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KINETICS AND MECHANISMS OF THE REACTIONS OF ALIPHATIC FREE RADICALS WITH ORGANOCOBALOXIMES AND FLUOROPENTAAMMINECOBALT(III) ION, AND OF IRON(III) WITH METHYLRHODOXIME

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

GENERAL INTRODUCTION

The kinetic and mechanistic studies presented in this dissertation pertain to the reactions of selected free radicals with two distinct types of cobalt(III) complexes. The coupling reaction between free radicals and alkyl(bis-dimethylglyoximato)cobalt(III) complexes, $RCo(dmgH)_2OH_2$, where R = benzyl, methyl, ethyl, and isopropyl, is the subject of Part I. This coupling reaction is illustrated, for the reaction between $\cdot C(CH_3)_2OH$ radical and $PhCH_2Co(dmgH)_2OH_2$, by Equation 1.

$$\cdot C(CH_3)_2OH + PhCH_2Co(dmgH)_2OH_2 \rightarrow PhCH_2C(CH_3)_2OH + Co^{II}(dmgH)_2OH_2 \quad (1)$$

This work represents the first report of such reactions as well as a kinetic study of them. In addition, this is the first kinetic study dealing with reactions of the α-ethoxyethyl radical obtained non-radiolytically. In Part II, the reduction of the inorganic complex fluoropentaamminecobalt(III), $Co(NH_3)_5F^{2+}$, by 2-hydroxy-2-propyl and α-ethoxyethyl radicals is examined. A detailed discussion of previously published work concerning the complexation of iron(III) ions by methyl(aquo)bis(dimethylglyoximato)rhodium(III), $CH_3Rh(dmgH)_2OH_2$, (1) will not be included, however, an abstract of the published paper appears in the Appendix.

The balance of this introduction consists of information of a general nature, pertinent to both sections. Background information concerning the methods employed in these studies is presented. Material more directly pertinent to the individual studies is given in the introductions to Parts I and II.

Kinetic studies involving the radicals 2-hydroxy-2-propyl, $\cdot C(CH_3)_2OH$, and α-ethoxyethyl, $\cdot CH(CH_3)OC_2H_5$, comprise the bulk of this dissertation. Reactions of these radicals with cobalt(III) amine complexes (2-10), inorganic macrocyclic cobalt(III) complexes (11), and other inorganic complexes of cobalt(III) (12, 13) have been extensively studied. With the exception of the reduction of $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ in strongly acidic solution by $\cdot C(CH_3)_2OH$ radical (10), these kinetic studies have all relied upon pulse radiolysis for generation of the desired radical.

Although pulse radiolysis is an extremely powerful tool for the direct determination of rate constants for radical reactions it does, however, have two serious disadvantages which limit its applicability. The first, and probably more important, is the limitation of pulse radiolysis to only the most reactive systems. The pulse radiolysis experiment generates a burst of radical at sufficiently high concentration to allow direct monitoring. This concentration is typically on the order of 10^{-5}M. At these high radical concentrations, self-reaction, which occurs with rate constants near the diffusion controlled limit, becomes a major contribution to the radical decay and hence only species whose reactions with the radical are sufficiently rapid to compete with the self-reaction are capable of being investigated. Considering the detection limits, the rates of radical self-reaction, and the practical substrate concentrations, this places a threshold limit of approximately 3×10^6 $M^{-1}s^{-1}$, upon any rate constant for a reaction between an aliphatic free radical and a cobalt(III) complex directly observable by pulse

radiolysis. An important case in point involves the reduction of $Co(NH_3)_6^{3+}$ by $\cdot C(CH_3)_2OH$, Equation 2.

$$Co(NH_3)_6^{3+} + \cdot C(CH_3)_2OH \rightarrow Co(NH_3)_6^{2+} + (CH_3)_2CO + H^+ \quad (2)$$

Pulse radiolytic kinetic data have been reported in the pH 4.5-12 region, however, at lower pH the reaction becomes too slow to monitor directly using pulse radiolysis (4). Yields of Co^{2+} produced, as expected from reaction 2, during continuous radiation experiments (4, 14) were used to establish the continued occurrence of reaction 2, but at a rate too low to monitor directly. Basically, the two experiments differ only in the concentration attained by the radical. The steady state concentration produced during continuous radiation is far lower than in the pulse, thereby allowing the radical to react with the cobalt(III) species, instead of with itself. The second major disadvantage of pulse radiolysis, for the present, involves the specialized equipment necessary to generate and monitor radicals pulse radiolytically, limiting these studies to a handful of laboratories possessing such specialized equipment.

