10^7	1.45×10^4	1.21×10^2
7.2×10^{-2}	1.0×10^8	1.45×10^5	1.21×10^3
7.2×10^{-3}	1.0×10^9	1.45×10^6	1.21×10^4
7.2×10^{-4}	1.0×10^{10}	1.45×10^7	1.21×10^5
7.2×10^{-5}	1.0×10^{11}	1.45×10^8	1.21×10^6
7.2×10^{-6}	1.0×10^{12}	1.45×10^9	1.21×10^7
7.2×10^{-7}	1.0×10^{13}	1.45×10^{10}	1.21×10^8
7.2×10^{-8}	1.0×10^{14}	1.45×10^{11}	1.21×10^9
7.2×10^{-9}	1.0×10^{15}	1.45×10^{12}	1.21×10^{10}
7.2×10^{-10}	1.0×10^{16}	1.45×10^{13}	1.21×10^{11}

Figure 13. Plot of experimental values of $[CoL_2^+]$ and least squares values of $[CoL_2^+]_{calc}$ *versus* time for the mechanism including equation 49.
$K_1 = 8.32 \times 10^6$, $K_2 = 3.31 \times 10^5$, $K_3 = 1.4 \times 10^4$, $K_{4a} = 1.93 \times 10^1$
$K_{4b} = 3.74 \times 10^5$, $k_{5a} = 1.14 \times 10^{-3}$, $k_{5b} = 2.54$, 5% O_2 gas.

A. $Co_0^{II} = 12 \times 10^{-3}$ *M*, $Co_0^{III} = 0$.

B. $Co_0^{II} = 6 \times 10^{-3}$ *M*, $Co_0^{III} = 0$.

C. $Co_0^{II} = 6 \times 10^{-3}$ *M*, $Co_0^{III} = 6 \times 10^{-3}$ *M*.

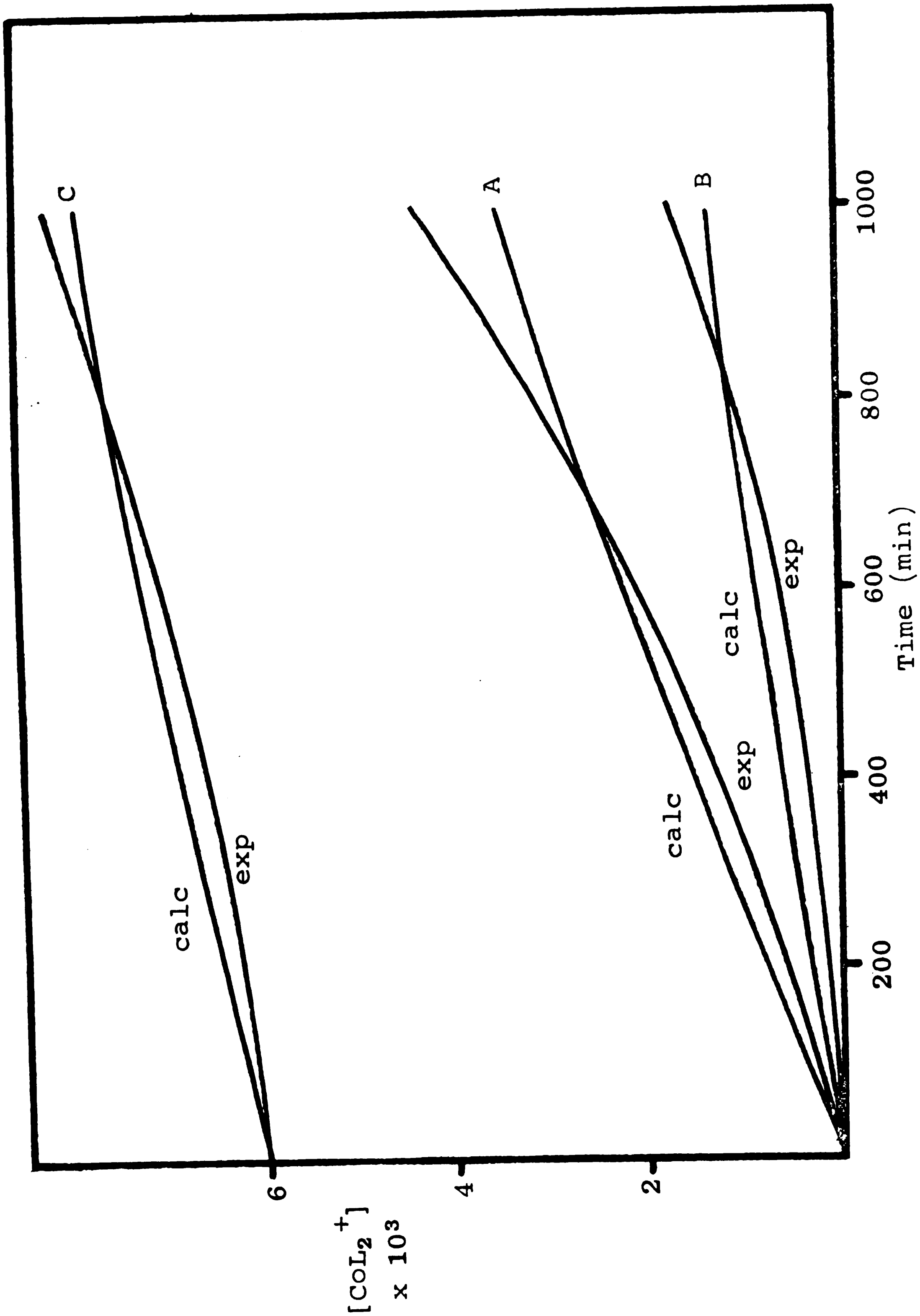


Figure 13.

Figure 14. Plot of experimental values of $[CoL_2^+]$ and least squares values of $[CoL_2^+]_{calc}$ *versus* time for the mechanism including equation 50.

$K_1 = 8.32 \times 10^6$, $K_2 = 3.31 \times 10^5$, $K_3 = 1.4 \times 10^4$, $K_{4a} = 3.62 \times 10^3$, $K_{4b} = 1.99 \times 10^3$, $k'_{5a} = 2.19$, $k_{5b} = 3.65 \times 10^{-1}$, 5% O_2 gas.

A. $Co_0^{II} = 12 \times 10^{-3}$ *M*, $Co_0^{III} = 0$.

B. $Co_0^{II} = 6 \times 10^{-3}$ *M*, $Co_0^{III} = 0$.

C. $Co_0^{II} = 6 \times 10^{-3}$ *M*, $Co_0^{III} = 6 \times 10^{-3}$ *M*.

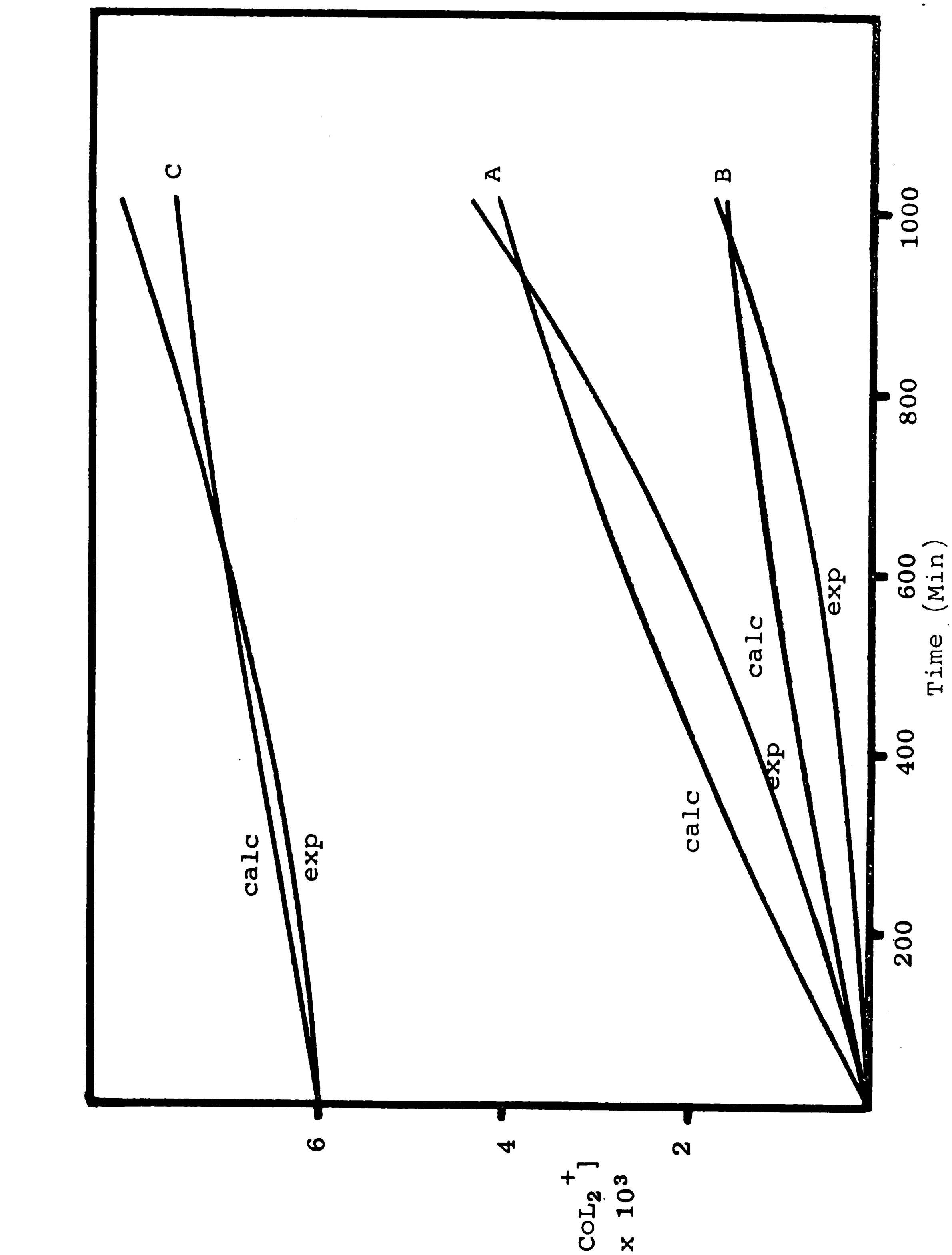

C
A
B
calc
exp
calc
exp
calc
exp
6
4
2
$[CoL_2^+] \times 10^3$
200
400
600
800
1000
Time (Min)

Figure 14.

a far greater oxygen dependence on the rate of formation of CoL_2^+ than is found experimentally. The addition of equation 121 to the mechanism yields no change in the shape of the graph of $[CoL_2^+]_{calc}$ _versus_ time.

There are several unexpected results which are probably related to the influence of the oxygen on the decomposition of the binuclear cobalt-histidine oxygen carrier. These results can be used to explain the lack of agreement between the calculated and experimental curves in Figures 12 and 13. These unexpected results as described below are evidence for the presence of an additional oxygen oxidation reaction. Since the additional oxidation was suspected, only the data from the experiments performed with 5% O_2 were used in the least squares procedure.

As the reaction proceeds, there is a small downward shift of the spectral peak at 500 mμ to about 485 mμ. This downward shift occurs at different rates for the oxygen, air and 5% O_2 gases.

The molar absorptivity at 500 mμ of a mixture of the three isomers of $(CoL_2)NO_3$ (prepared and purified as described in the Experimental section) is 84; the separated isomers have molar absorptivities at 500 mμ of approximately 100, 40 and 34.[107] However, the molar absorptivity of a solution of $(CoL_2)NO_3$, produced by bubbling air for several days through a solution containing a known number of moles of CoL_2 and then diluting with water to a known total volume, is reported to be 115.1[117] and 125.1 by this author. The absorbance of oxygenated solutions of CoL_2 is always greater than the absorbance of pure $(CoL_2)NO_3$. Studies of the oxygen uptake of CoL_2 solutions show that initially more than one mole of O_2 per two moles of CoL_2 is absorbed (about 1.14 to 1.32 moles of O_2 per two moles of CoL_2[106]). In addition, Csaszar, Kiss and Beck[144] found the presence of traces of unidentifiable organic residues after the oxygenation of CoL_2 is complete and they suggest the most probable cause as the oxidation of histidine by oxygen. To determine if the oxygen could attack the final product, $(CoL_2)NO_3$, a solution of 6.08×10^{-3} <u>M</u> $(CoL_2)NO_3$ was oxygenated for 900 minutes. The absorbance of this solution varied irregularly (within experimental error) from 0.501 to 0.509 (initial absorbance = 0.508, final absorbance = 0.505) and indicated that the oxygen does not attack the final product.

Since it is also possible for the initial oxygen uptake in excess of one mole of O_2 per two moles of CoL_2^+ to be due to the formation of CoL_2O_2, a calculation (as described in the Theoretical section, Part H) was performed to estimate K_{4a}, K_{4b} and moles of O_2 absorbed per two moles of CoL_2^+. The calculation is based on the knowledge that $K_{4a} \cdot K_{4b} = 7.2 \times 10^6$ and on the assumption of various values for the percentage of total cobalt that is $(CoL_2)_2O_2$ (before any decomposition of the oxygen carrier). The results of this calculation are shown in Table XIII.

Since it is not possible to confirm spectrophotometrically of chemically the presence of CoL_2O_2[59] and since, in the

Table XIII. Calculation of number of moles of O_2 initially absorbed per $2Co^{II}_{total}$ (initial) for $Co^{II}_t = 1.2 \times 10^{-2}$ <u>M</u> and pure O_2 gas (at 25°C), $K_{4a} \cdot K_{4b} = 7.2 \times 10^6$

Assumed % of Co as $(CoL_2)_2O_2$	$[(CoL_2)O_2]$ (x 10^3 <u>M</u>)	$[CoL_2]$ (x 10^3 <u>M</u>)	$[CoL_2O_2]$ (x 10^3 <u>M</u>)	K_{4a}	K_{4b}	O_2 initially absorbed per $2Co^{II}_t$
94	5.64	0.803	0.07	8×10^1	1×10^5	0.95
90	5.40	0.787	0.41	4.40×10^2	1.64×10^4	0.97
80	4.80	0.742	1.66	1.85×10^3	3.90×10^3	1.08
70	4.20	0.694	2.91	3.46×10^3	2.08×10^3	1.18
60	3.60	0.643	4.16	5.34×10^3	1.35×10^3	1.28
50	3.00	0.586	5.41	7.61×10^3	9.45×10^2	1.57

The maximum possible percentage of cobalt as $(CoL_2)_2O_2$ is about 94.5%.

kinetics of the formation of $(CoL_2)_2O_2$, the steady state approximation for CoL_2O_2 appears to be valid,[59] it is highly unlikely that more than 10% of the total cobalt is in the form of CoL_2O_2 immediately after oxygenation. By looking at Table XIII, one can see that the maximum O_2 absorbed per 2 Co^{II}_t that can be accounted for by the presence of CoL_2O_2 is about 1.07. Therefore, the presence of CoL_2O_2 cannot be used to explain the unexpectedly high experimental value for the initial O_2 absorption.

The shape of the graph of the apparent rate of formation of CoL_2^+ (assuming $\epsilon_{500} = 125.1$) changes markedly as the gas bubbled into the solution is varied from oxygen to air to 5% O_2-95% N_2 (see Figure 15). When pure oxygen is the gas, the apparent $[CoL_2^+]$ begins to decrease after approximately 2500 minutes from the start of the reaction. With air as the gas, the apparent $[CoL_2^+]$ appears to decrease after about 3000 minutes whereas with 5% O_2, the apparent $[CoL_2^+]$ continues to increase.

The above phenomena strongly suggest that there is an oxygen attack on some species in the reacting solutions. The absorbance of the solutions are initially increased by the oxygen attack which causes the increase in the ϵ_{500} from 87 to 125.

Whereas oxygen rapidly attacks solutions of lycine and Co^{2+}, as evidenced by CO_2 evolution, oxygen does not attack lycine without the Co^{2+}.[145] This suggests that histidine is not attacked by O_2 unless Co^{2+} is present. Therefore,

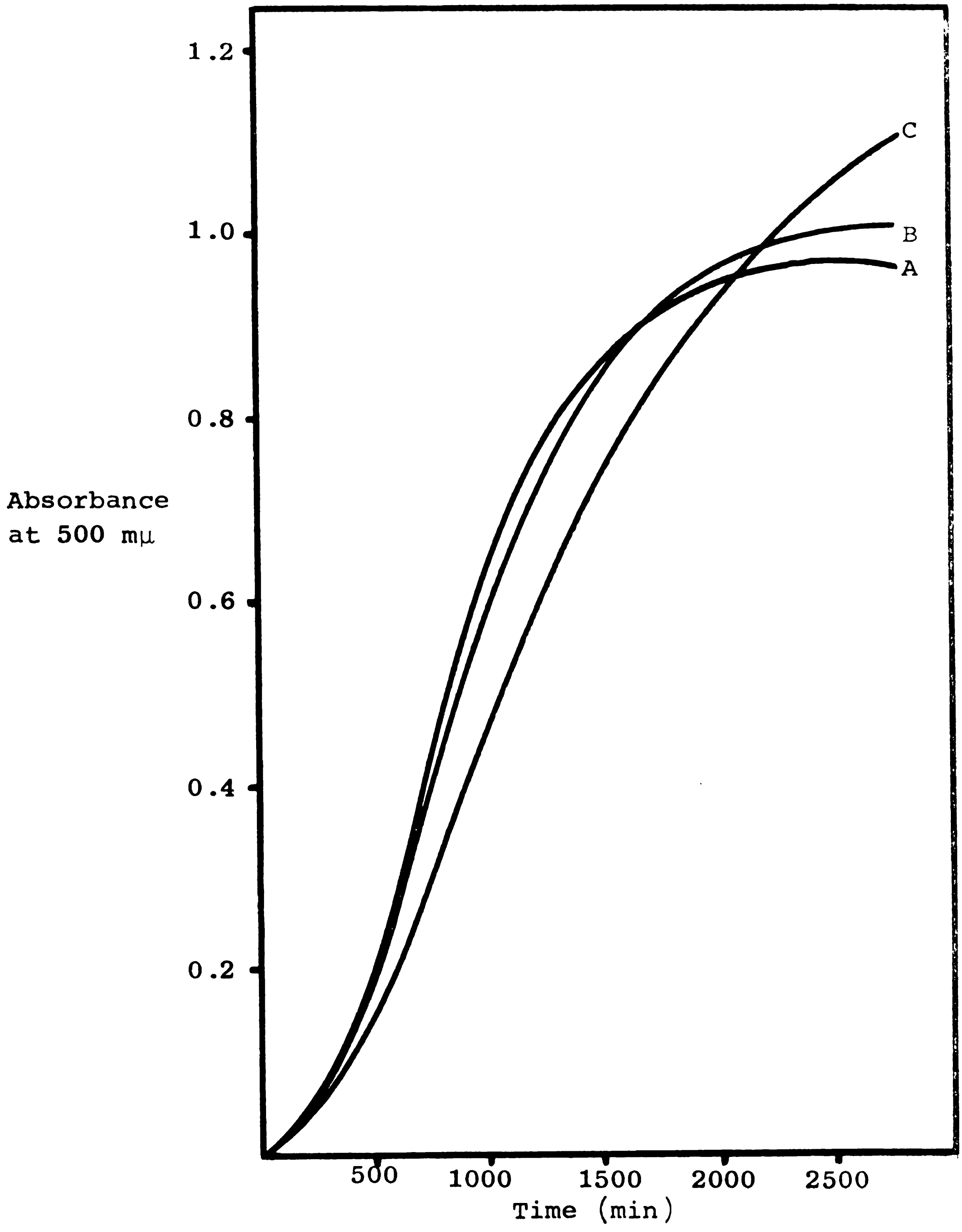


Figure 15. Absorbance *versus* time of cobalt-histidine solutions oxygenated with various gases, Co_0^{II} = 1.2 x 10^{-2} M. A = pure O_2 gas, B = air, C = 95% N_2 - 5% O_2.

the oxygen must attack one or more of the following: CoL^+, CoL_2, CoL_3^-, CoL_2O_2, $(CoL_2)_2O_2$.

The product of the oxygen attack was originally thought to be a cobalt amine complex. However, this was not likely since over 90% of the cobalt at the end of the reaction is recoverable as CoL_2NO_3.[117] Upon separation of the three isomers of CoL_2NO_3 by ion exchange, there is only a small quantity of yellow to brown residue which remains on the ion exchange column.[117] Since only a small quantity of the oxidation product is formed, it must have an absorptivity, ϵ_{500}, of several hundred to be able to raise the net molar absorptivity of the solution from 84 to 125. There are no known simple cobalt(II) or cobalt(III) complexes which have a large enough molar absorptivity in the visible region to cause the increase in the absorbance of the solution.

There is some evidence for the formation of traces of the superoxo cobalt ammine complex upon oxygenation of aqueous ammoniacal cobalt(II) solutions.[146] From the esr and visible spectra of oxygenated aqueous solutions of Co^{2+} and excess cyanide, it has been shown that the superoxo cobalt cyanide oxygen carrier is formed in one to two percent yield.[36,68] The recently isolated superoxo cobalt histidine complex has been shown to be stable even in strongly acidic solutions.[37] This superoxo complex has a broad peak at 477 mμ (ϵ_{477} = 502, ϵ_{500} = 498) and another broad peak at 677 mμ (ϵ = 601).[147]

A solution containing 1.2×10^{-2} $\underline{M}$ CoL_2 was oxygenated with a 5% O_2 - 95% N_2 gas mixture for several days. Spectra of the solutions (see Figures 16 to 19) show that with increasing time, there is an increase in the absorption in the region of 477 and 677 mμ and the peak at 500 mμ gradually shifts to 482 mμ. This is strong evidence for the presence of the superoxo complex. The solutions were quenched with both HCl and HNO_3. The spectra of both quenched solutions were identical which proves that the HNO_3 is not causing the oxidation. The absorbance due to the superoxo complex is greater with water rather than acid quench (see Figure 19) and indicates that the acid does slowly decompose the superoxo complex. This explains the slow rate of decrease in the absorbance after the solutions are quenched (see Figure 12).

An experiment to attempt to observe the known esr spectrum of the superoxo complex did not succeed due to the low concentration of the superoxo complex and the presence of trace paramagnetic impurities in the quartz and Pyrex tubing used for the sample tubes. There did appear to be a small signal from the sample in the quartz tube. At the high gain necessary to observe this signal, the noise level is high and the signal from the impurities in the quartz is high which makes it impossible to ascertain if the signal is from the superoxo complex. Therefore, the additional reaction which causes the poor correlation between the least squares calculation and the experiment is

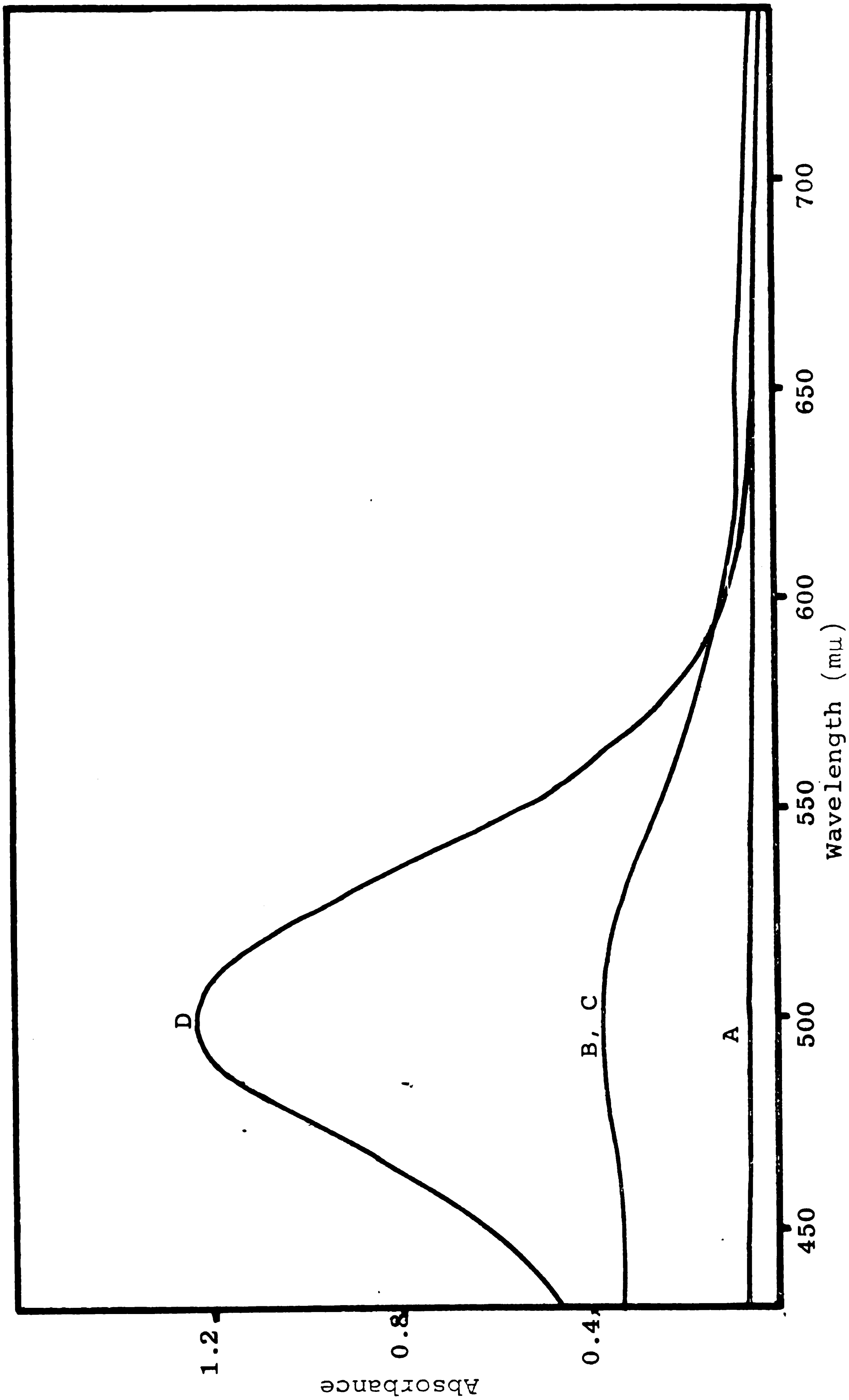
Figure 16. Visible spectra of solutions of $(CoL_2)NO_3$.

A. Baseline.

B. 5 ml sample oxygenated for 800 min and quenched with 1 ml of 4$\underline{M}$ HNO_3, (Co_0^{II} = 1.2 x $10^{-2}$$\underline{M}$, 5% O_2 gas), 25 minutes after quenching.

C. Same as B but quenched with 1 ml of 4$\underline{M}$ HCl.

D. 1.2 x $10^{-2}$$\underline{M}$ purified $(CoL_2)NO_3$.



Absorbance
1.2
0.8
0.4
Wavelength (mμ)
450
500
550
600
650
700
A
B, C
D

Figure 16.

Figure 17. Visible spectra of solutions of $(CoL_2)NO_3$.

A. Baseline.

B. 5 ml of sample oxygenated for 1563 min and quenched with 1 ml of 4$\underline{M}$ HNO_3, (Co_0^{II} = 1.2 x $10^{-2}\underline{M}$, 5% O_2 gas), 1 minute after quench.

C. 1.2 x $10^{-2}\underline{M}$ purified $(CoL_2)NO_3$.

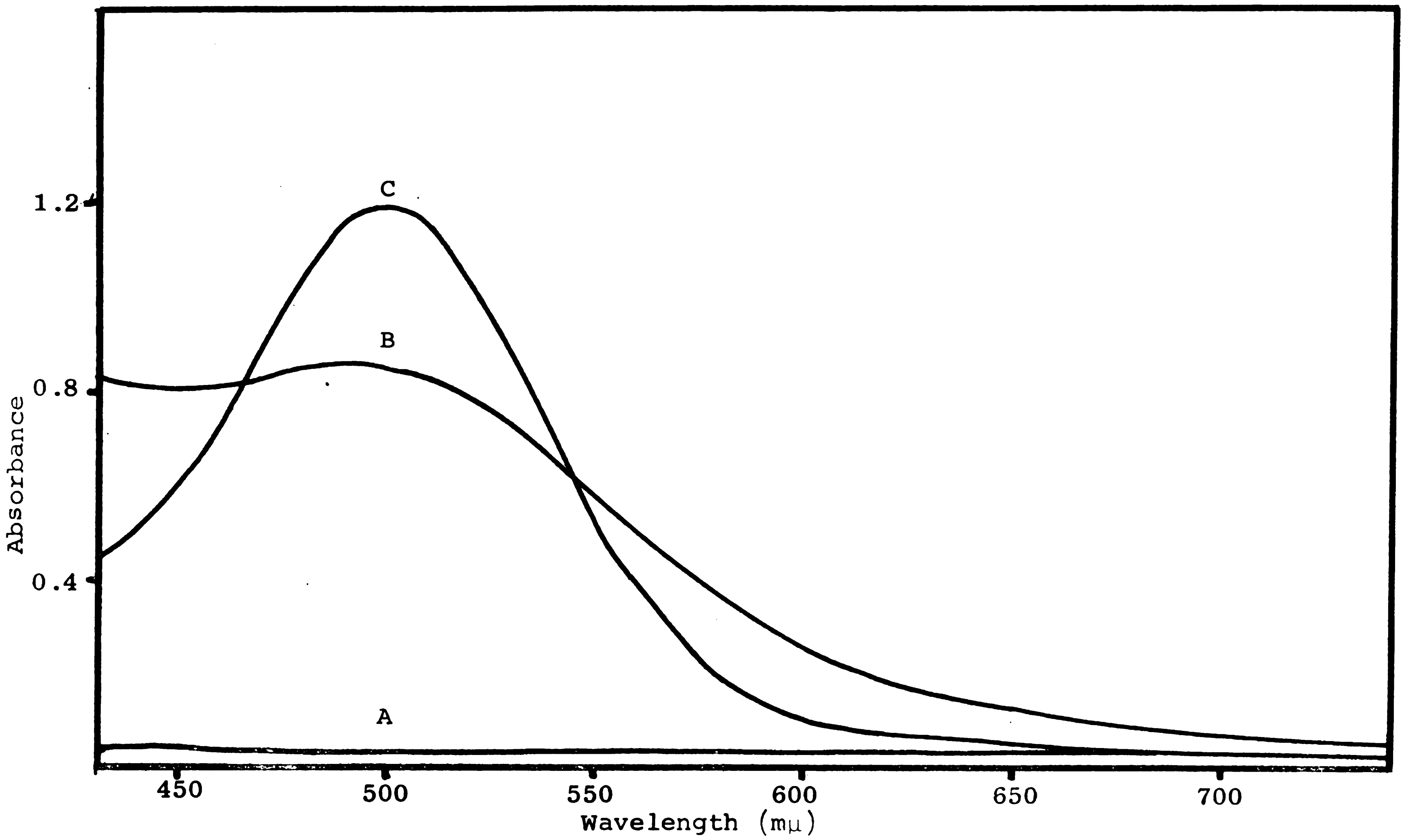


Figure 17.

Figure 18. Visible spectra of solutions of $(CoL_2)NO_3$.

A. Baseline.

B. 1.2×10^{-2} M purified $(CoL_2)NO_3$.

C. 5 ml of sample oxygenated for 2500 min and quenched with 1 ml of 4M HNO_3, ($Co_0^{II} = 1.2 \times 10^{-2}$ M, 5% O_2 gas), 1 minute after quench.

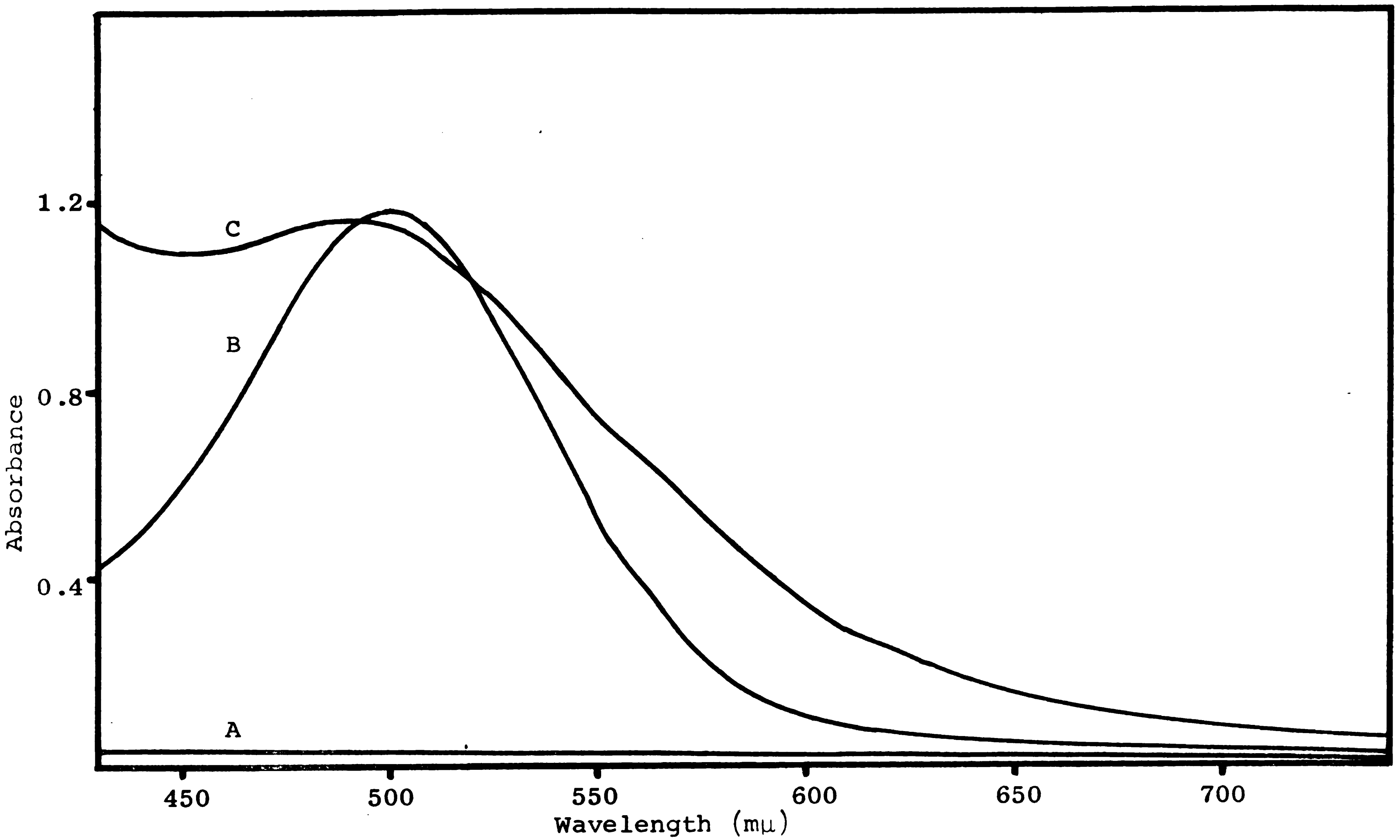


Figure 18.

Figure 19. Visible spectra of solutions of $(CoL_2)NO_3$.

A. Baseline.

B. 1.2×10^{-2} <u>M</u> purified $(CoL_2)NO_3$.

C. 5 ml of sample oxygenated for 5200 min and quenched with 1 ml of 4<u>M</u> HNO_3, ($Co_0^{II} = 1.2 \times 10^{-2}$ <u>M</u>, 5% O_2 gas), 1 minute after quench.

D. Same as C but quenched with 1 ml of 4<u>M</u> HCl.

E. Same as C but unquenched, 1 ml of water added instead of 1 ml of acid.

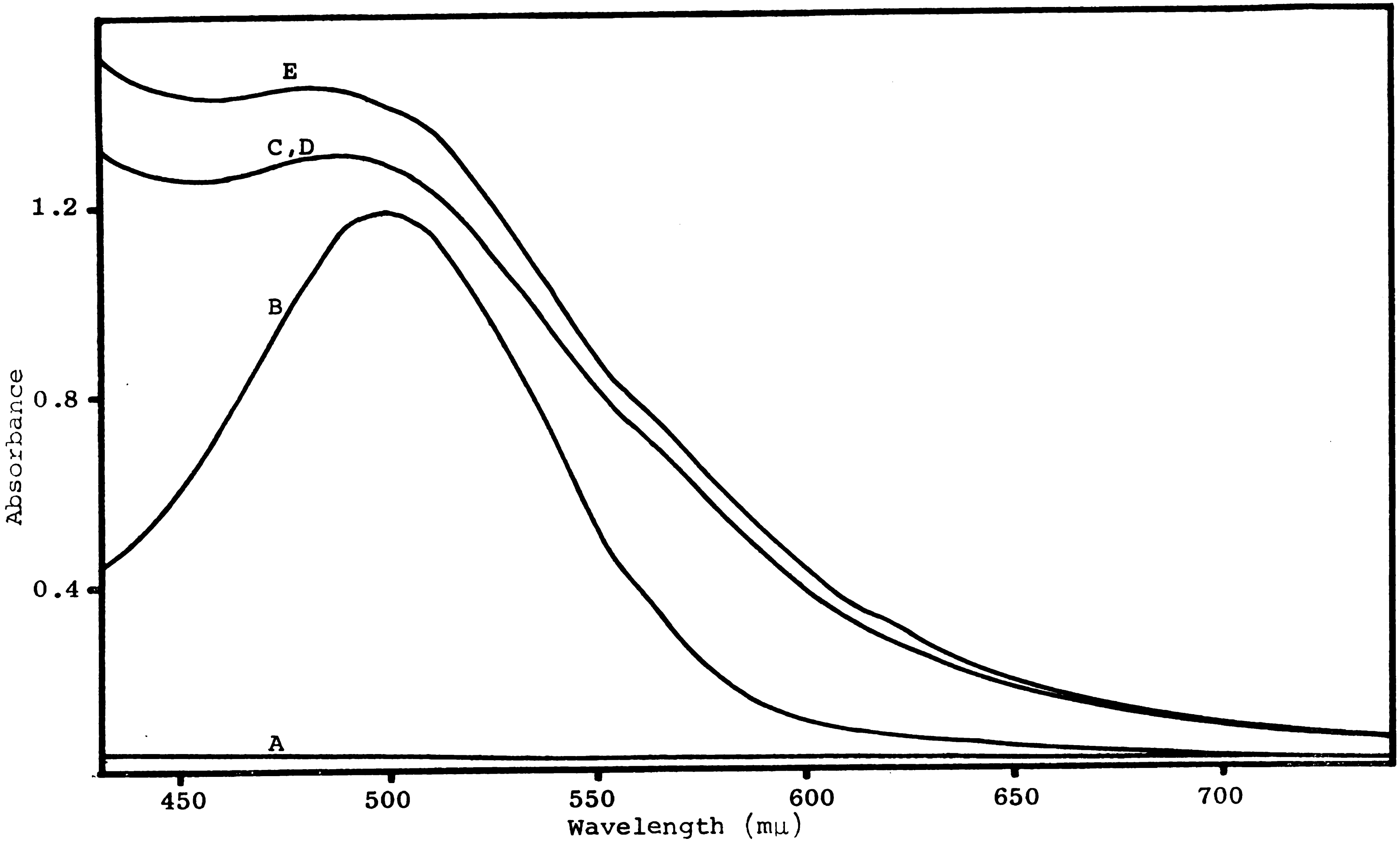

E
C,D
B
A
1.2
0.8
0.4
Absorbance
450
500
550
600
650
700
Wavelength (mμ)

Figure 19.

$$(CoL_2)_2O_2 + O_2 \longrightarrow (CoL_2)_2O_2^+ + O_2^- . \qquad (122)$$

At long reaction times, especially with pure O_2 as gas, there probably is a further oxidation which fragments the histidine. This would explain the decrease in the absorbance, after about 2400 minutes, of the solutions oxygenated by pure oxygen, the presence of unidentifiable organic residues as found by Csaszar, Kiss and Beck,[144] and the traces of yellow to brown residue as found by Zompa.[117]

Both proposed mechanisms (including either equation 49 or 50) appear to be about equally as good at predicting calculated values for $[CoL_2^+]$. The values for K_{4a}, K_{4b}, k_{5a}, k'_{5a}, and k_{5b} resulting from the least squares procedure are probably order of magnitude values.