Recently, a method of chemically generating the 2-hydroxy-2-propyl radical, free of the difficulties encountered in the pulse radiolytic experiment, from homolytic decomposition of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ has been developed (10, 15).

Organochromium(III) cations of the general formula $(H_2O)_5CrR^{2+}$, henceforth abbreviated CrR^{2+}, have been extensively studied. In 1957, Anet and Leblanc (16) reported the first preparation of a member of this family of organochromium species, benzylchromium(III), $CrCH_2Ph^{2+}$. The list of well-characterized species now includes; alkyls (R = CH_3,

CH_2CH_3, $CH(CH_3)_2$, etc.), haloalkyls (R = CH_2Cl, $CHCl_2$, CF_3, etc.), arylalkyls (R = CH_2Ph^{2+}, $CH_2C_6H_4$-m-CH_3, etc.), alkoxyalkyls (R = CH_2OCH_3, $CH(CH_3)OC_2H_5$), and hydroxyalkyls (R = CH_2OH, $CH(CH_3)OH$, $C(CH_3)_2OH$, etc.). The chemistry of this class of compounds has recently been reviewed (17, 18), and will not be elaborated upon here. With rare exception, the key step in the synthesis of organochromium cations involves the generation of an organic radical in the presence of $Cr^{2+}(aq)$.

$$\cdot R + Cr^{2+}(aq) \rightarrow CrR^{2+} \qquad (3)$$

Homolysis of the carbon-chromium bond to form R· and $Cr^{2+}(aq)$, simply the reverse of the reaction from which the organochromium was prepared, has

$$CrR^{2+} \rightarrow Cr^{2+}(aq) + \cdot R \qquad (4)$$

been definitely established for several $(H_2O)_5CrR^{2+}$ complexes. Its importance, relative to nonradical decomposition, as well as the magnitude of the rate constant for homolytic cleavage depend greatly upon the electronic and steric nature of the ligand R. For example, homolysis is the major pathway leading to decomposition of $CrC(CH_3)_2OH^{2+}$, in the presence of oxidants. A kinetic investigation (15) of the reaction of $CrC(CH_3)_2OH^{2+}$ with a variety of oxidants such as Cu^{2+}, Fe^{3+}, H_2O_2, VO^{2+}, and $Co(NH_3)_5X^{2+}$, where X = Br, Cl, F, in aqueous perchloric acid, gave a rate law first order in $[CrC(CH_3)_2OH^{2+}]$ and independent of the nature and concentration of the oxidant.

$$\frac{-d[CrC(CH_3)_2OH^{2+}]}{dt} = k[CrC(CH_3)_2OH^{2+}] \qquad (5)$$

The products (15) of reaction were those expected from oxidation of both Cr^{2+} and 2-hydroxy-2-propyl radical by the specific oxidant. These results were interpreted (15) as a rate limiting homolysis of the organochromium(III) ion, followed by rapid oxidation of $Cr^{2+}(aq)$ and $\cdot C(CH_3)_2OH$ radical by the oxidant present:

$$CrC(CH_3)_2OH^{2+} \xrightarrow{k} Cr^{2+}(aq) + \cdot C(CH_3)_2OH \qquad (6)$$

$$Cr^{2+}(aq) \xrightarrow{\text{fast oxidation}} \text{Products} \qquad (7)$$

$$\cdot C(CH_3)_2OH \xrightarrow{\text{fast oxidation}} \text{Products} \qquad (8\text{-}9)$$

The experimental rate constant k for Equation 5 was identified with that of homolysis. The value is $0.127 \pm 0.003\ s^{-1}$ at 25.0°C, characterized by $\Delta H^{\ddagger} = 27.2 \pm 0.5$ K cal mol^{-1} and $\Delta S^{\ddagger} = 28.6 \pm 0.3$ cal $mol^{-1}\ K^{-1}$.

Kinetic studies of pyridinomethylchromium(III) ion (19-21); benzylchromium(III) ion (22); difunctional complexes of bis(benzylchromium(III)) cations (23, 24); other α-hydroxyalkyl, and α-alkoxyalkylchromium(III) complexes (25-28) have similarly demonstrated the importance of homolysis for these species.