Additional experiments must be performed in which the solutions are quenched for several days to destroy any superoxo cobalt-histidine complex and also experiments which include measuring of the absorbance at 677 mμ (by using 5 cm cells) to estimate the concentration of the superoxo complex so that corrections can be made for the presence and the absorbance at 500 mμ of the superoxo complex.

There is the possibility that the apparent catalytic activity of CoL_2^+ (as shown in equation 51) is due instead to the following reaction:

$$CoL_2O_2 + CoL_2^+ \longrightarrow (CoL_2)_2O_2^+ . \qquad (123)$$

If equation 123 rather than equation 122 is the major source of formation of the superoxo complex, $(CoL_2)_2O_2^+$, then an increase in $[CoL_2^+]$ will result in an increase in the rate of formation of $(CoL_2)_2O_2^+$ which will increase the absorbance of the solution at 500 mμ. Since the $[CoL_2^+]$ is determined by the absorbance of the solution at 500 mμ, an increase in the absorbance at this wavelength due to equation 123 will cause the $[CoL_2^+]$ to appear to affect the rate of formation of CoL_2^+. Therefore, experiments will have to be performed to ascertain the influence of CoL_2^+ on the rate of formation of CoL_2^+.

REFERENCES

REFERENCES

1. Basolo, F. and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed., John Wiley and Sons, Inc., New York, 1967.

2. Benson, S. W., "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., New York, 1960, p. 63.

3. Fremy, E., Ann. Chim. Phys., 35, 257 (1852).

4. Fremy, E., Ann., 83, 289 (1852).

5. Vortmann, G., Ber., 10, 1451 (1877).

6. Vortmann, G., ibid., 15, 1890 (1882).

7. Vortmann, G., Monatsh., 6, 404 (1885).

8. Vortmann, G., and O. Blasberg, Ber., 22, 2648(1889).

9. Werner, A. and A. Mylius, Z. Anorg. Allgem. Chem., 16, 245 (1898).

10. Jorgensen, S. M., J. Prakt. Chem., 31, 69 (1885).

11. Werner, A. and F. Beddow, Z. Anorg. Chem., 16, 109 (1898).

12. Werner, A., Z. Anorg. Chem., 21, 96 (1899).

13. Werner, A., Ber. Deut. Chem. Ges., 40, 2103, 4426, 4434, 4605, 4834 (1907).

14. Werner, A., ibid., 41, 3879, 3912 (1908).

15. Werner, A., Justus Liebigs Ann. Chem., 375, 1 (1910).

16. Werner, A., Ber. Deut. Chem. Ges., 46, 3674 (1913).

17. Werner, A., ibid., 47 1961 (1914).

18. Werner, A., Justus Liebigs Ann. Chem., 406, 261 (1914).

19. Gluud, W., K. Keller and H. Nordt, Ber. Ges. Kohlentech. (Halle), 4, 210 (1933).

20. Hearon, J., D. Burk and A. L. Schade, J. Natl. Cancer Inst., 9, 337 (1949).

21. Vogt, L. H., Jr., H. M. Faigenbaum and E. Wiberley, Chem. Rev., 63, 269 (1963).

22. "Gmelins Handbuch der anorganischen Chemie," 8 ed., System No. 58, part B, pp. 322 FF., Verlag Chemie G.M.B.H., Berlin, Germany, 1932, Suppl., Weinheim, 1964, pp. 615FF.

23. Goodman, G. L., H. G. Hecht and J. A. Weil, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D.C., 1965, p. 90.

24. Connor, J. A., and E. A. V. Ebsworth in "Advances in Inorganic Chemistry and Radiochemistry," Vol. 6, H. J. Emeléus and A. G. Sharpe, Ed., Academic Press, New York, 1964, pp. 279-381.

25. Fallab, S., Angew. Chem. (Int. Ed.), 6, 496 (1967).

26. Sykes, A. G., and J. A. Weil, Prog. Inorg. Chem. (in press).

27. Chester, A. W., Advan. Chem. Ser., 62, 78 (1967).

28. Erdem, B., and S. Fallab, Chimia, 19, 463 (1965).

29. Haim, A., and W. K. Wilmarth, J. Am. Chem. Soc., 83 509 (1961).

30. Gleu, K. and K. Rehm, Z. Anorg. Allgem. Chem., 237, 79 (1938).

31. Ohyagi, Y., Bull. Chem. Soc. Japan, 15, 186 (1940).

32. Mori, M., J. A. Weil and M. Ishiguro, J. Am. Chem. Soc., 90, 615 (1968).

33. Bernal, I., E. A. V. Ebsworth and J. A. Weil, Proc. Chem. Soc., 57 (1959).

34. Ebsworth, E. A. V., and J. A. Weil, J. Phys. Chem., 63, 1890 (1959).

35. Mori, M., J. A. Weil and J. K. Kinnaird, J. Phys. Chem., 71, 103 (1967).

36. Bayston, J. H., F. D. Looney and M. E. Winfield, Australian J. Chem., 16, 557 (1963).

37. Weil, J. A., and J. K. Kinnaird, Inorg. Nucl. Chem. Letters, 5, 251 (1969).

38. Mast, R. D., and A. G. Sykes, Chem. Commun., 270 (1965).

39. Marsh, R. E., and W. P. Schaefer, Acta. Cryst., B24, 246 (1968).

40. Linhard, M., and M. Weigel, Z. Anorg. Allgem. Chem., 308, 254 (1961).

41. Okaya, Y., unpublished results as described in Reference 23.

42. Dunitz, J. D., and L. E. Orgel, J. Chem. Soc., 2594 (1953).

43. Brosset, C., and N. Vannerberg, Nature, 190, 714 (1961).

44. Bekaroglu, O., and S. Fallab, Helv. Chim. Acta, 46, 2120 (1963).

45. Vlcek, A. A., Collect. Czech. Chem. Commun., 25, 3036 (1960).

46. Vlcek, A. A., Trans. Faraday Soc., 56, 1137 (1960).

47. Bayer, E., and P. Schretzmann, Structure and Bonding, 2, 181 (1967).

48. Schaefer, W. P., Inorg. Chem., 7, 725 (1968).

49. Thewalt, U., submitted to J. Am. Chem. Soc., as described in Reference 26.

50. Schaefer, W. P., and R. E. Marsh, J. Am. Chem. Soc., 88, 178 (1966).

51. Schaefer, W. P., and R. E. Marsh, Acta Cryst., 21, 735 (1966).

52. Christoph, G. G., R. E. Marsh and W. P. Schaefer, Inorg. Chem., 8, 291 (1969).

53. Thewalt, U. and R. E. Marsh, J. Am. Chem. Soc., 89, 6364 (1967).

54. The Chemical Society (London), "Tables of Interatomic Distances," Special Publication 11, 1958.

55. Halverson, F., J. Phys. Chem. Solids, 23, 207 (1962).

56. Cotton, F. A., and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, 1962, p. 282.

57. Jouan, R., J. Chim. Phys., 56, 277 (1959).

58. Fallab, S., Chimia, 19, 174 (1965).

59. Simplicio, J., and R. G. Wilkins, J. Am. Chem. Soc., 89, 6092 (1967).

60. Simplicio, J., and R. G. Wilkins, J. Am. Chem. Soc., 91, 1325 (1969).

61. Descamps, M. A., Compt. Rend., 67, 330 (1868).

62. Adamson, A. W., J. Am. Chem. Soc., 73, 5710 (1951).

63. Glasstone, S., and J. C. Speakman, Analyst, 55, 93 (1930).

64. MacDiarmid, A. C., and N. F. Hall, J. Am. Chem. Soc., 75, 5204 (1953).

65. Muller, E., and W. Schulttig, Z. Anorg. Allgem. Chem., 134, 327 (1924).

66. Rupp, E., and F. Pfennig, Chem. Z., 34, 322 (1910).

67. Mondain-Monval, P., and R. Paris, Compt. Rend., 198, 1154 (1934).

68. Bayston, J. H., R. N. Beale, N. K. King and M. E. Winfield, Aust. J. Chem., 16, 954 (1963).

69. Jezowska-Trzebiatowska, B., J. Mrozinski and W. Wojciechowski, J. Prakt. Chem., 34, 97 (1966).

70. Bayston, J., N. K. King and M. E. Winfield, "Advances in Catalysis," Vol. 9, Academic Press, New York, 1957, p. 312.

71. De Vries, B., J. Catal., 1, 489 (1962).

72. Chadwick, B. M., and A. G. Sharpe, Adv. Inorg. Chem. Radiochem., 8, 83 (1966).

73. Hume, D. N. and I. M. Kolthoff, J. Am. Chem. Soc., 71, 867 (1949).

74. Schaefer, W. P., Inorg. Chem., 7, 725 (1968).

75. Ray, P. R., and H. Bhar, J. Indian Chem. Soc., 5, 497 (1928).

76. Szego, L., and P. Ostinelli, Gazz. Chim. Ital., 60, 950 (1930).

77. Biltz, W., W. Eschweiler and A. Bodenseik, Z. Anorg. Allgem. Chem., 170, 161 (1928).

78. Descamps, A., Compt. Rend., 87, 1039 (1878).

79. Rosenheim, A., and J. Koppel, Z. Anorg. Chem., 17, 35 (1898).

80. Nast, R., H. Ruppert-Mesche and M. Helbig-Neubauer, Z. Anorg. Allgem. Chem., 312, 314 (1961).

81. Griffith, W. P., and G. Wilkinson, J. Chem. Soc., 2757 (1959).

82. Cotton, F. A., T. G. Dunne and J. S. Wood, Inorg. Chem., 3, 1495 (1964).

83. Iguchi, M., J. Chem. Soc. Japan , 63, 634 (1942) as described in C. A., 41, 2975D (1947).

84. King, N. K., and M. E. Winfield, J. Am. Chem. Soc., 83, 3366 (1961).

85. Banks, R. G. S., and J. M. Pratt, Chem. Commun., 776 (1967).

86. Mills, G. A., S. W. Weller and A. Wheeler, J. Phys. Chem., 63, 403 (1959).

87. Treadwell, W. D., and D. Huber, Helv. Chim. Acta, 26, 10 (1943).

88. Ginsberg, A. P., Trans. Metal Chem., 1, 111 (1965).

89. Schindewolf, U., Ber. Bunsenges. Phys. Chem., 67, 2191 (1963).

90. King, N. K., and M. E. Winfield, J. Am. Chem. Soc., 80, 2060 (1958).

91. Pratt, J. M., and R. P. J. Williams, J. Chem. Soc. (A), 1291 (1967).

92. Alexander, J. J., and H. B. Gray, J. Am. Chem. Soc., 89, 3356 (1967).

93. Caulton, K. G., Inorg. Chem., 7, 392 (1968).

94. Candlin, J. P., J. Halpern and S. Nakamura, J. Am. Chem. Soc., 85, 2517 (1963).

95. Fraser, K. A., H. A. Long, R. Candlin and M. M. Harding, Chem. Commun., 334 (1965).

96. McDonald, C. C., and W. D. Phillips, J. Am. Chem. Soc., 85, 3736 (1963).

97. Harding, M. M., and H. A. Long, J. Chem. Soc. (A), 2554 (1968).

98. Sano, Y., and H. Tanabe, J. Inorg. Nucl. Chem., 25, 11 (1963).

99. Burk, D., J. Z. Hearon, L. Caroline and A. L. Scade, J. Biol. Chem., 165, 723 (1946).

100. Hearon, J. Z., J. Nat. Cancer Inst., 9, 1 (1948).

101. Burk, D., J. Z. Hearon, H. Levy and A. L. Schade, Federation Proc., 6, 242 (1947).

102. Hearon, J. Z., ibid., 259, 260 (1947).

103. Burk, D., S. Fiala, J. Z. Hearon, M. Hesselbach, H. Levy and A. L. Schade, Federation Proc., 7, 148 (1948).

104. Earnshaw, A., and L. F. Larkworthy, Nature, 192, 1068 (1961).

105. Michaelis, L., Arch. Biochem., 14, 17 (1942).

106. Zompa, L. J., C. S. Sokol and C. H. Brubaker, Jr., Chem. Commun., 701 (1967).

107. Zompa, L. J., Chem. Commun., 783 (1969).

108. Bagger, S., Acta Chem. Scand., 23, 975 (1969).

109. Daniels, F., J. H. Mathews, J. W. Williams, P. Bender and R. A. Alberty, "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1956, p. 336-339.

110. Youden, W. J., "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, 1951, p. 41-45.

111. Wentworth, W. E., J. Chem. Ed., 42, 96 (1965).

112. Amdur, I., and G. G. Hammes, "Chemical Kinetics", McGraw-Hill Book Co., New York, 1966.

113. See Reference 2, *in toto*.

114. Frost, A. A., and R. G. Pearson, "Kinetics and Mechanisms," second edition, John Wiley and Sons, New York, 1961.

115. "The Handbook of Chemistry and Physics," 37th edition, Chemical Rubber Publishing Co., Cleveland, 1955, p. 253, Equations 89 and 99.

116. Smail, L. L., "Calculus," Appleton-Century-Crofts, Inc., New York, 1949, p. 100-101.

117. Zompa, L. J., and C. H. Brubaker, Jr., personal communication, 1969.

118. Furman, N. H., ed.,"Standard Methods of Chemical Analysis," sixth ed., Vol. 1, D. Van Nostrand Co., Inc., Princeton, N.J., 1962, pps. 385-386.

119. Willard, H. H., N. H. Furman and C. E. Bricker, "Elements of Quantitative Analysis," fourth ed., D. Van Nostrand Co., Inc., Princeton, N.J., 1956, pps. 133-135.

120. Harned, H. S., and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold Publishing Corp., New York, 1950.

121. Burnett, M. G., P. J. Connolly and C. Kemball, J. Chem. Soc. (A), 800 (1967).

122. Samuel, J., Z. Physik, 70, 43 (1931).

123. Birk, J. P., and J. Halpern, J. Am. Chem. Soc., 90, 304 (1968).

124. Truesdale, G. A., and A. L. Downing, Nature, 173, 1236 (1954).

125. Guzzetta, F. H., and W. B. Hadley, Inorg. Chem., 3, 259 (1964).

126. Halpern, J., personal communication, 1969.

127. Pratt, J. M., and P. R. Silverman, J. Chem. Soc. (A), 1286 (1967).

128. Piringer, O., and A. Farcas, Z. Phys. Chem., 46, 190 (1965).

129. Reinstein, J. G., E. Griswold and J. Kleinberg, Inorg. Chem., 8, 2499 (1969).

130. Piringer, O., Abh. Deut. Akad. Wiss. Berlin, kl. Chem. Biol., Geol., 821 (1964).

131. Simandi, L., and F. Nagy, Acta Chim. Hung., 46, 101 (1965).

132. Bayston, J. H., and M. E. Winfield, J. Catalysis, 3, 123 (1964).

133. Kwiatek, J., I. L. Mador and J. K. Seylor, J. Am. Chem. Soc., 84, 305 (1962).

134. Banks, R. G. S., and J. M. Pratt, J. Chem. Soc. (A), 854 (1968).

135. Grube, G., Z. Elektrochem., 32, 561 (1926).

136. Farcas, A., and L. Farcas, J. Chem. Phys., 2, 468 (1934).

137. Sokol, C. S., and C. H. Brubaker, Jr., J. Inorg. Nucl. Chem., 30, 3267 (1968).

138. Sillen, L. G., and A. E. Martell, ed., "Stability Constants of Metal-Ion Complexes," Chem. Soc. Special Pub. 17, The Chemical Society, London, 1964.

139. Albert, A., J. Biochem., 50, 690 (1952).

140. Crumbliss, A. L., and F. Basolo, Science, 164, 1168 (1969).

141. Crumbliss, A. L., and F. Basolo, J. Am. Chem. Soc., 92, 55 (1970).

142. Hoffman, B. M., D. L. Diemente and F. Basolo, J. Am. Chem. Soc., 92, 61 (1970).

143. Miller, F., J. Simplicio and R. G. Wilkins, J. Am. Chem. Soc., 91, 1962 (1969).

144. Csaszar, J., L. Kiss and M. T. Beck, Naturwiss., 45, 210 (1958).

145. Laussegger, H., and C. H. Brubaker, Jr., personal communication, 1969.

146. Charles, R. G., and S. Barnartt, J. Inorg. Nucl. Chem., 22, 69 (1961).

147. Weil, J. A., personal communication, 1970.

APPENDIX

APPENDIX

A. Derivatives for the Non-linear Least Squares Calculation.

By defining the following terms:

$$E_1 = 2/\sqrt{b^2 - 4ac} \tag{124}$$

$$E_2 = \frac{-bB_1}{a\sqrt{b^2 - 4ac}} \tag{125}$$

$$T_{1n} = 2c(\sqrt{B_2 - B_3\ Co_0^{III}} - B_1) + b - \sqrt{b^2 - 4ac} \tag{126}$$

$$T_{1d} = 2c(\sqrt{B_2 - B_3\ Co_0^{III}} - B_1) + b + \sqrt{b^2 - 4ac} \tag{127}$$

$$T_{2n} = (\sqrt{B_2 - B_3\ Co_0^{III}} - B_1)^2 \tag{128}$$

$$T_{2d} = c(\sqrt{B_2 - B_3 Co_0^{III}} - B_1)^2 + b(\sqrt{B_2 - B_3 Co_0^{III}} - B_1) + a \tag{129}$$

$$T_{3n} = 2c(\sqrt{B_2 - B_3\ Co^{III}} - B_1) + b - \sqrt{b_2 - 4ac} \tag{130}$$

$$T_{3d} = 2c(\sqrt{B_2 - B_3\ Co^{III}} - B_1) + b + \sqrt{b_2 - 4ac} \tag{131}$$

$$T_{4n} = (\sqrt{B_2 - B_3\ Co^{III}} - B_1)^2 \tag{132}$$

$$T_{4d} = c(\sqrt{B_2 - B_3 Co^{III}} - B_1)^2 + b(\sqrt{B_2 - B_3 Co^{III}} - B_1) + a \tag{133}$$

$$E_3 = B_1/a \tag{134}$$

and substituting these terms into equation 78, one obtains:

$$t = (E_1 + E_2)\log\left(\frac{T_{1n}/T_{1d}}{T_{3n}/T_{3d}}\right) + E_3\log\left(\frac{T_{2n}/T_{2d}}{T_{4n}/T_{4d}}\right) \quad . \qquad (135)$$

For simplicity, the following terms are defined:

$$f(\Sigma\, r_i) = f(Co^{III},\ K_1, K_2, K_3, K_{4a}, K_{4b}, k_{5a} \text{ or } k'_{5a}, k_{5b}) \qquad (136)$$

and ∂r_i is the derivative with respect to one of the variables of equation 135.