Homolysis of $(H_2O)_5CrR^{2+}$ complexes results in a convenient, controlled source of the constituent radical in solution. Since the radical is generated slowly with time, its steady state concentration remains very small, hence radical self-reaction becomes unimportant. This chemical generation of ·R from organochromium homolysis functions to extend

the range of monitorable rate constants several orders of magnitude. In specialized cases, where the radical produced from homolysis proves unreactive, homolysis serves as a convenient source of $Cr^{2+}(aq)$ at low concentration. Under appropriate conditions, this low steady-state concentration of $Cr^{2+}(aq)$ can be used to generate a useful radical by the "Modified Fenton's Reagent" method, reaction with a hydroperoxide, or an activated organic halide (17).

Two fundamentally distinct methods of competition kinetics have been developed based on homolysis of CrR^{2+} complexes. These two complementary methods function together to extend greatly the scope of kinetically characterized radical-substrate reactions. The first of these relies upon the reversibility of the homolysis reaction. Competitive kinetic inhibition of homolysis occurs in the presence of a measured excess of $Cr^{2+}(aq)$ and a substrate, unreactive toward $Cr^{2+}(aq)$ on the time scale of the CrR^{2+} homolysis, whose reaction rate with $\cdot R$ is under investigation. This situation is represented by Equations 10 and 11.

$$CrR^{2+} \rightleftarrows Cr^{2+}(aq) + \cdot R \qquad (10)$$

$$\cdot R + S \rightarrow \text{Products} \qquad (11)$$

This method has been successfully demonstrated by Espenson, et al. (10) for the reduction of $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ in strongly acidic solution by $\cdot C(CH_3)_2OH$ radical. This method also appears to be applicable to the reduction of 2-iodopropane, Equation 12, by $\cdot C(CH_3)_2OH$ radical (29).

$$\cdot C(CH_3)_2OH + (CH_3)_2CHI \rightarrow (CH_3)_2CO + H^+ + I^- + \cdot CH(CH_3)_2 \qquad (12)$$

The other method, useful when one or more substrate reacts rapidly with $Cr^{2+}(aq)$, involves promoting homolysis by rapidly and continuously removing $Cr^{2+}(aq)$ in the presence of two substrates which react competitively with the radical, Equations 10, 13, 11a and 11b.

$$CrR^{2+} \longrightarrow Cr^{2+}(aq) + \cdot R \qquad (10)$$

$$Cr^{2+}(aq) + S \xrightarrow{fast} Cr(III)\ Products \qquad (13)$$

$$\cdot R \xrightarrow{S'} P_1 \qquad (11a)$$

$$\cdot R \xrightarrow{S''} P_2 \qquad (11b)$$

Provided one rate constant is known, the other can be obtained from an analysis of the product ratios. This latter competition method forms the basis of the kinetic studies presented herein.

PART I. THE REACTIONS OF THE 2-HYDROXY-2-PROPYL, α-ETHOXYETHYL, AND OTHER SELECTED ALIPHATIC FREE RADICALS WITH ALKYL(AQUO)-COBALOXIMES

INTRODUCTION

Bis(dimethylglyoximato)cobalt complexes are referred to as "cobaloximes", both for convenience and because of their similarity to cobalamins which are Vitamin B_{12} derivatives. Organocobaloximes, whose structure is shown in Figure I-1, are regarded in a formal sense as complexes of cobalt(III) with a carbanion. This formalism is, however, not meant to imply the existence of an ionic cobalt-carbon bond. On the contrary, reactions of organocobaloximes, as well as their marked stability in aqueous acidic solution can be explained only in terms of covalent bonding interactions.

Free-radical reactions involving organometallic complexes can be broadly catagorized as: 1) electron transfer, 2) atom transfer, 3) displacement, and 4) oxidative addition with or without subsequent reductive elimination. Although the latter two categories are the most pertinent to this work, and as such will receive the most attention, it is instructive to consider briefly examples of the former categories.