By substituting equation 135 into equation 136,

$$f(\Sigma r_i) = (E_1+E_2)\log\left(\frac{T_{1n}T_{3d}}{T_{1d}T_{3n}}\right) + E_3 \log\left(\frac{T_{2n}T_{4d}}{T_{2d}T_{4n}}\right) - t. \qquad (137)$$

The generalized partial derivative of equation 137 is

$$\frac{\partial f(\Sigma r_i)}{\partial r_i} = (E_1+E_2)\,\frac{\partial\left[\log\left(\frac{T_{1n}T_{3d}}{T_{1d}T_{3n}}\right)\right]}{\partial r_i} + \log\left(\frac{T_{1n}T_{3d}}{T_{1d}T_{3n}}\right)\frac{\partial(E_1+E_2)}{\partial r_i}$$

$$+ E_3\,\frac{\partial\left[\log\left(\frac{T_{2n}T_{4d}}{T_{2d}T_{4n}}\right)\right]}{\partial r_i} + \log\left(\frac{T_{2n}T_{4d}}{T_{2d}T_{4n}}\right)\frac{\partial E_3}{\partial r_i} - \frac{\partial t}{\partial r_i} \,. \qquad (138)$$

For all r_i,

$$\frac{\partial t}{\partial r_i} = 0. \qquad (139)$$

Since $\dfrac{\partial \log y}{\partial x} = \dfrac{1}{y}\dfrac{\partial y}{\partial x}$, one obtains

$$\frac{\partial f(\Sigma r_i)}{\partial r_i} = \frac{(E_1+E_2)T_{1d}T_{3n}}{T_{1n}T_{3d}}\,\frac{\partial\left(\frac{T_{1n}T_{3d}}{T_{1d}T_{3n}}\right)}{\partial r_i} + \log\left(\frac{T_{1n}T_{3d}}{T_{1d}T_{3n}}\right)\left(\frac{\partial E_1}{\partial r_i} + \frac{\partial E_2}{\partial r_i}\right)$$

$$+ \frac{E_3T_{2d}T_{4n}}{T_{2n}T_{4d}}\,\frac{\partial\left(\frac{T_{2n}T_{4d}}{T_{2d}T_{4n}}\right)}{\partial r_i} + \log\left(\frac{T_{2n}T_{4d}}{T_{2d}T_{4n}}\right)\frac{\partial E_3}{\partial r_i} \quad . \qquad (140)$$

Two of the above terms can be expanded as follows:

$$\frac{\partial\left(\frac{T_{1n}T_{3d}}{T_{1d}T_{3n}}\right)}{\partial r_i} = \frac{T_{1d}T_{3n}\left(T_{1n}\frac{\partial T_{3d}}{\partial r_i} + T_{3d}\frac{\partial T_{1n}}{\partial r_i}\right) - T_{1n}T_{3d}\left(T_{1d}\frac{\partial T_{3n}}{\partial r_i} + T_{3n}\frac{\partial T_{1d}}{\partial r_i}\right)}{T_{1d}^2\ T_{3n}^2} \tag{141}$$

$$\frac{\partial\ \frac{T_{2n}T_{4d}}{T_{2d}T_{4n}}}{\partial r_i} = \frac{T_{2d}T_{4n}\left(T_{2n}\frac{\partial T_{4d}}{\partial r_i} + T_{4d}\frac{\partial T_{2n}}{\partial r_i}\right) - T_{2n}T_{4d}\left(T_{2d}\frac{\partial T_{4n}}{\partial r_i} + T_{4n}\frac{\partial T_{2d}}{\partial r_i}\right)}{T_{2d}^2\ T_{4n}^2}. \tag{142}$$

The generalized derivatives of the variables from equations 124 to 134 are as follows:

$$\frac{\partial E_1}{\partial r_i} = \frac{4a\frac{\partial c}{\partial r_i} + 4c\frac{\partial a}{\partial r_i} - 2b\frac{\partial b}{\partial r_i}}{(b^2 - 4ac)^{3/2}} \tag{143}$$

$$\frac{\partial E_2}{\partial r_i} = \frac{bB_1\left[\frac{a\left(2b\frac{\partial b}{\partial r_i} - 4a\frac{\partial c}{\partial r_i} - 4c\frac{\partial a}{\partial r_i}\right)}{2\sqrt{b^2 - 4ac}} + \sqrt{b^2-4ac}\ \frac{\partial a}{\partial r_i}\right]}{a^2(b^2 - 4ac)} - \frac{\left(b\frac{\partial B_1}{\partial r_i} + B_1\frac{\partial b}{\partial r_i}\right)}{a\sqrt{b^2 - 4ac}} \tag{144}$$

$$\frac{\partial T_{1n}}{\partial r_i} = 2c\left(\frac{1}{2\sqrt{B_2}}\ \frac{\partial B_2}{\partial r_i} - \frac{\partial B_1}{\partial r_i}\right) + 2(\sqrt{B_2} - B_1)\frac{\partial c}{\partial r_i} + \frac{\partial b}{\partial r_i} - \frac{1}{2\sqrt{b^2 - 4ac}}\left(2b\frac{\partial b}{\partial r_i} - 4a\frac{\partial c}{\partial r_i} - 4c\frac{\partial a}{\partial r_i}\right) \tag{145}$$

$$\frac{\partial T_{1d}}{\partial r_i} = 2c\left(\frac{1}{2\sqrt{B_2}}\ \frac{\partial B_2}{\partial r_i} - \frac{\partial B_1}{\partial r_i}\right) + 2(\sqrt{B_2} - B_1)\ \frac{\partial c}{\partial r_i} + \frac{\partial b}{\partial r_i}$$

$$+ \frac{1}{2\sqrt{b^2-4ac}}\left(2b\ \frac{\partial b}{\partial r_i} - 4a\ \frac{\partial c}{\partial r_i} - 4c\ \frac{\partial a}{\partial r_i}\right) \tag{146}$$

$$\frac{\partial T_{2n}}{\partial r_i} = 2(\sqrt{B_2} - B_1)\left(\frac{1}{2\sqrt{B_2}}\frac{\partial B_2}{\partial r_i} - \frac{\partial B_1}{\partial r_i}\right) \tag{147}$$

$$\frac{\partial T_{2d}}{\partial r_i} = 2c\left(\frac{1}{2\sqrt{B_2}}\frac{\partial B_2}{\partial r_i} - \frac{\partial B_1}{\partial r_i}\right) + (\sqrt{B_2} - B_1)^2\ \frac{\partial c}{\partial r_i}$$

$$+ b\left(\frac{1}{2\sqrt{B_2}}\frac{\partial B_2}{\partial r_i} - \frac{\partial B_1}{\partial r_i}\right) + (\sqrt{B_2} - B_1)\ \frac{\partial b}{\partial r_i} + \frac{\partial a}{\partial r_i} \tag{148}$$

$$\frac{\partial T_{3n}}{\partial r_i} = 2c\left[\frac{1}{2\sqrt{B_2-B_3Co^{III}}}\left(\frac{\partial B_2}{\partial r_i} - B_3\ \frac{\partial Co^{III}}{\partial r_i} - Co^{III}\frac{\partial B_3}{\partial r_i}\right) - \frac{\partial B_1}{\partial r_i}\right]$$

$$+ 2(\sqrt{B_2-B_3Co^{III}} - B_1)\frac{\partial c}{\partial r_i} + \frac{\partial b}{\partial r_i} \tag{149}$$

$$- \frac{1}{2\sqrt{b^2-4ac}}\left(2b\ \frac{\partial b}{\partial r_i} - 4a\ \frac{\partial c}{\partial r_i} - 4c\ \frac{\partial a}{\partial r_i}\right)$$

$$\frac{\partial T_{3d}}{\partial r_i} = 2c\left[\frac{1}{2\sqrt{B_2-B_3Co^{III}}}\left(\frac{\partial B_2}{\partial r_i} - B_3\ \frac{\partial Co^{III}}{\partial r_i} - Co^{III}\ \frac{\partial B_3}{\partial r_i}\right) - \frac{\partial B_1}{\partial r_i}\right]$$

$$+ 2(\sqrt{B_2-B_3Co^{III}} - B_1)\frac{\partial c}{\partial r_i} + \frac{\partial b}{\partial r_i} + \frac{1}{2\sqrt{b^2-4ac}}\left(2b\ \frac{\partial b}{\partial r_i} - 4a\ \frac{\partial c}{\partial r_i}\right.$$

$$\left. - 4c\ \frac{\partial a}{\partial r_i}\right) \tag{150}$$

$$\frac{\partial T_{4n}}{\partial r_i} = 2c\left(\sqrt{B_2-B_3Co^{III}}-B_1\right)\left[\frac{\left(\frac{\partial B_2}{\partial r_i} - B_3\frac{\partial Co^{III}}{\partial r_i} - Co^{III}\frac{\partial B_3}{\partial r_i}\right)}{2\sqrt{B_2-B_3Co^{III}}} - \frac{\partial B_1}{\partial r_i}\right] \quad (151)$$

$$\frac{\partial T_{4d}}{\partial r_i} = 2c\left(\sqrt{B_2-B_3Co^{III}}-B_1\right)\left[\frac{\left(\frac{\partial B_2}{\partial r_i} - B_3\frac{\partial Co^{III}}{\partial r_i} - Co^{III}\frac{\partial B_3}{\partial r_i}\right)}{2\sqrt{B_2-B_3Co^{III}}} - \frac{\partial B_1}{\partial r_i}\right]$$

$$+ \left(\sqrt{B_2-B_3Co^{III}}-B_1\right)^2\frac{\partial c}{\partial r_i} + b\left[\frac{\left(\frac{\partial B_2}{\partial r_i} - B_3\frac{\partial Co^{III}}{\partial r_i} - Co^{III}\frac{\partial B_3}{\partial r_i}\right)}{2\sqrt{B_2-B_2Co^{III}}} - \frac{\partial B_1}{\partial r_i}\right]$$

$$+ \left(\sqrt{B_2-B_3Co^{III}}- B_1\right)\frac{\partial b}{\partial r_i} + \frac{\partial a}{\partial r_i} \quad (152)$$

$$\frac{\partial E_3}{\partial r_i} = \frac{a\frac{\partial B_1}{\partial r_i} - B_1\frac{\partial a}{\partial r_i}}{a^2} \ . \quad (153)$$

For the non-linear least squares calculation, the derivatives with respect to K_{4b}, k_{5a} or k'_{5a}, k_{5b} and Co^{III} can be obtained from the following derivatives:

$$\frac{\partial B_1}{\partial K_{4b}} = 0 \quad (154)$$

$$\frac{\partial B_1}{\partial (k_{5a} \text{ or } k'_{5a})} = 0 \quad (155)$$

$$\frac{\partial B_1}{\partial k_{5b}} = 0 \quad (156)$$

$$\frac{\partial B_1}{\partial Co^{III}} = 0 \qquad (157)$$

$$\frac{\partial B_2}{\partial K_{4b}} = 8\ K_{4a}[O_2]Co_t \qquad (158)$$

$$\frac{\partial B_2}{\partial (k_{5a} \text{ or } k'_{5a})} = 0 \qquad (159)$$

$$\frac{\partial B_2}{\partial k_{5b}} = 0 \qquad (160)$$

$$\frac{\partial B_2}{\partial Co^{III}} = 0 \qquad (161)$$

$$\frac{\partial B_3}{\partial K_{4b}} = 8K_{4a}[O_2] \qquad (162)$$

$$\frac{\partial B_3}{\partial (k_{5a} \text{ or } k'_{5a})} = 0 \qquad (163)$$

$$\frac{\partial B_3}{\partial k_{5b}} = 0 \qquad (164)$$

$$\frac{\partial B_3}{\partial Co^{III}} = 0 \qquad (165)$$

$$\frac{\partial a}{\partial K_{4b}} = 0 \qquad (166)$$

$$\frac{\partial a}{\partial (k_{5a} \text{ or } k'_{5a})} = 0 \qquad (167)$$

$$\frac{\partial a}{\partial k_{5a}} = 2K_{4a}[O_2]Co_t \qquad (168)$$

$$\frac{\partial a}{\partial Co^{III}} = 0 \qquad (169)$$

$$\frac{\partial b}{\partial k_{5a}} = \frac{1}{2} \qquad (170)$$

$$\frac{\partial b}{\partial k'_{5a}} = \frac{1}{2K_{4b}} \tag{171}$$

$$\frac{\partial b}{\partial k_{5b}} = -\frac{1}{2K_{4b}}\left(\frac{1}{K_1K_2[L^-]^2} + \frac{1}{K_2[L^-]} + 1 + K_3[L^-] + K_{4a}[O_2]\right) \tag{172}$$

$$\frac{\partial b}{\partial Co^{III}} = 0 \tag{173}$$

$$\frac{\partial c}{\partial K_{4b}} = \frac{k_{5b}}{4K_{4b}^2} \tag{174}$$

$$\frac{\partial c}{\partial (k_{5a} \text{ or } k'_{5a})} = 0 \tag{175}$$

$$\frac{\partial c}{\partial k_{5b}} = \frac{-1}{4K_{4b}} \tag{176}$$

$$\frac{\partial c}{\partial Co^{III}} = 0 \tag{177}$$

$$\frac{\partial Co^{III}}{\partial K_{4b}} = 0 \tag{178}$$

$$\frac{\partial Co^{III}}{\partial (k_{5a} \text{ or } k'_{5a})} = 0 \tag{179}$$

$$\frac{\partial Co^{III}}{\partial k_{5b}} = 0 \tag{180}$$

$$\frac{\partial Co^{III}}{\partial Co^{III}} = 1 \ . \tag{181}$$

For the mechanism including equation 49

$$\frac{\partial b}{\partial K_{4b}} = \frac{k_{5b}}{2K_{4b}^2}\left(\frac{1}{K_1K_2[L^-]} + \frac{1}{K_2[L^-]} + 1 + K_3[L^-] + K_{4a}[O_2]\right) \tag{182}$$

and for the mechanism including equation 50 instead of equation 49

$$\frac{\partial b}{\partial K_{4b}} = \frac{k_{5b}\left(\frac{1}{K_1K_2[L^-]^2} + \frac{1}{K_2[L^-]} + 1+K_3[L^-]+K_{4a}[O_2]\right) - k_{5a}}{2K_{4b}^2} \quad . \qquad (183)$$

By substituting equations 154 to 183 into equations 143 to 153, then substituting the results into equations 141 and 142 and finally substituting the results into equation 140, one obtains all the necessary derivatives of the type

$$\frac{\partial f(\Sigma\, r_i)}{\partial r_i} \quad .$$

To obtain the final derivatives required for the least squares calculation, the term q_i is defined as r_i except that Co^{III} is not included (see equation 136).

The final derivatives are

$$\frac{\partial Co^{III}}{\partial q_i} = \frac{\frac{\partial f(\Sigma r_i)}{\partial q_i}}{\frac{\partial f(\Sigma r_i)}{\partial Co^{III}}} \quad . \qquad (184)$$

Thus, the final derivatives are obtained by substituting equations 140 into equation 184.

B. <u>Derivative for the Ligand Concentration Calculations</u>

By substituting equation 65 into 84, one obtains

$$f(L^-) = \left(\frac{-B_1 + \sqrt{B_2 - B_3 Co^{III}}}{B_3}\right) 2E + (-B_1 + \sqrt{B_2 - B_3 Co^{III}})^2 \,\frac{(n-2)}{B_3}$$

$$+ (n-2)Co^{III} - [L^-]A_H = 0. \qquad (185)$$

To be able to calculate the $[L^-]$ by the Newton method, it is necessary to obtain $\partial f[L^-]/\partial[L^-]$ which is as follows:

$$\frac{\partial f[L^-]}{\partial [L^-]} = \left(\frac{-B_1+\sqrt{B_2-B_3Co^{III}}}{B_3}\right)(2)\left[(n-3)K_3-\frac{2n}{K_1K_2[L^-]^3}-\frac{(n-1)}{K_2[L^-]^2}\right]$$

$$+ E\left[\frac{\left(\frac{2}{K_1K_2[L^-]^3}+\frac{1}{K_2[L^-]^2}-K_3\right)}{4K_{4a}K_{4b}[O_2]}+\frac{B_1\left(K_3-\frac{2}{K_1K_2[L^-]^3}-\frac{1}{K_2[L^-]^2}\right)}{4K_{4a}K_{4b}[O_2]\sqrt{B_2-B_3Co^{III}}}\right]$$

$$+ (n-2)\left(\sqrt{B_2-B_3Co^{III}}-B_1\right)\left(\frac{2}{B_3}\right)\left[\frac{2}{K_1K_2[L^-]^3}+\frac{1}{K_2[L^-]^2}-K_3\right.$$

$$\left.+\frac{B_1\left(K_3-\frac{2}{K_1K_2[L^-]^3}-\frac{1}{K_2[L^-]^2}\right)}{\sqrt{B_2-B_3Co^{III}}}\right]-A_H \quad . \qquad (186)$$

C. Computer Programs

1. Linear Least Squares.

```
      PROGRAM LINEARLS
      DIMENSION X(200),Y(200),IDENT(10)
C THIS PROGRAM WILL CALCULATE THE LEAST SQUARES SLOPE,INTERCEPT AND THE STANDARD
C DEVIATIONS OF THE SLOPE AND INTERCEPT FOR A STRAIGHT LINE CONTAINING 200 OR
C FEWER EXPERIMENTAL POINTS.THIS PROGRAM CAN BE USED TO CALCULATE MULTIPLE RUNS.
C THE FIRST DATA CARD SHOULD HAVE THE NUMBER OF EXPERIMENTAL POINTS IN COLUMNS 1
C TO 3.THE SECOND DATA CARD SHOULD IDENTIFY THE RUN USING COLUMNS 1 TO 80.THEN
C YOU SHOULD HAVE ONE DATA CARD FOR EACH EXPERIMENTAL POINT USING COLUMNS 1 TO
C 10 FOR THE VALUE OF X AND COLUMNS 11 TO 20 FOR THE VALUE OF Y. THEN YOU CAN
C HAVE ANOTHER SET OF CARDS FOR THE NEXT RUN, ETC. AFTER THE LAST DATA CARD OF
C THE LAST RUN, THERE SHOULD BE ONE BLANK DATA CARD.
   99 READ (60,1) N
    1 FORMAT (I3)
      SUMX=0 $ SUMY=0 $ SUMXSQ=0 $ SUMYSQ=0 $ SUMXY=0
```

```
C N IS THE NUMBER OF DATA POINTS ON THE STRAIGHT LINE,ANTERCPT IS THE INTERCEPT.
      IF (N) 100,100,2
    2 READ (60,11)(IDENT(I),I=1,10,1)
   11 FORMAT (10A8)
      DO 4 I=1,N,1
      READ (60,3) X(I),Y(I)
    3 FORMAT (2F10.0)
      SUMX=SUMX+X(I) $ SUMXSQ=SUMXSQ+X(I)**2 $ SUMXY=SUMXY+X(I)*Y(I)
      SUMY=SUMY+Y(I) $ SUMYSQ=SUMYSQ+Y(I)**2
    4 CONTINUE
      Q=N $ SLOPE=(Q*SUMXY-SUMX*SUMY)/(Q*SUMXSQ-SUMX**2)
      ANTERCPT=(SUMXSQ*SUMY-SUMX*SUMXY)/(Q*SUMXSQ-SUMX**2)
      C=SUMX*SUMY $ D=SUMX**2 $ E=SUMY**2 $ SUMXYN=C/Q $ B=D/Q $ EN=E/Q
      F=SUMXY-SUMXYN $ FSQ=F**2 $ G=SUMXSQ-B $ SSQN=SUMYSQ-EN-FSQ/G
      SSQ=SSQN/(Q-2) $ H=FSQ/G $ STDEVSLO=SQRTF(SSQ/G)
      STDEVINT=SQRTF(SSQ*SUMXSQ/(Q*SUMXSQ-D))
      WRITE (61,12)(IDENT(I),I=1,10,1)
   12 FORMAT (*-*,10A8)
```

```
      WRITE (61,7) N
    7 FORMAT(*-*,*THE NUMBER OF DATA POINTS ON THE STRAIGHT LINE =*,I3)
      WRITE(61,20)SUMX,SUMY,SUMXSQ,SUMYSQ,SUMXY,C,D,F                    OPTIONAL
   20 FORMAT(* *,*SUMX=*,F15.6,5X,*SUMY=*,F15.6,5X,*SUMXSQ=*,F15.6,5X,*SOPTIONAL
     1UMYSQ=*,F15.6,/,* SUMXY=*,F15.6,5X,*SUMX SUMY=*,F15.6,5X,*(SUMX)SQOPTIONAL
     2=*,F15.6,5X,*(SUMY)SQ=*,F15.6)                                     OPTIONAL
      WRITE(61,22)SUMXYN,B,EN,F,FSQ,G,SSQN,SSQ,H                         OPTIONAL
   22 FORMAT(* *,*(SUMX SUMY)/N=*,F15.6,5X,*(SUMX)SQ/N=*,F15.6,5X,*(SUMYOPTIONAL
     1)SQ/N=*,F15.6,5X,*SUMXY-(SUMX SUMY)/N=*,F15.6,/,* (SUMXY-(SUMX SUMOPTIONAL
     2Y)/N)SQUARED=*,F15.6,5X,*SUMXSQ-(SUMX)SQ/N=*,F15.6,5X,*(N-2)S SQUAOPTIONAL
     3RED=*,F15.6,5X,/,* S SQUARE=*,F15.6,5X,*(SUMXY-SUMX SUMY/N)SQ/(SUMOPTIONAL
     4XSQ-(SUMX)SQ/N))=*,F15.6)                                          OPTIONAL
      WRITE (61,8)
    8 FORMAT (*-*,*POINT NUMBER*,11X,*X*,18X,*Y*)
      WRITE (61,9)(I,X(I),Y(I),I=1,N,1)
    9 FORMAT(* *,I3,11X,2(F15.7,2X))
      WRITE (61,10)SLOPE,STDEVSLO,ANTERCPT,STDEVINT
   10 FORMAT(*-*,*SLOPE=*,F15.7,*PLUS OR MINUS*,F15.5,/,*INTERCEPT=*,F15
```

```
   1,7,*PLUS OR MINUS*,F15.7)
    GO TO 99
100 CONTINUE
    END
```

The boxed in lines of the two following programs indicate computer cards that are different for the mechanism including equation 49 (which is derivation G) and for the mechanism including equation 50 in place of equation 49 (derivation H). The programs as shown are for derivation G. If, in converting the computer card from derivation G to derivation H, the only change is to change a "G" to an "H", the change is not listed at the end of the program. Any other changes are listed at the end of the program. The numbers at the far right of each line are for identification.

2. <u>Non Least Squares Calculation Program.</u>

```
      PROGRAM KINTSLCT                                                    1
C   THIS DECK INCLUDES THE CORRECTION OF 7/23/69 ON THE TERM EXP12.
C   THIS DECK INCLUDES THE CORRECTION OF 7/23/69 ON THE TERM EXP12.
C   THIS DECK INCLUDES THE CORRECTION OF 7/23/69 ON THE TERM EXP12.
C   THIS DECK INCLUDES THE CORRECTION OF 7/23/69 ON THE TERM EXP12.
C     THIS DECK IS BASED ON THE ORIGINAL CATALYTIC MECHANISM.  (DERIVATION G).
C     THIS DECK IS BASED ON THE ORIGINAL CATALYTIC MECHANISM.  (DERIVATION G).
C     THIS DECK IS BASED ON THE ORIGINAL CATALYTIC MECHANISM.  (DERIVATION G).
C     THIS DECK IS BASED ON THE ORIGINAL CATALYTIC MECHANISM.  (DERIVATION G).
      COMMON T,CC,CX,CO,LABORT,I,LTEST,ALIG,A1H,A2H,A3H,HCONC,N,ALIGGESS  2
     1,ALIGG                                                              3
      DIMENSION T(100),CX(100),CC(100),ALIGGESS(11),P(10),ALIGG(100)      4
      TYPE REAL K4A                                                       4A
C   THIS IS A TEST OF THE MOST PROBABLE CATALYTIC MECHANISM.              5
C   THIS IS A TEST OF THE MOST PROBABLE CATALYTIC MECHANISM.              6
```

```
C    THIS IS A TEST OF THE MOST PROBABLE CATALYTIC MECHANISM.          7
     SENSE LIGHT 0                                                     7A
  10 READ 1,R                                                          8
   1 FORMAT (10A8)                                                     9
     READ 2,CO,A1,A2,A3,A4A,A4B,A5A,A5B                                10
   2 FORMAT (8F10.0)                                                   11
     IF (SENSE LIGHT 1)13,14                                           11A
  14 K4A=A4A/(1.212*10.0**(-3))                                        11B
  13 SENSE LIGHT 1                                                     11C
     READ 3,A1H,A2H,A3H,HCONC,ALICTRYY,ALMRATIO,LTEST                  12
   3 FORMAT (6F10.0,I10)                                               13
     IF((A1+A2+A3+A4A+A4B+A5A+A5B).EQ.0.0) GO TO 11                    14
     PRINT 12                                                          15
  12 FORMAT (* THIS IS A TEST OF CATALYTIC MECHANISM G. A4A IS EQUAL TO    16
    1 (K4A)(OXYGEN CONC.), OXYGEN CONC. =1.212E-3 FOR PURE OXYGEN,*,/,*   16A
    2 2.424E-4 FOR AIR AND 6.06E-5 FOR 5 PERCENT OXYGEN.*)             17
     PRINT 4,R                                                         18
   4 FORMAT (//,10A8)                                                  19
```

```
      PRINT 5,CO,ALMRATIO,A1,A2,A3,A4A,A4B,A5A,A5B,ALIGTRYY,A1H,A2H,A3H,
     1HCONC,K4A
    5 FORMAT(* *,*THE CONC. OF TOTAL COBALT=*,E10.3,5X,*LIGAND TO METAL
     1RATIO =*,F5.2,* TO 1*,/,1X,*K1 =*,E10.3,5X,*K2 =*,E10.3,5X,*K3 =*,
     2E10.3,/,*A4A =*,E10.3,4X,*A4B =*,E10.3,4X,*A5A =*,E10.3,/,*A5B =*,
     3E10.3,4X,*A4A = (K4A)(OXYGEN CONCENTRATION)*,/,* INITIAL GUESS OF
     4LIGAND CONC. =*,E10.3,5X,*K1H =*,E10.3,5X,*K2H =*,E10.3,5X,*K3H =*
     5,E10.3,/,* HYDROGEN ION CONCENTRATION =*,E10.3,5X,*K4A =*,E10.3)
      ALIGEST=(ALMRATIO-2.0)*CO/(1.0+A1H*HCONC+A1H*A2H*HCONC**2+A1H*A2H*
     1A3H*HCONC**3)
      PRINT 514, ALIGEST
  514 FORMAT (* *,*ESTIMATED VALUE OF LIGAND CONCENTRATION =*,E10.3)
      I=1
    6 READ 7,IDENT,T(I),CX(I)
    7 FORMAT (I1,F4,F10.0)
      IF (IDENT.GT.1) GO TO 10
      ALIGGESS(1)=ALIGTRYY
      CALL ALIGCALC(A1,A2,A3,A4A,A4B,A5A,A5B,ALMRATIO)
```

```
      IF (LABORT.EQ.0)GO TO 11                                          38
      IF (T(I).EQ.0.0)105,103
  105 ALIG=ALIGG(I)  $  TIME=T(I)  $  GO TO 988
  103 ALIG=(ALIGG(I)+ALIGG(I-1))/2.0  $  TIME=T(I)-T(I-1)
  988 CALL CO3CALC(A1,A2,A3,A4A,A4B,A5A,A5B,TIME)                       39
      IF(LABORT.EQ.0.AND.CC(I-1).GT.(0.999*CO))15,16                    39A
   15 READ 7,IDENT,T(I),CX(I)                                           39B
      IF (IDENT.EQ.9)16,15                                              39C
   16 IF (LABORT.EQ.0)GO TO 11                                          40
      PRINT 8,T(I),CX(I),CC(I),ALIGG(I)                                 41
    8 FORMAT (* *,*T(I) =*,F6.1,5X,*CX(I) =*,E14.6,5X,*CC(I) =*,F14.6,5X 42
     1,*LIGAND CONCENTRATION =*,F14.6)                                  43
      I=I+1  $  GO TO 6                                                 44
   11 CONTINUE                                                          45
      SENSE LIGHT 0                                                     46
      END
```