Sterically hindered alkyl radicals have been shown, with certain oxidants, to undergo a direct outer-sphere oxidation. Kochi, et al. (30) have interpreted the oxidation of tert-butyl radicals by lead (IV) complexes as proceeding via this outer-sphere pathway.

$$\cdot C(CH_3)_3 + Pb(IV) \rightarrow Pb(III) + {}^{+}C(CH_3)_3 \qquad (14)$$

In addition, the oxidation of isopropyl, tert-butyl, α-hydroxyalkyl and α-alkoxyalkyl radicals by $IrCl_6^{2-}$ (31, 32) has been shown to proceed

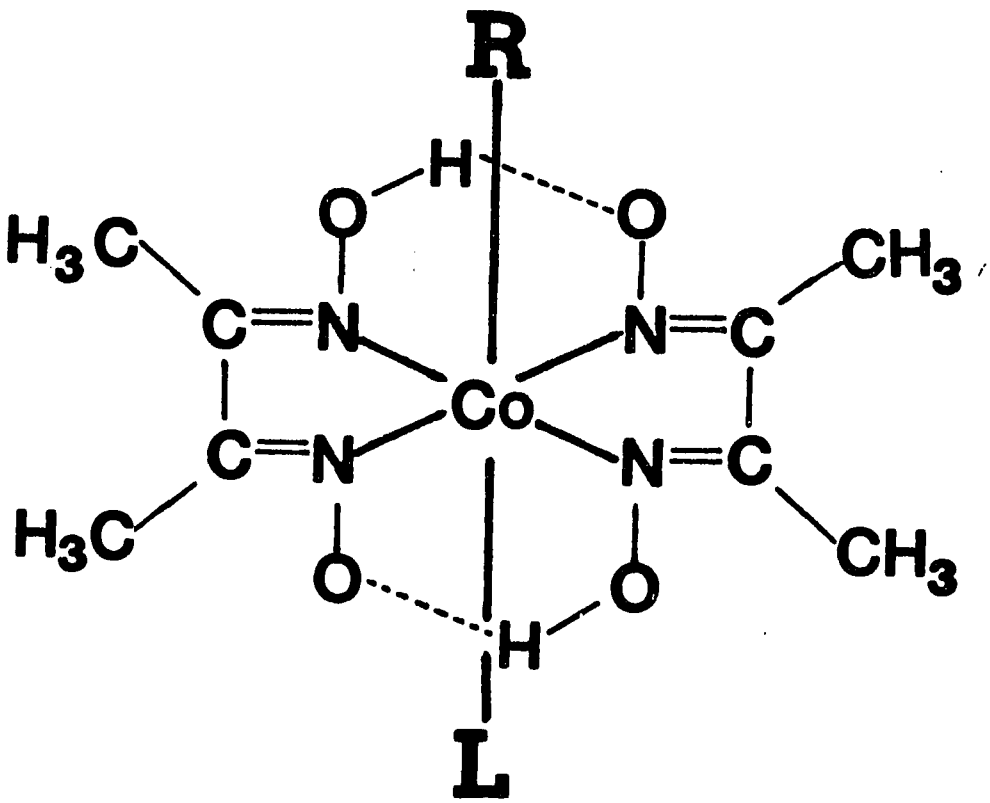

Figure I-1. Molecular structure of an organocobaloxime, where R = alkyl or aryl group and L = any appropriate base, usually H_2O, as in this work, pyridine, phosphine, or amine

predominantly, for alkyl radicals, and exclusively, for hydroxy- and alkoxyalkyl radicals, via an outer-sphere pathway.

$$\cdot R + IrCl_6^{2-} \rightarrow R^+ + IrCl_6^{3-} \qquad (15)$$

Atom transfer from a metal complex to an attacking radical is most common among halogen and hydride complexes. Kochi (33) has reported the reaction of ethyl radical with $Cu^{II}Cl_2$, where a chlorine atom is transferred to the radical.

$$CH_3CH_2\cdot + CuCl_2 \rightarrow CH_3CH_2Cl + CuCl \qquad (16)$$

Kuivila (34) has studied the reaction of methyl radical with Bu_3SnH, in which methane is produced.