3. Non-linear Least Squares Calculation.

```
      PROGRAM DERIVG                                                          1
C     THIS DECK INCLUDES THE CORRECTION OF 7/23/69 ON EXP12,
      COMMON T(500),CC(500),CX(500),LABORT,I,LTEST,ALIG,A1H,A2H,A3H,HCON      2
     1C,N,ALIGGESS(11),ALIGG(500),ALMRATIO(500),R(10,500),L,CONCOXYG(50      2A
     2),LL,CO(500),CO37ERO(500),CXX(500),CO2(500),COL(500),COL2(500),COL     2B
     3202(500),COL2202(500)                                                   3
      DIMENSION KA(500),AA(500,4),M(4,4),DPC(500),BB(3,3),ALIGTRYY(500),      4
     1IRUN(500),IRUNMIN(15),IRUNMAX(15),ALIGGG(500),CO3(500)                  4A
      TYPE REAL M                                                             5
      TYPE INTEGER R                                                          5A
      PRINT 1009                                                              5B
 1009 FORMAT (*THIS DECK INCLUDES THE CORRECTION OF 7/23/69 ON EXP12.*,/      5C
     1,*THIS DECK IS BASED ON THE CATALYTIC MECHANISM (DERIVATION G),*,/      5D
     1,*  THE PARAMETERS K4B,K5A,K5B ARE VARIED BY THE LEAST SQUARES PRO      5D
     1CEDURE,*,/,*A1 IS K1, (THE FIRST STEPWISE FORMATION CONSTANT OF TH    5D-A
```

```
2E METAL-LIGAND COMPLEX),                                           *,/,*   5D-P
3A2 IS K2, (THE SECONDSTEPWISE FORMATION CONSTANT OF THE METAL-LIGA   5E
4ND COMPLEX),                      *,/,*A3 IS K3, (THE THIRD STEPWISE   5F
5 FORMATION CONSTANT FOR THE LIGAND-METAL COMPLEX),*,/,*A4A IS K4A,   5G
6 (THE FIRST STEPWISE FORMATION CONSTANT FOR THE METAL-LIGAND-OXYGE   5H
7N COMPLEX),*,/,*A4B IS K4B, (THE SECOND STEPWISE FORMATION CONSTAN   5I
8T FOR THE METAL-LIGAND-OXYGEN COMPLEX),*,/,*A5A IS K5A, (THE COBAL   5J
9T 2 KINETIC DECOMPOSITION STEP OF THE REACTION),*,/,*A5B IS K5B, (   5K
1THE COBALT 3 KINETIC DECOMPOSITION STEP OF THE REACTION)     *,/,*   5L
2A1H IS THE FIRST PROTONATION CONSTANT FOR THE LIGAND.        *,/,*   5M
3A2H IS THE SECOND PROTONATION CONSTANT FOR THE LIGAND.       *,/,*   5N
4A3H IS THE THIRD PROTONATION CONSTANT FOR THE LIGAND.        *,/,*   5-O
5AA(I, J OR K) IS A DETERMINANT WHICH IS USED TO STORE THE DATA TO   5P
6SOLVE THE SYSTEM OF SIMULTANEOUS LINEAR EQUATIONS OF THE NON-LINEA   5Q
7R*,/,*          LEAST SQUARES PROCEDURE,                     *,/,*   5R
8AD6 IS THE QUANTITY TO ADD TO THE GUESS OF K5A IN THE EVENT THAT T   5S
9HE LEAST SQUARES PROCEDURE PRODUCES A NEGATIVE PARAMETER.    *,/,*   5T
1AD7 IS THE QUANTITY TO ADD TO THE GUESS OF K5B IN THE EVENT THAT T   5U
```

```
2HE LEAST SQUARES PROCEDURE PRODUCES A NEGATIVE PARAMETER.      *,/,*     5V
3ALIG IS THE AVERAGE VALUE OF THE LIGAND CONCENTRATION BETWEEN ADJA       5W
4CENT EXPERIMENTAL POINTS OF THE SAME KINETIC RUN.                *,/,*     5X
5ALIGG(I) IS THE VALUE OF THE LIGAND ION CONCENTRATION FOR EXPERIME       5Y
6NTAL POINT I AS CALCULATED BY SUBROUTINE ALIGCALC.               *,/,*     5Z
7ALIGGG IS THE VALUE OF THE LIGAND CONCENTRATION USED IN THE LEAST        5AA
8SQUARES CALCULATION,*,/,*ALIGEST IS A SIMPLE ESTIMATE OF THE LIGAN       5AB
9D CONCENTRATION BASED ON THE QUANTITY OF LIGAND IN EXCESS OF TWICE       5AC
1 THE METAL ION CONC. *,/,*ALIGGESS IS THE TRIAL OF THE VALUE OF TH       5AD
2E VALUE OF THE LIGAND CONCENTRATION.                             *,/,*     5AE
3ALIGTRYY IS THE INITIAL GUESS OF THE LIGAND CONCENTRATION.     *,/,*     5AF
4ALMRATIO IS THE LIGAND TO METAL RATIO.                           *,/,*     5AG
5BB IS A DETERMINANT THAT IT USED TO SOLVE THE LEAST SQUARES SIMULT       5AH
6ANEOUS LINEAR EQUATIONS,*,/,*CC IS THE CALCULATED VALUE OF COBALT        5AI
73 IN MOLES PER LITER.                                            *,/,*     5AJ
8CO IS THE INITIAL CONCENTRATION OF COBALT 2 IN THE REACTION SAMPLE       5AK
9.*,/,*CONCOXYG IS THE CONCENTRATION OF OXYGEN IN THE REACTION SOLU       5AL
1TION (BASED ON THE OXYGEN GAS SOLUBILITY AT THE OXYGEN PARTIAL *,/       5AM
```

```
2,*           PRESSURE) AND CALCULATED IN MOLES PER LITER.       *,/,*    5AN
3CO3 IS THE CALCULATED VALUE OF THE COBALT 3 CONCENTRATION LESS THE       5ANA
3 COBALT 3 ADDED INITIALLY.                                       *,/,*    5ANB
3CO3ZERO IS THE INITIAL CONCENTRATION OF COBALT 3 IN THE REACTION S       5AO
4AMPLE.*,/,*CX IS THE EXPERIMENTAL VALUE OF COBALT 3 IN THE REACTIO       5AP
5N VESSEL IN MOLES PER LITER.*,/,*CXX IS THE EXPERIMENTAL VALUE OF        5AQ
5THE COBALT 3 CONCENTRATION LESS THE COBALT 3 ADDED INITIALLY.*,/,*       5AQA
6DD IS THE FACTOR BY WHICH THE LEAST SQUARES CORRECTION ON THE CONS       5AR
7TANTS IS DECREASED.                                               *,/     5AS
8,*DDC(I) = COBALT 3 (EXPERIMENTAL) - COBALT 3 (CALCULATED) FOR DAT       5AT
9A POINT I.*,/,*DMIN IS THE MINIMUM PERMITTED VALUE OF THE SYMMETRI       5AU
1C LEAST SQUARES DETERMINANT.                                     *,/,*    5AV
2DXMAX6 IS THE SMALLEST PERMITTED CORRECTION ON K5A.              *,/,*    5AW
3DXMAX7 IS THE SMALLEST PERMITTED CORRECTION ON K5B.              *,/,*    5AX
4HCONC IS THE HYDROGEN ION CONCENTRATION (ASSUMED TO BE CONSTANT) I       5AY
5N THE REACTION SAMPLE.                                           *,/,*    5AZ
6I IS AN INDEXING VARIABLE FOR THE EXPERIMENTAL DATA POINT NUMBER.*       5BA
7,/,*ICONST IS THE TOTAL NUMBER OF EXPERIMENTAL DATA POINTS READ IN       5BB
```

```
8TO THE COMPUTER.                                                *,/,*     5BC
9 IRUN = 0 ,  NO PARTICULAR SIGNIFICANCE.                        *,/,*     5BD
1 IRUN = 1 ,    FIRST DATA POINT FROM AN EXPERIMENTAL RUN.       *,/,*     5BE
2 IRUN = 2 ,  FIRST LEAST SQUARES DATA POINT OF AN EXPERIMENTAL RUN        5BF
3,*,/,* IRUN = 3, LAST LEAST SQUARES DATA POINT OF AN EXPERIMENTAL         5BG
4RUN,*,/,* IRUN = 4, LAST DATA POINT OF AN EXPERIMENTAL RUN,*,/,* I        5BH
5RUN = 5, FIRST DATA POINT AND FIRST LEAST SQUARES DATA POINT OF EX        5BI
6ERIMENTAL RUN,*,/,* IRUN = 6, LAST DATA POINT AND LAST LEAST SQUAR        5BJ
7ES DATA POINT OF EXPERIMENTAL RUN,*,/,*IRUNMIN IS AN INDEX VARIABL        5BK
8E FOR THE FIRST DATA POINT OF KINETIC RUN LL WHICH IS TO BE INCLUD        5BL
9ED IN THE LEAST SQUARES PROCEDURE,*,/,*IRUNMAX IS AN INDEX VARIABL        5BM
1E FOR THE LAST DATA POINT OF KINETIC RUN LL WHICH IS TO BE INCLUDE       5BN
2D IN THE LEAST SQUARES PROCEDURE,*,/,*KA(I)=0  INDICATES THAT THE         5BO
3EXPERIMENTAL POINT I IS TO BE INCLUDED IN THE LEAST SQUARES CALCUL        5BP
4ATION,*,/,*KA(I) =1  INDICATES THAT THE EXPERIMENTAL POINT I IS NO        5BQ
5T TO BE INCLUDED IN THE LEAST SQUARES CALCULATION,*,/,*KA(I) = 9          5BR
6INDICATES THAT POINT (I-1) IS THE LAST EXPERIMENTAL DATA POINT FRO        5BS
7M KINETIC RUN K,*,/,*L IS AN INDEXING VARIABLE FOR A DO LOOP. ITS         5BT
```

```
8MAXIMUM VALUE IS THE MAXIMUM PERMITTED NUMBER OF NON-LINEAR LEAST      5BU
9SQUARES*,/,*             ITERATIONS,*,/,*LABORT = 1 WHEN A SURROUTINE   5BV
1 CAN SUCCESSFULLY COMPLETE ITS CALCULATIONS,*,/,*LABORT = 0 WHEN A     5BW
2 SUBROUTINE CANNOT SUCCESSFULLY COMPLETE ITS CALCULATIONS,    *,/,*    5BX
3LL IS AN INDEX VARIABLE TO IDENTIFY THE KINETIC RUN,          *,/,*    5BY
4LLMAX IS THE TOTAL NUMBER OF KINETIC RUNS BEING FED INTO THE COMPU     5BZ
5TER,*,/,*LLMAX IS THE TOTAL NUMBER OF EXPERIMENTAL KINETIC RUNS BE     5CA
6ING READ INTO THE COMPUTER,*,/,*LLL IS A DIMENSION VARIABLE FOR BC     5CB
7D VARIABLE R TO ALLOW R 80 SPACES,*,/,*LMAX IS THE MAXIMUM NUMBER      5CC
8OF LEAST SQUARES ITERATIONS PERMITTED,*,/,*LTEST INDICATES WHETHER     5CD
9 CERTAIN INTERMEDIATES IN THE CALCULATION OF COBALT 3 AND LIGAND C     5CE
1ONCENTRATION WILL BE PRINTED OUT,*,/,*M(J,K) IS THE SUM OVER I OF      5CF
2THE PAIRWISE PRODUCTS OF AA(I,J) AND AA(I,K),*,/,*NN IS THE NUMBER     5CG
3PARAMETERS INCLUDED IN THE LEAST SQUARES PROCEDURE,*,/,*R IS THE T     5CH
4ITLE OF THE EXPERIMENTAL RUN, IT IS A BCD VARIABLE,*,/,*T IS TIME      5CI
5 IN MINUTES,                                                  *,/,*    5CJ
6X1 TO X5B ARE THE CURRENT COMPUTER VALUES FOR K1 TO K5B,      *,/,*    5CK
7XX1 TO XX7 ARE INTERMEDIATE VARIABLES FOR STORAGE OF CURRENT VALUE     5CL
```

```
      8S OF K1 TO K56*)
      READ 225,DXMAX5,DXMAX6,DXMAX7,DMIN                                  5CM
  225 FORMAT (40X,4F10.0)                                                 6
      READ 226,AD5,AD6,AD7,LMAX,LTEST                                     7
  226 FORMAT (40X,3F10.0,I9,I1)                                           8
      XX1=0.0  $  XX2=0.0  $  XX3=0.0  $  XX4=0.0  $  XX5=0.0             9
      XX6=0.0  $  XX7=0.0  $  L=0  $  I=1  $  LL=0                        10
      READ 501,A1,A2,A3,A4A,A4B,A5A,A5B                                   11
  501 FORMAT (7F10.0)                                                     12
      READ 1004,A1H,A2H,A3H,DD,HCONC,FACTOR                               13
 1004 FORMAT (6F10.0)                                                     14
      EPSILON=125.1/FACTOR                                                15
      PRINT 1005,A1,A2,A3,A4A,A4B,A5A,A5B,A1H,A2H,A3H,HCONC,DD,FACTOR,EP  15AA
     1SILON                                                               15A
 1005 FORMAT (*2 A1 =*,E10.3,5X,* A2 =*,E10.3,5X,* A3 =*,E10.3,5X,*A4A =  15AB
     1*,E10.3,5X,*A4B =*,E10.3,/,* A5A =*,E10.3,5X,*A5B =*,E10.3,5X,*A1H  15B
     2 =*,E10.3,5X,*A2H =*,E10.3,5X,*A3H =*,E10.3,/,* HYDROGEN ION CONCE  16
     3NTRATION =*,E10.3,5X,*DIVISOR OF CORRECTION TERMS OF K VALUES =*,F  17
                                                                          18
```

```
   44,1,/,* FACTOR =*,F7.3,5X,*MOLAR ABSORPTIVITY =*,F8.2)              18AA
 97 LL=LL+1                                                             18A
100 READ 500, (R(LLL,I),LLL=1,10)                                       19
500 FORMAT (10A8)                                                       20
    READ 227, ALMRATIO(I),CO(I),ALIGTRYY(I),CONCOXYG(I),CO3ZERO(I)      21
227 FORMAT (5F10.0)                                                     22
    IF (ALMRATIO(I).EQ.0.0) GO TO 108                                   22A
    PRINT 502, (R(LLL,I),LLL=1,10)                                      22B
502 FORMAT (1H1,10A8)                                                   23
    PRINT 503, CO(I),ALMRATIO(I),ALIGTRYY(I),CONCOXYG(I),CO3ZERO(I)     24
503 FORMAT(* *,*THE CONC. OF TOTAL COBALT=*,E10.3,5X,*LIGAND TO METAL   25
   1RATIO =*,F2,* TO 1*,/,* INITIAL GUESS OF LIGAND CONC =*,E10.3,5X,*  26
   2OXYGEN CONCENTRATION =*,E10.3,*      INITIAL CONCENTRATION OF COBA  27
   3LT 3 =*,E10.3)                                                      28
    IF (ALMRATIO.GE.2.0)102,101                                         29-31
101 PRINT 104                                                           32
104 FORMAT (* *,*THERE IS AN ERROR IN THE LIGAND TO METAL RATIO. THERE  33
   1FORE THIS PROGRAM IS BEING ABORTED.*)                               34
```

```
      GO TO 1000                                                          35
  102 ALIGEST=(ALMRATIO(I)-2.0)*CO(I)/(1.0+A2H*HCONC+A1H*A2H*HCONC**2+A1  36
     1H*A2H*A3H*HCONC**3)                                              37-44
  106 NN=3                                                                45
      PRINT 514, ALIGEST,LL                                               46
  514 FORMAT (* *,*ESTIMATED VALUE OF LIGAND CONCENTRATION =*,E10.3,5X,*  47
     1DATA SET NUMBER*,I3)                                                47A
  107 READ 504,KA(I),T(I),CXX(I),IRUN(I)                                  48
  504 FORMAT (I1,F4.0,E15.0,I5)                                           49
      IF (IRUN(I).EQ.2.OR.IRUN(I).EQ.5) IRUNMIN(LL)=I                     49A
      IF (IRUN(I).EQ.3.OR.IRUN(I).EQ.6) IRUNMAX(LL)=I                     49B
      CXX(I)=CXX(I)*FACTOR  $  CX(I)=CXX(I)+CO3ZERO(I)                    49C
      IF(CXX(I).GT.(0.98*CO(I)))CXX(I)=CO(I)*0.98                         49D
      CX(I)=CXX(I)+CO3ZERO(I)                                             49E
      IF (KA(I).GT.1) GO TO 97  $  ALIGGESS(1)=ALIGTRYY(I)                50
      CALL ALIGCALC(A1,A2,A3,A4A,A4B,A5A,A5B)                             51
      IF (LABORT.EQ.0) GO TO 1000                                         51A
      CALL COBLTCLC (A1,A2,A3,A4A,A4B,A5A,A5B)                            51AA
```

```
      IF (T(I).EQ.0.0)105,103                                              51AB
 105  ALIG=ALIGG(I)  $  TIME=T(I)  $  GO TO 988                            51B
 103  ALIG=(ALIGG(I)+ALIGG(I-1))/2.0  $  TIME=T(I)-T(I-1)                  51C
 988  CALL CO3CALC(A1,A2,A3,A4A,A4B,A5A,A5B,TIME)                          51D
      IF (LABORT.EQ.0)GO TO 1000                                           51E
      IF (LABORT.EQ.2) 520,521                                             51F
 520  ICONST=I  $  IRUN(I-1)=4                                             51G
 522  READ 504,KA(I),T(I),CXX(I),IRUN(I)                                   51H
      CX(I)=CXX(I)+CO3ZERO(I)  $  IF (KA(I).EQ.9) 523,522                  51I
 523  I=ICONST-1  $  GO TO 97                                              51J
 521  PRINT 600,KA(I),I,T(I),CC(I),CX(I),ALIGG(I),TIME,ALIG                52
 600  FORMAT(* KA=*,I2,* I=*,I3,* TIME=*,F6.1,* C(CALC)=*,E10.4,* C(EXP)   53
     1=*,E10.4,* LIGAND CONC.=*,E10.4,* ELAPSED TIME=*,F5.1,* AV. LIGAND   54
     2 CONC.=*,E10.4)                                                      54A
      I=I+1  $  ALMRATIO(I)=ALMRATIO(I-1)  $  CONCOXYG(I)=CONCOXYG(I-1)    55
      CO(I)=CO(I-1)  $  ALIGTRYY(I)=ALIGTRYY(I-1)                          55A
      CO3ZERO(I)=CO3ZERO(I-1)  $  DO 557 LLL=1,10,1                        55B
 557  R(LLL,I)=R(LLL,I-1)                                                  55C
```

```
    GO TO 107                                                              55D
108 PRINT 146                                                              55E
146 FORMAT (*1*)                                                           55F
    IMAX=I-1 $ LLMAX=LL-1 $ X1=A1 $ X2=A2 $ X3=A3 $ X4A=A4A $ X4B=A4B      56
    X5A=A5A  $  Y5B=A5B  $  DO 144 I=1,IMAX                                57
144 PRINT 145,T(I),CO2(I),COL(I),COL2(I),COL2O2(I),COL22O2(I)              57AA
145 FORMAT(* TIME =*,F6.1,3X,*(CO 2)2* =*,E11.4,3X,*(COL)* =*,E11.4,3X     57AB
   1,*(COL2) =*,E11.4,3X,*(COL2O2) =*,E11.4,3X,*(COL2)2 O2 =*,E11.4)       57AC
     DO 170 L=1,IMAX                                                       57A
    LL=0                                                                   57B
    DO 109 I=1,IMAX                                                        58
    IF (IRUN(I).EQ.1.OR.IRUN(I).EQ.5) LL=LL+1                              58A
    ALIG=(ALIGG(IRUNMIN(LL))+ALIGG(IRUNMAX(LL)))/2.0 $ ALIGGG(I)=ALIG      58B
    B1=1.0/(A1*A2*ALIG**2)+1.0/(A2*ALIG)+1.0+A3*ALIG+A4A*CONCOXYG(I)       59
    B3=8.0*A4A*A4B*CONCOXYG(I)  $  IF (T(I).EQ.0.0)310,311                 59A
310 ACOTSQ=B1**2+B3*CO(I)  $  GO TO 312                                    59B
311 ACOTSQ=B1**2+B3*CO(I)-B3*CC(I-1)+B3*CO3ZERO(I)                         60
312 ACOLSQ=B1**2+B3*CO(I)-B3*CC(I)+B3*CO3ZERO(I)                           61
```

```
    92=B1**2+B3*(CO(I)+CO3ZERO(I))  $  IF (ACOLSQ)700,705,705          61A
700 PRINT 701,ACOLSQ,ALIG,CC(I)                                          62
701 FORMAT(* *,*ACOL SQUARED =*,E11.3,5X,*LIGAND CONC. =*,E11.3,5X,*CO   63
   1BALT(III) =*,E11.3,/,* THIS PROGRAM IS BEING ABORTED SINCE ONE OF    64
   2THE SQUARE ROOTS IS IMAGINARY.*,27X,*KNFTMULT CARD 65*)              65
    GO TO 1002                                                           66
705 IF (ACOTSQ)706,710,710                                               67
706 PRINT 707,ACOTSQ,CC(I)                                               68
707 FORMAT(* *,*ACOT SQUARED =*,E11.3,5X,*COBALT(III) CALC. =*,E11.3,/   69
   1,* THIS PROGRAM IS BEING ABORTED SINCE ONE OF THE SQUARE ROOTS IS    70
   2IMAGINARY.*,27X,*KNFTMULT CARD 71*)                                  71
    GO TO 1002                                                           72
710 ACOL=SQRTF(ACOLSQ) $ ACOT=SQRTF(ACOTSQ)                              73
    A=2.0*A4A*CONCOXYG(I)*A5B*(CO(I)+CO3ZERO(I))                         74
    B=A5A/2.0-A5B*B1/(2.0*A4B)  $  C=A5B/((-4.0)*A4B)                    75-76
    CONST=SQRTF(B**2-4.0*A*C)  $  EXP11=2.0/CONST                        77
    EXP12=(-1.0)*B*B1/(A*CONST)  $  T1NUM=2.0*C*(ACOT-B1)+B-CONST        78
    T1DEN=2.0*C*(ACOT-B1)+B+CONST  $  EXP2=B1/A  $  T2NUM=(ACOT-B1)**2   79
```

```
      T2DEN=C*(ACOT-B1)**2+B*(ACOT-B1)+A
      T3NUM=2.0*C*(ACOL-B1)+B-CONST  $  T3DEN=2.0*C*(ACOL-B1)+B+CONST
      T4NUM=(ACOL-B1)**2  $  T4DEN=C*(ACOL-B1)**2+B*(ACOL-B1)+A
      T1=T1NUM/T1DEN  $  T2=T2NUM/T2DEN  $  T3=T3NUM/T3DEN
      T4=T4NUM/T4DEN  $  T13=T1/T3  $  T24=T2/T4
      DB1=0.0  $  DA=0.0  $  DB3=8.0*A4A*CONCOXYG(I)  $  DCO3=0.0
      DC=0.0  $  DB2=8.0*A4A*CONCOXYG(I)*(CO(I)+CO3ZERO(I))
      DB=A5B*B1/(2.0*A4B**2)
      DEXP11=(4.0*A*DC+4.0*C*DA-2.0*B*DB)/(B**2-4.0*A*C)**1.5
      DEXP12=(B*B1*(A*(2.0*B*DB-4.0*A*DC-4.0*C*DA)/(2.0*CONST)+CONST*DA)
     1-A*CONST*(B*DB1+B1*DB))/(A*CONST)**2
      DT1NUM=2.0*C*(DB2/(2.0*ACOT)-DB1)+2.0*DC*(ACOT-B1)+DB-(2.0*B*DB-4.
     10*A*DC-4.0*C*DA)/(2.0*CONST)
      DT1DEN=2.0*C*(DB2/(2.0*ACOT)-DB1)+2.0*DC*(ACOT-B1)+DB+(2.0*B*DB-4.
     10*A*DC-4.0*C*DA)/(2.0*CONST)
      DT2NUM=2.0*(ACOT-B1)*((DB2-CO3ZERO*DB3)/(2.0*ACOT)-DB1)
      DT2DEN=2.0*C*((DB2-CO3ZERO*DB3)/(2.0*ACOT)-DB1)+DC*(ACOT-B1)**2+B*
     1((DB2-CO3ZERO*DB3)/(2.0*ACOT)-DB1)+DB*(ACOT-B1)+DA
```

```
 DEXP2=(A*DB1-B1*DA)/A**2                                                98
 DT3NUM=2.0*C*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)+2.0*(ACOL-B1      99
1)*DC+DB*(2.0*B*DB-4.0*A*DC-4.0*C*DA)/(2.0*CONST)                        100
 DT3DEN=2.0*C*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)+2.0*(ACOL-B1      101
1)*DC+DB*(2.0*B*DB-4.0*A*DC-4.0*C*DA)/(2.0*CONST)                        102
 DT4NUM=2.0*(ACOL-B1)*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)           103
 DT4DEN=2.0*C*(ACOL-B1)*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)+DC      104
1*(ACOL-B1)**2+B*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)+(ACOL-B1)      105
2*DB+DA                                                                  106
 DFUNCT=((EXP11+EXP12)/T13)*((T1DEN*T3NUM*(T1NUM*DT3DEN+T3DEN*DT1NU      107
1M)-T1NUM*T3DEN*(T2DEN*DT3NUM+T3NUM*DT1DEN))/(T1DEN*T3NUM)**2)+LOGF      108
2(T13)*(DEXP11+DEXP12)+(EXP2/T24)*((T2DEN*T4NUM*(T2NUM*DT4DEN+T4DEN      109
3*DT2NUM)-T2NUM*T4DEN*(T2DEN*DT4NUM+T4NUM*DT2DEN))/(T2DEN*T4NUM)**2      110
4)+LOGF(T24)*DEXP2                                                       111
 DFUNCK4B=DFUNCT                                                     112-223
 DB1=0.0  $  DB2=0.0  $  DB3=0.0  $  DA=0.0  $  DB=0.5                   112
 DC=0.0  $  DCO3=0.0                                                 113-224
 DEXP11=(4.0*A*DC+4.0*C*DA-2.0*B*DB)/(B**2-4.0*A*C)**1.5                 225
```

```
 DEXP12=(B*B1+(A*(2.0*B*DB-4.0*A*DC-4.0*C*DA)/(2.0*CONST)+CONST*DA)
1-A*CONST*(B*DB1+B1*DB))/(A*CONST)**2
 DT1NUM=2.0*C*(DB2/(2.0*ACOT)-DB1)+2.0*DC*(ACOT-B1)+DB-(2.0*B*DB-4.
10*A*DC-4.0*C*DA)/(2.0*CONST)
 DT1DEN=2.0*C*(DB2/(2.0*ACOT)-DB1)+2.0*DC*(ACOT-B1)+DB+(2.0*B*DB-4.
10*A*DC-4.0*C*DA)/(2.0*CONST)
 DT2NUM=2.0*(ACOT-B1)*((DB2-CO3ZERO*DB3)/(2.0*ACOT)-DB1)
 DT2DEN=2.0*C*((DB2-CO3ZERO*DB3)/(2.0*ACOT)-DB1)+DC*(ACOT-B1)**2+B*
1((DB2-CO3ZERO*DB3)/(2.0*ACOT)-DB1)+DB*(ACOT-B1)+DA
 DEXP2=(A*DB1-B1*DA)/A**2
 DT3NUM=2.0*C*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)+2.0*(ACOL-B1
1)*DC+DB-(2.0*B*DB-4.0*A*DC-4.0*C*DA)/(2.0*CONST)
 DT3DEN=2.0*C*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)+2.0*(ACOL-B1
1)*DC+DB+(2.0*B*DB-4.0*A*DC-4.0*C*DA)/(2.0*CONST)
 DT4NUM=2.0*(ACOL-B1)*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)
 DT4DEN=2.0*C*(ACOL-B1)*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)+DC
1*(ACOL-B1)**2+B*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)+(ACOL-B1)
2*DB+DA
```

```
 DFUNCT=((EXP11+EXP12)/T13)*((T1DEN*T3NUM*(T1NUM*DT3DEN+T3DEN*DT1NU
1M)-T1NUM*T3DEN*(T2DEN*DT3NUM+T3NUM*DT1DEN))/(T1DEN*T3NUM)**2)+LOGF
2(T13)*(DEXP11+DEXP12)+(EXP2/T24)*((T2DEN*T4NUM*(T2NUM*DT4DEN+T4DEN
3*DT2NUM)-T2NUM*T4DEN*(T2DEN*DT4NUM+T4NUM*DT2DEN))/(T2DEN*T4NUM)**2
4)+LOGF(T24)*DEXP2
 DFUNCK5A=DFUNCT
 DB1=0.0  $  DB2=0.0  $  DB3=0.0  $  DB=B1/((-2.0)*A4B)  $  DC03=0.
 DA=2.0*A4A*CONCOXYG(I)*(C0(I)+C03ZERO)   $  DC=1.0/((-4.0)*A4B)
 DEXP11=(4.0*A*DC+4.0*C*DA-2.0*B*DB)/(B**2-4.0*A*C)**1.5
 DEXP12=(B*B1+(A*(2.0*B*DB-4.0*A*DC-4.0*C*DA)/(2.0*CONST)+CONST*DA)
1-A*CONST*(B*DB1+B1*DB))/(A*CONST)**2
 DT1NUM=2.0*C*(DB2/(2.0*ACOT)-DB1)+2.0*DC*(ACOT-B1)+DB-(2.0*B*DB-4.
10*A*DC-4.0*C*DA)/(2.0*CONST)
 DT1DEN=2.0*C*(DB2/(2.0*ACOT)-DB1)+2.0*DC*(ACOT-B1)+DB+(2.0*B*DB-4.
10*A*DC-4.0*C*DA)/(2.0*CONST)
 DT2NUM=2.0*(ACOT-B1)*((DB2-C03ZERO*DB3)/(2.0*ACOT)-DB1)
 DT2DEN=2.0*C*((DB2-C03ZERO*DB3)/(2.0*ACOT)-DB1)+DC*(ACOT-B1)**2+B*
1((DB2-C03ZERO*DB3)/(2.0*ACOT)-DB1)+DB*(ACOT-B1)+DA
```

```
      DEXP2=(A*DB1-B1*DA)/A**2
      DT3NUM=2.0*C*((DB2-B3*DC03-CC(I)*DB3)/(2.0*ACOL)-DB1)+2.0*(ACOL-B1
     1)*DC+DB-(2.0*B*DB-4.0*A*DC-4.0*C*DA)/(2.0*CONST)
      DT3DEN=2.0*C*((DB2-B3*DC03-CC(I)*DB3)/(2.0*ACOL)-DB1)+2.0*(ACOL-B1
     1)*DC+DB+(2.0*B*DB-4.0*A*DC-4.0*C*DA)/(2.0*CONST)
      DT4NUM=2.0*(ACOL-B1)*((DB2-B3*DC03-CC(I)*DB3)/(2.0*ACOL)-DB1)
      DT4DEN=2.0*C*(ACOL-B1)*((DB2-B3*DC03-CC(I)*DB3)/(2.0*ACOL)-DB1)+DC
     1*(ACOL-B1)**2+B*((DB2-B3*DC03-CC(I)*DB3)/(2.0*ACOL)-DB1)+(ACOL-B1)
     2*DB+DA
      DFUNCT=((EXP11+EXP12)/T13)*((T1DEN*T3NUM*(T1NUM*DT3DEN+T3DEN*DT1NU
     1M)-T1NUM*T3DEN*(T2DEN*DT3NUM+T3NUM*DT1DEN))/(T1DEN*T3NUM)**2)+LOGF
     2(T13)*(DEXP11+DEXP12)+(EXP2/T24)*((T2DEN*T4NUM*(T2NUM*DT4DEN+T4DEN
     3*DT2NUM)-T2NUM*T4DEN*(T2DEN*DT4NUM+T4NUM*DT2DEN))/(T2DEN*T4NUM)**2
     4)+LOGF(T24)*DEXP2
      DFUNCK5B=DFUNCT
      DB1=0.0  $  DB2=0.0  $  DB3=0.0  $  DA=0.0  $  DB=0.0  $  DC=0.0
      DC03=1.0
      DEXP11=(4.0*A*DC+4.0*C*DA-2.0*B*DB)/(B**2-4.0*A*C)**1.5
```

```
 DEXP12=(B*B1*(A*(2.0*B*DB-4.0*A*DC-4.0*C*DA)/(2.0*CONST)+CONST*DA)
1-A*CONST*(B*DB1+B1*DB))/(A*CONST)**2
 DT1NUM=2.0*C*(DB2/(2.0*ACOT)-DB1)+2.0*DC*(ACOT-B1)+DB-(2.0*B*DB-4.
10*A*DC-4.0*C*DA)/(2.0*CONST)
 DT1DEN=2.0*C*(DB2/(2.0*ACOT)-DB1)+2.0*DC*(ACOT-B1)+DB+(2.0*B*DB-4.
10*A*DC-4.0*C*DA)/(2.0*CONST)
 DT2NUM=2.0*(ACOT-B1)*(DB2/(2.0*ACOT)-DB1)
 DT2DEN=2.0*C*(DB2/(2.0*ACOT)-DB1)+DC*(ACOT-B1)**2+B*(DB2/(2.0*ACOT
1)-DB1)+DB*(ACOT-B1)+DA
 DEXP2=(A*DB1-B1*DA)/A**2
 DT3NUM=2.0*C*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)+2.0*(ACOL-B1
1)*DC+DB-(2.0*B*DB-4.0*A*DC-4.0*C*DA)/(2.0*CONST)
 DT3DEN=2.0*C*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)+2.0*(ACOL-B1
1)*DC+DB+(2.0*B*DB-4.0*A*DC-4.0*C*DA)/(2.0*CONST)
 DT4NUM=2.0*(ACOL-B1)*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)
 DT4DEN=2.0*C*(ACOL-B1)*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)+DC
1*(ACOL-B1)**2+B*((DB2-B3*DCO3-CC(I)*DB3)/(2.0*ACOL)-DB1)+(ACOL-B1)
2*DB+DA
```

```
      DFUNCT=((EXP11+EXP12)/T13)*((T1DEN*T3NUM*(T1NUM*DT3DEN+T3DEN*DT1NU
     1M)-T1NUM*T3DEN*(T2DEN*DT3NUM+T3NUM*DT1DEN))/(T1DEN*T3NUM)**2)+LOGF
     2(T13)*(DEXP11+DEXP12)+(EXP2/T24)*((T2DEN*T4NUM*(T2NUM*DT4DEN+T4DEN
     3*DT2NUM)-T2NUM*T4DEN*(T2DEN*DT4NUM+T4NUM*DT2DEN))/(T2DEN*T4NUM)**2
     4)+LOGF(T24)*DEXP2
      DFUNCC03=DFUNCT
      AA(I,1)=DFUNCK4B/DFUNCC03   $   AA(I,2)=DFUNCK5A/DFUNCC03
      AA(I,3)=DFUNCK5B/DFUNCC03
  109 AA(I,4)=CX(I)-CC(I)
      DO 110 J=1,4
      DO 110 K=1,4
      M(J,K)=0
      DO 111 I=1,IMAX
      IF (KA(I).EQ.1) GO TO 111
      M(J,K)=M(J,K)+AA(I,J)*AA(I,K)
  111 CONTINUE
  110 CONTINUE
      DO 112 J=1,3,1
```

```
      DO 112 K=1,3,1
      BB(J,K)=M(J,K)
  112 CONTINUE
      CALL DTERM (NN,BB,D)
      IF (ABSF(D).LT.ABSF(DMIN)) GO TO 180
      DO 113 J=1,3,1
      DO 113 K=1,3,1
      BB(J,K)=M(J,K)
  113 CONTINUE
      DO 114 J=1,3,1
      BB(J,1)=M(J,4)
  114 CONTINUE
      CALL DTERM (NN,BB,D1)
      DO 115 J=1,3,1
      DO 115 K=1,3,1
      BB(J,K)=M(J,K)
  115 CONTINUE
      DO 116 J=1,3,1
```

```
      BB(J,2)=M(J,4)                                                      336
  116 CONTINUE                                                            337
      CALL DTERM (NN,BB,D2)                                               338
      DO 117 J=1,3,1                                                      338A
      DO 117 K=1,3,1                                                      339
      BB(J,K)=M(J,K)                                                      340
  117 CONTINUE                                                            341
      DO 118 J=1,3,1                                                      342
      BB(J,3)=M(J,4)                                                      343
  118 CONTINUE                                                            344
      CALL DTERM (NN,BB,D3)                                               345
      X4AOLD=X4A  $  X4BOLD=X4B  $  X4B=X4B+D1/(DD*D)  $  DK4B=D1/D       346
      X4A=7.2*10**6/X4B                                                   347-378
      X5AOLD=X5A  $  X5A=X5A+D2/(DD*D)  $  DK5A=D2/D                      379-381
      X5BOLD=X5B  $  X5B=X5B+D3/(DD*D)  $  DK5B=D3/D                      382
      PRINT 505,L                                                         383
  505 FORMAT(/,* ITERATION NO. *,I2,/)                                    384
      PRINT 508,D,X4AOLD,X4BOLD,X5AOLD,X5BOLD,DK4B,DK5A,DK5B,X4A,X4B,X5A  385
```

```
      1,X5B
  508 FORMAT (/,* DETERMINANT =*,E13.6,4X,*OLD K4A =*,E14.6,4X,*OLD K4B
      1=*,E14.6,4X,*OLD K5A =*,E14.6,4X,*OLD K5B =*,E14.6,/,61X,*DK4B =*,
      2E14.6,7X,*DK5A =*,E14.6,7X,*DK5B =*,E14.6,/,31X,*NEW K4A =*,E14.6,
      34X,*NEW K4B =*,E14.6,4X,*NEW K5A =*,E14.6,4X,*NEW K5B =*,E14.6)
       DDC1=0 $ DDC2=0 $ IM=0  $  LL=0
  126 DO 199 I=1,IMAX  $  IF (T(I).EQ.0.0)530,531
  530 ALIG=ALIGG(I)  $  TIME=T(I)  $  GO TO 533
  531 ALIG=(ALIGG(I)+ALIGG(I-1))/2.0  $  TIME=T(I)-T(I-1)
  533 CALL CO3CALC (X1,X2,X3,X4A,X4B,X5A,X5B,TIME)
      IF (LABORT.EQ.0) GO TO 1002
  190 DDC(I)=CX(I)*CC(I)  $  NT=T(I)
      IF (KA(I).EQ.1) GO TO 160
      DDC1=DDC1+ABSF(DDC(I))  $  DDC2=DDC2+DDC(I)**2  $  IM=IM+1
      IF(X1.LT.0..OR.X2.LT.0..OR.X3.LT.0..OR.X4A.LT.0..OR.X4B.LT.0..OR.X
     15A.LT.0..OR.X5B.LT.0.)198,550
  198 PRINT 197
  197 FORMAT (* *,* VALUES ARE NOT PRINTED SINCE ONE OR MORE OF THE SIX
```

```
   1CONSTANTS ARE NEGATIVE.*)
    GO TO 162
550 IF (IRUN(I).EQ.1.OR.IRUN(I).EQ.5)551,160
551 LL=LL+1
    PRINT 552, (R(LLL,I),LLL=1,10),CO(I),ALMRATIO(I),ALIGTRYY(I),CONCO
   1XYG(I),ALIGGR(I),LL
552 FORMAT (1H ,10A8,/,* TOTAL COBALT =*,E10.3,5X,*LIGAND TO METAL RAT
   1IO =*,F3,* TO 1*,5X,* INITIAL GUESS OF LIGAND CONC. =*,E13.3,/,* O
   2XYGEN CONC. =*,E10.3,5X,*LIGAND CONC. USED IN LEAST SQUARES CALC =
   3*,E10.3,/,* EXPERIMENTAL DATA SET NUMBER *,I3,*,*,/)
    PRINT 509
509 FORMAT (/,1X,3HFIT,2X,4HTIME,3X,8HDDC/DK4B,4X,8HDDC/DK5A,4X,8HDDC/
   1DK5B,4X,7HC(CALC),5X,6HC(EXP),4X,10HDIFFERENCE,4X,*NEW  COBALT 3*,
   2/,84X,* (LESS COBALT 3 ADDED INITIALLY)*,/)
160 CO3(I)=CC(I)*CO3ZERO(I)
    PRINT 510,KA(I),NT,AA(I,1),AA(I,2),AA(I,3),CC(I),CX(I),DDC(I),CO3(
   1I)
510 FORMAT (1X,I1,3X,I4,7(2X,E10.3))
```

```
199 CONTINUE
    DDC1=DDC1/IM $ DDC2=SQRTF(DDC2)/IM
    PRINT 511,DDC1,DDC2
511 FORMAT(/,25X,20HMEAN DEVIATION      =,E15.4,/,25X,20HSTANDARD DEVIA
   7TION =,E15.4,/)
    IF(ABSF(DK5A).LT.DXMAX6.AND.ABSF(DK5B).LT.DXMAX7)651,170
651 PRINT 652
652 FORMAT (* *,*THE ABOVE VALUES OF K1 TO K5B ARE THE CONVERGED VALUE
   1S.*)
    GO TO 1002
162 XX1=A1  $  XX2=A2  $  XX3=A3  $  XX4B=A4B+AD5
    XX4A=7.2*10**6/XX4B  $  XX5A=A5A+AD6  $  XX5B=A5B+AD7  $  X1=XX1
    X2=XX2  $  X3=XX3  $  X4A=XX4A  $  X4B=XX4B  $  X5A=XX5A
    X5B=XX5B  $  A1=X1  $  A2=X2  $  A3=X3  $  A4A=X4A  $  A4B=X4B
    A5A=X5A  $  A5B=X5B
    PRINT 164,X1,X2,X3,X4A,X4B,X5A,X5B
164 FORMAT(* *,*X1 =*,E11.3,*   X2 =*,E11.3,*   X3 =*,E11.3,*   X4A =*
   1,E11.3,*   X4B =*,E11.3,*   X5A =*,E11.3,*   X5B =*,E11.3)
```

```
      IF(X1.LT.0..OR.X2.LT.0..OR.X3.LT.0..OR.X4A.LT.0..OR.X4B.LT.0..OR.X
     15A.LT.0..OR.X5B.LT.0.)750,128
  750 PRINT 752
  752 FORMAT(* *,*THIS CALCULATION IS BEING ABORTED SINCE THE CORRECTION
     1 TERMS PRODUCES A NEGATIVE CONSTANT.*)
      GO TO 1002
  128 DO 163 I=1,IMAX  $  IF (T(I).EQ.0.0)534,535
  534 ALIG=ALIGG(I)  $  TIME=T(I)  $  GO TO 536
  535 ALIG=(ALIGG(I)+ALIGG(I-1))/2.0  $  TIME=T(I)-T(I-1)
  536 CALL CO3CALC (X1,X2,X3,X4A,X4B,X5A,X5B,TIME)
      IF (LABORT.EQ.0) GO TO 1002
  163 CONTINUE
  170 CONTINUE
      PRINT 512,LMAX
  512 FORMAT(/,1X,I2,* ITERATIONS WITHOUT CONVERGENCE*,/)
      GO TO 1002
  180 PRINT 513,D
  513 FORMAT(/,* THE DETERMINANT IS TOO SMALL*,/,* D =*,E15.6,/)
```

```
      GO TO 1002                                                      446
 1000 IF (L.EQ.0)1003,1002                                            447
 1003 READ 1001,KA(I),T(I),CXX(I)                                     448
 1001 FORMAT (I1,F4.0,E15.0)                                          449
      IF (KA(I).EQ.1)GO TO 1003                                       450
      READ 500, (R(LLL,I),LLL=1,10)                                   451
      READ 227, ALMRATIO(I),CO(I),ALIGTRYY(I),CONCOXYG(I),CO3ZERO(I)  451A
      IF (ALMRATIO(I).EQ.0.0)1002,1003                                452
 1002 CONTINUE                                                        453
      END                                                             454
```

To convert "Derivg" to "Derivh" the following computer cards must be changed: (the numbers at the right are for identification only)

```
B  =A5A/(2.0*A4B)-4.0*A5B*A4A*B1/B3 $ C=A5B/((-4.0)*A4B)    75-76
DB= (A5B*B1-A5A)/(2.0*A4B**2)                                87
DB1=0.0 $ DB2=0.0 $ DB3=0.0 $ DA=0.0 $ DB=1.0/(2.0*A4B)     112.
```

```
      SUBROUTINE DTERM (NN,A,D)
      COMMON T(500),CC(500),CX(500),LABORT,I,LTEST,ALIG,A1H,A2H,A3H,HCON
     1C,N,ALIGGESS(11),ALIGG(500),ALMRATIO(500),R(10,500),L,CONCOXYG(500
     2),LL,CO(500),CO3ZERO(500),CXX(500),CO2(500),COL(500),COL2(500),COL
     3202(500),COL2202(500)
      DIMENSION A(3,3)
C      EVALUATION OF A 3 BY 3 DETERMINANT.
      D=1.
   10 DO 34 MM=1,NN
      KP=0
      Z=0.0
      DO 12 K=MM,NN
      IF (Z-ABSF(A(K,MM)))11,12,12
   11 Z=ABSF(A(K,MM))
      KP=K
   12 CONTINUE
      IF (MM-KP)13,20,20
   13 DO 14 J=MM,NN
```

```
      Z=A(MM,J)
      A(MM,J)=A(KP,J)
   14 A(KP,J)=Z
      D=-D
   20 IF (MM-NN)31,40,40
   31 LP1=MM+1
      DO 34 K=LP1,NN
      IF (A(K,MM))32,34,32
   32 RATIO=A(K,MM)/A(MM,MM)
      DO 33 J=LP1,NN
   33 A(K,J)=A(K,J)-RATIO*A(L,J)
   34 CONTINUE
   40 DO 41 K=1,NN
   41 D=D*A(K,K)
      RETURN
      END
```

```
      SUBROUTINE ALIGCALC (A1,A2,A3,A4A,A4B,A5A,A5B)                     1
      COMMON T(500),CC(500),CX(500),LABORT,I,LTEST,ALIG,A1H,A2H,A3H,HCON 2
     1C,N,ALIGGESS(11),ALIGG(500),ALMRATIO(500),P(10,500),L,CONCOXYG(500 2A
     2),LL,CO(500),CO37ERO(500),CXX(500),CO2(500),COL(500),COL2(500),COL 2B
     3202(500),COL2202(500)                                               3
C     ONLY FOR A LIGAND TO METAL RATIO OF EQUAL TO OR GREATER THAN 2 TO 1,
C     ONLY FOR A LIGAND TO METAL RATIO OF EQUAL TO OR GREATER THAN 2 TO 1,
C     ONLY FOR A LIGAND TO METAL RATIO OF EQUAL TO OR GREATER THAN 2 TO 1,
      IF (ALMRATIO(I).LT.2.0)14,13                                       3A
   14 PRINT 15                                                           3B
   15 FORMAT (* *,* THERE IS AN ERROR IN THE VALUE OF THE LIGAND TO META 3C
     1L RATIO,*)                                                         3D
      GO TO 3                                                            3E
   13 DO 1 N=1,10,1                                                      4
      D=1.0/(A1*A2*ALIGGESS(N)**2)+1.0/(A2*ALIGGESS(N))+1.0+A3*ALIGGESS( 5
     1N)+A4A*CONCOXYG(I)                                                 6
      ACOL=SQRTF(D**2+8.0*A4A*A4B*CONCOXYG(I)*(CO(I)-CXX(I)))            7
      E=ALMRATIO(I)/(A1*A2*ALIGGESS(N)**2)+(ALMRATIO(I)-1.0)/(A2*ALIGGES 8
```

```
1S(N))+ALMRATIO(I)-2.0+(ALMRATIO(I)-3.0)*A3*ALIGGESS(N)+(ALMRATIO(I      9
2)-2.0)*A4A*CONCOXYG(I)                                                   9A
 AH=1.0+A1H*HCONC+A1H*A2H*HCONC**2+A1H*A2H*A3H*HCONC**3                   10
 G=(ALMRATIO(I)-3.0)*A3-2.0*ALMRATIO(I)/(A1*A2*ALIGGESS(N)**3)-(ALM       11
1RATIO(I)-1.0)/(A2*ALIGGESS(N)**2)                                        12
 F=2.0/(A1*A2*ALIGGESS(N)**3)+1.0/(A2*ALIGGESS(N)**2)-A3                  13
 FLIG=(ACOL-D)*E/(4.0*A4A*CONCOXYG(I)*A4B)+((ACOL-D)/(4.0*A4A*CONCO       14
1XYG(I)*A4B))**2*(2.0*ALMRATIO(I)-4.0)*A4A*CONCOXYG(I)*A4B+(ALMRATI       15
2O(I)-2.0)*CXY(I)-ALIGGESS(N)*AH                                          15A
 DFLIG=G*(ACOL-D)/(4.0*A4A*CONCOXYG(I)*A4B)+E*(F/(4.0*A4A*CONCOXYG(       16
1I)*A4B)-D*F/(4.0*A4A*CONCOXYG(I)*A4B*ACOL))+(ALMRATIO(I)-2.0)*(ACO       17
2L-D)*(F-D*F/ACOL)/(4.0*A4A*CONCOXYG(I)*A4B)-AH                           17A
 ALIGGESS(N+1)=ALIGGESS(N)-FLIG/DFLIG                                     18
 IF (LTEST.EQ.2.OR.LTEST.EQ.1.AND.L.GT.0)16,10                            19
16 PRINT 11,N,ALIGGESS(N),ALIGGESS(N+1)                                   20
11 FORMAT(* *,*N =*,I3,5X,*OLD GUESS OF LIGAND CONC. =*,E11.3,5X,*NEW     21
 1 GUESS OF LIGAND CONC. =*,E11.3)                                        22
10 ADIFRAT1=(ALIGGESS(N+1)-ALIGGESS(N))/ALIGGESS(N)                       23
```

```
      ADIFRAT2=(ALIGGESS(N+1)-ALIGGESS(N))/ALIGGESS(N+1)
      IF(ABSF(ADIFRAT1).LT.(0.001*ALIGGESS(N)).AND.ABSF(ADIFRAT2).LT.(0.
     1001*ALIGGESS(N+1))) 18,1
   18 ALIGG(I)=ALIGGESS(N+1)   $   GO TO 3
    1 CONTINUE
      PRINT 2
    2 FORMAT (* *,*THIS PROGRAM IS BEING ABORTED SINCE THE LIGAND CONCEN
     1TRATION CANNOT BE CALCULATED.*)
      LABORT=0   $   GO TO 4
    3 LABORT=1
    4 CONTINUE
      RETURN
      END

      SUBROUTINE C^3CALC(A1,A2,A3,A4A,A4B,A5A,A5B,TIME)
      COMMON T(500),CC(500),CX(500),LABORT,I,LTEST,ALIG,A1H,A2H,A3H,HCON
     1C,N,ALIGGESS(11),ALIGG(500),AL^MRATIO(500),R(10,500),L,CONCOXYG(5^0
```

```
  2),LL,CO(500),CO3ZERO(500),CXX(500),CO2(500),COL(500),COL2(500),COL     2B
  3202(500),COL2202(500)                                                  3
   IF (T(I).EQ.0.)98,99                                                   4
 98 CC(I)=CO3ZERO(I)  $  GO TO 200                                        5
 99 B1=1.0/(A1*A2*ALIG**2)+1.0/(A2*ALIG)+1.0+A3*ALIG+A4A*CONCOXYG(I)      6
   B3=8.0*A4A*A4B*CONCOXYG(I)  $  B2=B1**2+B3*(CO(I)+CO3ZERO(I))          7
   CC(I)=CX(I)  $  KK=0  $  ACOTSQ=B2-B3*CC(I-1)                          8
   CH=0.0  $  CHA=0.0  $  MULT=0  $  ACOLSQ=B2-B3*CC(I)                   8A
   IF (ACOTSQ)400,405,405                                                 8B
400 PRINT 401, ACOTSQ,B1,B2,CO(I)                                         9
401 FORMAT (* *,*ACOT SQUARED =*,E15.6,5X,*B1 =*,E15.6,5X,*B2 =*,E15.6    10
  1,5X,*CO =*,E15.6,/,* THIS PROGRAM IS BEING ABORTED SINCE ACOT SQUA     11
  2RED IS NEGATIVE.*,39X,*CO3CALC CARD 12*)                               12
   GO TO 250                                                              13
405 IF (ACOLSQ)406,410,410                                                14
406 PRINT 402, ACOTSQ,ACOLSQ,B1,B2,B3,CO(I),CC(I)                         15
402 FORMAT (* *,*ACOT SQUARED =*,E15.6,5X,*ACOL SQUARED =*,E15.6,5X,*B    16
  11 =*,E15.6,/,* B2 =*,E15.6,5X,*B3 ,*,E15.6,5X,*CO =*,E15.6,/,* CC(     17
```

```
   2I) =*,E15.6,*THIS PROGRAM IS BEING ABORTED SINCE THE SQUARE ROOT I      18
   3S IMAGINARY,*,13X,*CO3CALC CARD 19*)                                    19
    GO TO 250                                                               20
410 C=A5B/((-4.0)*A4B)  $  ACOL=SQRTF(ACOLSQ)                               21
    A=2.0*A4A*CONCCXYG(I)*A5B*(CO(I)+CO3ZERO(I))                            21A
    B=A5A/2.0*A5B*B1/(2.0*A4B)  $  CONSTSQ=B**2-4.0*A*C                     21B
    ACOT=SQRTF(ACOTSQ)  $  IF (CONSTSQ)411,413,413                          21C
411 PRINT 412,A,C,B,CONSTSQ                                                 21D
412 FORMAT (* *,*A =*,E11.3,5X,*C =*,E11.3,5X,*B =*,E11.3,5X,*CONSTSQ       21E
   1=*,E11.3,/,* THIS PROGRAM IS BEING ABORTED SINCE THE SQUARE ROOT I      21F
   2S IMAGINARY,*,35X,*CO3CALC CARD 21G*)                                   21G
    GO TO 250                                                               21H
413 CONST=SQRTF(B**2-4.0*A*C)  $  U1=TIME                                   22
    U2 =(2.0/CONST-B*B1/(A*CONST))*LOGF(((2.0*C*(ACOT-B1)+B-CONST)/(2.      23
   1*C*(ACOT-B1)+B+CONST))/((2.*C*(ACOL-B1)+B-CONST)/(2.0*C*(ACOL-B1)+      23A
   2B+CONST)))+(B1/A)*LOGF(((ACOT-B1)**2/(C*(ACOT-B1)**2+B*(ACOT-B1)+A      23B
   3))/((ACOL-B1)**2/(C*(ACOL-B1)**2+B*(ACOL-B1)+A)))                       23C
    IF (L.EQ.0)504,501                                                      23D
```

```
 504 IF EXPONENT FAULT 500,501                                              23DA
 500 PRINT 503                                                              23E
 503 FORMAT (* THERE IS EITHER AN EXPONENT UNDERFLOW OR EXPONENT OVERFL     23F
    1OW IN THE CALCULATIONS FOR THE NEXT DATA POINT.*,/,* THEREFORE THI     23G
    2S DATA SET IS BEING ABORTED.*)                                         23H
     LABORT=2  $  GO TO 201                                                 23I
 501 UDIFF=U2-U1  $  CHANGE=1.0  $  LSTEP=24                                24
     IF (LTEST.EQ.2.OR.LTEST.EQ.1.AND.L.GT.0)2007,482                       25
2007 PRINT 2000,CC(I),U1,U2,UDIFF,KK,LSTEP                                  26
2000 FORMAT(* *,*  CC(I) =*,E15.6,5X,*U1  =*,E15.6,5X,*U2  =*,E15.6,5X,     27
    1*UDIFF  =*,E15.6,5X,*KK =*,I3,5X,*STATEMENT NO.*,I3)                   28
 482 IF(UDIFF)100,300,101                                                   29
 100 LSIGN=(-1)  $  GO TO 102                                               30
 101 LSIGN=1                                                                31
 102 CC(I)=CC(I)*10.                                                        32-34
     IF (CC(I).GT.(CO(I)+CO3ZERO(I)))600,475                                35
 600 MULT=1 $ MM=0 $ CC(I)=CC(I)/10.0 $ ADD=1.0 $ AD=1.0 $ CCC=CC(I)       36
 601 CC(I)=CC(I)+CCC*ADD/10.**AD                                            37
```

```
    IF (CC(I).GT.(CO(I)+CO3ZERO(I)))602,603                              38
602 CC(I)=CC(I)-CCC*ADD/10.0**AD $ AD=AD+1.0 $ MM=MM+1 $ CCC=CC(I)       39
    IF (CC(I).GT.(0.999*(CO(I)+CO3ZERO(I))).AND.CC(I).LT.(CO(I)+CO3ZER   40
   1O(I)))625,601                                                        40A
603 ACOLSQ=B2-B3*CC(I)                  $  IF(ACOLSQ)415,414,414         40B
415 PRINT 416, ACOLSQ,CO(I),CC(I),B2,B3                                  40B
416 FORMAT (* ACOL SQUARED =*,E15.6,5X,*CO =*,E15.6,5X,*CC(I) =*,E15.6   40C
   1,/,* B2 =*,E15.6,5X,*B3 =*,E15.6,57X,*CO3CALC CARD 40D*)             40D
    GO TO 250                                                            40E
414 ACOL=SQRTF(ACOLSQ)  $  UA1=TIME                                      41
    UA2=(2.0/CONST-B*B1/(A*CONST))*LOGF(((2.0*C*(ACOT-B1)+B-CONST)/(2.   42
   1*C*(ACOT-B1)+B+CONST))/((2.*C*(ACOL-B1)+B-CONST)/(2.0*C*(ACOL-B1)+   42A
   2B+CONST)))+(B1/A)*LOGF(((ACOT-B1)**2/(C*(ACOT-B1)**2+B*(ACOT-B1)+A   42B
   3))/((ACOL-B1)**2/(C*(ACOL-B1)**2+B*(ACOL-B1)+A)))                    42C
    IF (L.EQ.0)505,506                                                   42D
505 IF EXPONENT FAULT 507,506                                            42E
507 PRINT 503                                                            42F
    LABORT=2  $  GO TO 211                                               42G
```

```
506 UADIFF=UA2-UA1  $  MM=MM+1                                        43
    IF (LTEST.EQ.2.OR.LTEST.EQ.1.AND.L.GT.0)617,616                  43A
617 PRINT 609,CC(I),UA1,UA2,UADIFF,AD,ADD,MM                          44
609 FORMAT(* *,*CC(I) =*,E14.6,3X,*UA1 =*,E14.6,3X,*UA2 =*,E14.6,3X,*U   45
   1ADIFF =*,E14.6,3X,*AD =*,F5.1,3X,*ADD =*,F5.1,3X,*MM =*,I4)      46
610 IF (UADIFF)604,300,605                                            47
604 LSIGNA=(-1) $ GO TO 606                                           48
605 LSIGNA=1                                                          49
606 IF (LSIGN.EQ.LSIGNA)607,608                                       50
608 CHA=AD  $  GO TO 120                                              51
607 IF (ABSF(UDIFF).LT.ABSF(UADIFF))113,616                           52
616 U1=UA1 $ U2=UA2 $ UDIFF=UADIFF $ LSIGN=LSIGNA                     53
    IF (AD.GT.10.)611,613                                             54
611 PRINT 612                                                         55
612 FORMAT(* *,*THE EXPONENT IS GREATER THAN 10 INDICATING THAT SOMETH   56
   1ING IS WRONG.*)                                                   57
    GO TO 250                                                         58
613 IF (MM.GT.100)614,601                                             59
```

```
614 PRINT 615                                                              60
615 FORMAT(* *,*MM IS GREATER THAN 100 INDICATING THAT THE CALCULATION     61
   1S ARE TRAPPED IN A LOOP, THEREFORE, THE CALCULATIONS ARE BEING ABO     62
   2RTED,*)                                                                63
    GO TO 250                                                              64
475 ACOLSQ=B2-B3*CC(I)                   $  IF(ACOLSQ)418,417,417          64A
418 PRINT 419, ACOLSQ,CO(I),CC(I),B2,B3                                    64B
419 FORMAT (* ACOL SQUARED =*,E15.6,5X,*CO =*,E15.6,5X,*CC(I) =*,E15.6     64C
   1,/,* B2 =*,E15.6,5X,*B3 =*,E15.6,57X,*CO3CALC CARD 64D*)               64D
    GO TO 250                                                              64E
417 ACOL=SQRTF(ACOLSQ)   $  UA1=TIME                                       65
    UA2=(2.0/CONST-B*B1/(A*CONST))*LOGF(((2.0*C*(ACOT-B1)+B-CONST)/(2.     66
   1*C*(ACOT-B1)+B+CONST))/((2.0*C*(ACOL-B1)+B-CONST)/(2.0*C*(ACOL-B1)+    66A
   2B+CONST)))+(B1/A)*LOGF(((ACOT-B1)**2/(C*(ACOT-B1)**2+B*(ACOT-B1)+A     66B
   3))/((ACOL-B1)**2/(C*(ACOL-B1)**2+B*(ACOL-B1)+A)))                      66C
    IF (L.EQ.0) 508,509                                                    66D
508 IF EXPONENT FAULT 510,509                                              66E
510 PRINT 503                                                              66F
```

```
      LABORT=2  $  GO TO 201
  509 LSTEP=67  $  MULT=1  $  UADIFF=UA2-UA1  $  KK=KK+1
      IF (LTEST.EQ.2.OR.LTEST.EQ.1.AND.L.GT.0)2009,483
 2009 PRINT 2001,CC(I),UA1,UA2,UADIFF,KK,LSTEP
 2001 FORMAT(* *,*  CC(I) =*,E15.6,5X,*UA1 =*,E15.6,5X,*UA2 =*,E15.6,5X,
     1*UADIFF =*,E15.6,5X,*KK =*,I3,5X,*STATEMENT NO.*,I3)
  483 IF(UADIFF)103,300,104
  103 LSIGNA=(-1) $ GO TO 105
  104 LSIGNA=1
  105 IF(LSIGNA.EQ.LSIGN)106,120
  106 IF(ABSF(UADIFF).LT.ABSF(UDIFF))107,113
  107 CHANGE=CHANGE+1. $ U1=UA1 $ U2=UA2 $ UDIFF=UADIFF $ LSIGN=LSIGNA
      IF(CHANGE.GT.5.)108,110
  108 PRINT 109,CC(I)
  109 FORMAT(* *,*THE CALCULATED VALUE OF COBALT THREE IS GREATER THAN*,
     1E10.3,*THEREFORE THE GUESSES OF A1,A3,A4 ARE NOWHERE NEAR THE CORR
     2ECT VALUES.*,//)
      GO TO 250
```

```
110 IF (KK.GT.300)111,102
111 PRINT 112
112 FORMAT(* *,*THERE ARE MORE THAN 300 ITERATIONS IN CALCULATING THIS
   1 VALUE OF COBALT 3 INDICATING THAT THE CALCULATIONS ARE TRAPPED IN
   2 A LOOP,*,/,* *,*THEREFORE THE CALCULATION IS BEING ABORTED,*)
    GO TO 250
113 CHANGE=1.
114 U1=UA1 $ U2=UA2 $ UDIFF=UADIFF $ LSIGN=LSIGNA
    CC(I)=CC(I)/10.  $  MULT=(-1)  $  KK=KK+1
    ACOLSQ=B2-B3*CC(I)                    $  IF(ACOLSQ)445,450,450
445 PRINT 446,ACOLSQ,CO(I),CC(I),B2,B3
446 FORMAT (* ACOL SQUARED =*,E15.6,5X,*CO =*,E15.6,5X,*CC(I) =*,E15.6
   1,/,* B2 =*,E15.6,5X,*B3 =*,E15.6,57X,*CO3CALC CARD 95A*)
    GO TO 250
450 ACOL=SQRTF(ACOLSQ)  $  UA1=TIME
    UA2=(2.0/CONST-B*B1/(A*CONST))*LOGF(((2.0*C*(ACOT-B1)+B-CONST)/(2.
   1*C*(ACOT-B1)+B+CONST))/((2.*C*(ACOL-B1)+B-CONST)/(2.0*C*(ACOL-B1)+
   2B+CONST)))+(B1/A)*LOGF(((ACOT-B1)**2/(C*(ACOT-B1)**2+B*(ACOT-B1)+A
```

```
      3))/((ACOL-B1)**2/(C*(ACOL-B1)**2+B*(ACOL-B1)+A)))                101-102
      IF (L.EQ.0)512,513                                                102A
  512 IF EXPONENT FAULT 514,513                                         102B
  514 PRINT 503                                                         102C
      LABORT=2  $  GO TO 201                                            102D
  513 UADIFF=UA2-UA1  $ LSTEP=103                                       103
      IF (LTEST.EQ.2.OR.LTEST.EQ.1.AND.L.GT.0)2010,484                  104
 2010 PRINT 2001,CC(I),UA1,UA2,UADIFF,KK,LSTEP                          105
  484 IF(UADIFF)115,300,116                                             106
  115 LSIGNA=(-1) $ GO TO 117                                           107
  116 LSIGNA=1                                                          108
  117 IF(LSIGNA.EQ.LSIGN)118,120                                        109
  118 CHANGE=CHANGE+1. $ U1=UA1 $ U2=UA2 $ LSIGN=LSIGNA $ UDIFF=UADIFF   110
      IF(CHANGE.GT.5.)108,119                                           111
  119 IF (KK.GT.300)111,114                                             112
  120 CH=1.                                                             113
  121 CHA=CHA+1.                                                        114
  122 CHANGEA=CC(I)*CH/1?.**CHA                                         115
```

```
      IF(MULT)123,123,124                                                116
123   COL2PLA=CC(I)+CHANGEA $ GO TO 125                                  117
124   COL2PLA=CC(I)-CHANGEA                                              118
125   IF (COL2PLA.GT.(CO(I)+CO3ZERO(I)).AND.MULT.EQ.(-1))619,618         119
619   COL2PLA=CC(I)-CHANGEA  $  GO TO 120                                120
618   U1=UA1 $ U2=UA2 $ UDIFF=UADIFF $ LSIGN=LSIGNA                      121
      IF (COL2PLA.LT.(CO(I)+CO3ZERO(I)).AND.COL2PLA.GT.(0.999*(CO(I)+CO3  121A
     1ZERO(I))))GO TO 625                                                121B
      ACOLSQ=B2-B3*COL2PLA                  $  IF(ACOLSQ)465,470,470     122
625   CC(I)=CO(I)+CO3ZERO(I)  $  UA2=TIME  $  GO TO 200                  122A
465   PRINT 466,ACOLSQ                                                   123
466   FORMAT (* *,*ACOL SQUARED =*,E15.6)                                124
      GO TO 250                                                          125
470   ACOL=SQRTF(ACOLSQ)  $  UA1=TIME                                    126
      UA2=(2.0/CONST-B*B1/(A*CONST))*LOGF(((2.0*C*(ACOT-B1)+B-CONST)/(2.  127
     1*C*(ACOT-B1)+B+CONST))/((2.*C*(ACOL-B1)+B-CONST)/(2.0*C*(ACOL-B1)+  128
     2B+CONST)))+(B1/A)*LOGF(((ACOT-B1)**2/(C*(ACOT-B1)**2+B*(ACOT-B1)+A  129
     3))/((ACOL-B1)**2/(C*(ACOL-B1)**2+B*(ACOL-B1)+A)))                  129A
```

```
      IF (L.EQ.0)515,516
  515 IF EXPONENT FAULT 517,516
  517 PRINT 503
      LABORT=2  $  GO TO 201
  516 UADIFF=UA2-UA1 $ LSTEP=130
      IF (LTEST.EQ.2.OR.LTEST.EQ.1.AND.L.GT.0)2011,485
 2011 PRINT 2002,COL2PLA,UA1,UA2,UADIFF,KK,LSTEP
 2002 FORMAT(* *,*COL2PLA =*,E15.6,5X,*UA1 =*,E15.6,5X,*UA2 =*,E15.6,5X,
     1*UADIFF =*,E15.6,5X,*KK =*,I3,5X,*STATEMENT NO.*,I3)
  485 IF(ABSF(UADIFF-UDIFF).LT.ABSF(.0001*UDIFF).AND.ABSF(UADIFF-UDIFF).
     1LT.ABSF(.0001*UADIFF).AND.ABSF(COL2PLA-CC(I)).LT.ABSF(.0001*(CC(I)
     1-CO3ZERO(I))))GO TO 300
      IF(UADIFF)126,300,127
  126 LSIGNA=(-1) $ GO TO 128
  127 LSIGNA=1
  128 KK=KK+1
      IF (KK.GT.300)111,129
  129 CC(I)=COL2PLA
```

```
      IF(LSIGN.EQ.ISIGNA)130,131                                          144
  130 CH=CH+1. $ GO TO 122                                                145
  131 MULT=(-1)*MULT $ GO TO 120                                          146
  300 IF(KK.GT.20.AND.ABSF(UADIFF-UDIFF).LT..001*UDIFF.AND.ABSF(UADIFF-U  147
     1DIFF).LT..001*UADIFF.AND.ABSF(COL2PLA-CC(I)).LT..0001*(CC(I)-CO3ZE  148
     1RO(I)))200,301                                                      148A
  301 IF (ABSF(UADIFF).LT.5.0*10.**(-6))200,302                           149
  302 PRINT 303                                                           150
  303 FORMAT(* *,*UDIFF OR UADIFF IS EQUAL TO ZERO.*)                     151
  250 LABORT=0  $  GO TO 201                                              152
  200 LABORT=1                                                            153
  201 CONTINUE                                                            154
      RETURN                                                              155
      END                                                                 156
```

To convert this subroutine to derivation H, the following computer card must be changed:

B = A5A/(2.0*A4B)-4.0*A5B*A4A*B1 B3   21B.

```
SUBROUTINE CABLTCLC (A1,A2,A3,A4A,A4B,A5A,A5B)                              1
COMMON T(500),CC(500),CX(500),LABORT,I,LTEST,ALIG,A1H,A2H,A3H,HCON          2
1C,N,ALIGGESS(11),ALIGG(500),ALMRATIO(500),R(10,500),L,CONCOXYG(500         2A
2),LL,CO(500),CO3ZERO(500),CXX(500),CO2(500),COL(500),COL2(500),COL         2B
3202(500),COL2202(500)                                                      3
AC=2.0*A4A*A4B*CONCOXYG(I)*ALIGG(I)**4*(A1*A2)**2                           4
BC=1.0+A1*ALIGG(I)+A1*A2*ALIGG(I)**2+A1*A2*A4A*CONCOXYG(I)*ALIGG(I          5
1)**2                                                                       5A
CCC=CX(I)-CO(I)-CO3ZERO(I)                                                  5B
CO2(I)=((-BC)+SQRTF(BC**2-4.0*AC*CCC))/(2.0*AC)                             6
COL(I)=A1*CO2(I)*ALIGG(I)  $  COL2(I)=COL(I)*A2*ALIGG(I)                    7
COL202(I)=A4A*CONCOXYG(I)*COL2(I)                                           8
COL2202(I)=A4B*COL202(I)*COL2(I)                                            8A
RETURN                                                                      9
END                                                                         10
```