$$\cdot CH_3 + Bu_3SnH \rightarrow CH_4 + Bu_3Sn\cdot \qquad (17)$$

The latter two categories, oxidative addition followed by reductive elimination and a concerted displacement, S_H2, are often quite difficult to distinguish from one another. Indeed, the oxidative addition pathway becomes a concerted displacement in the limit of infinitely short adduct lifetime. The reaction of tert-butoxy radical with trimethylboron, Equation 18, proceeds by a direct homolytic substitution mechanism. The

$$(CH_3)_3CO\cdot + B(CH_3)_3 \rightarrow (CH_3)_3COB(CH_3)_2 + \cdot CH_3 \qquad (18)$$

total absence of an esr signal (35), even at temperatures below $-110^{\circ}C$, corresponding to a four-coordinate alkylboron intermediate was used to establish the validity of the direct homolytic pathway. The same technique has been used to demonstrate that the reaction of the same

radical with $P(CH_3)_3$ (36), written as an S_H2 displacement in Equation 19, actually occurs by prior oxidative addition of the radical to the

$$(CH_3)_3CO\cdot + P(CH_3)_3 \rightarrow (CH_3)_3COP(CH_3)_2 + \cdot CH_3 \quad (19)$$

phosphorus center to produce a paramagnetic phosphorus(IV) intermediate which subsequently decomposes via α and β elimination pathways.

$$(CH_3)_3CO\cdot + P(CH_3)_3 \rightarrow (CH_3)_3\dot{C}OP(CH_3)_3 \quad (20)$$

$$(CH_3)_3\dot{C}OP(CH_3)_3 \rightarrow (CH_3)_3COP(CH_3)_2 + \cdot CH_3 \quad (21)$$

$$(CH_3)_3\dot{C}OP(CH_3)_3 \rightarrow (CH_3)_3C\cdot + OP(CH_3)_3 \quad (22)$$

The detailed mechanism followed during metal complex-radical reactions is often not well-understood. In addition, the products and stoichiometry of the reaction do not provide a distinction between mechanisms. As illustrated above, the products of the oxidative addition and displacement pathways are identical and it is often only the kinetic behavior which serves to make a mechanistic distinction feasible. This is not an isolated occurrence; according to its stoichiometry, the oxidation of alkyl radicals to carbonium ions by Cu(II) is an electron transfer process.

$$\cdot R + Cu^{2+} \rightarrow R^+ + Cu^+ \quad (23)$$

However, detailed kinetic studies for R = methyl (37-39) have shown that it proceeds via the formation of a directly observable transient organocopper(III) intermediate. Similar studies (2, 40-43) have established

$$\cdot CH_3 + Cu^{2+} \rightarrow CuCH_3^{2+} \xrightarrow{H_2O} Cu^{+} + CH_3OH + H^{+} \quad (24)$$

the generality of this oxidative pathway. A similar example of the ambiguity regarding the products and stoichiometry of radical reactions can be found in the formation of alkyl chlorides from alkyl radicals and $CuCl_2$ by what appears to be an atom transfer reaction. Isotopic

$$\cdot R + CuCl_2 \rightarrow RCl + CuCl \quad (25)$$

labeling studies (44) have shown the presence of a solvent-dependent electron transfer pathway.

$$\cdot R + CuCl_2 \rightarrow [R^{+}CuCl_2^{-}] \quad (26)$$

$$[R^{+}CuCl_2^{-}] \rightarrow RCl + CuCl \quad (27)$$

In strong contrast to the wealth of homolytic displacement reactions observed for boron, tin, and lead, authenticated examples for sp^3 hybridized carbon are still quite rare. Two such examples of homolytic substitution at a saturated carbon atom involve the reaction of Cr(II) with organocobaloximes (45) and organocobalamins (46), and the reaction of bis(cyclohexanedionedioximato)cobalt(II), $Co(chgH)_2py$, with organocobaloximes (47). Espenson and coworkers have shown (45, 46) that the

$$Cr^{2+}(aq) + RCo(dmgH)_2OH_2 \rightarrow CrR^{2+} + Co(dmgH)_2OH_2 \quad (28)$$

$$RCo(dmgH)_2py + Co(chgH)_2py \not\rightleftharpoons Co(dmgH)_2py + RCo(chgH)_2py \quad (29)$$

rate constants for the Cr(II) reactions exhibit a very marked decrease with increasing substitution at the α and β positions of the alkyl ligand.

The reactivity order, methyl > ethyl > isopropyl > neopentyl, spanning some five orders of magnitute from methyl to neopentyl, is completely consistent with the highly restricted transition state, Figure I-2, necessary for alkyl transfer via bimolecular homolytic substitution at a saturated carbon atom. In addition, the reactivity order, primary R> secondary R, as well as the strict first-order dependence upon $Cr^{2+}(aq)$ concentration, precludes the intermediacy of radicals or carbonium ions.

Proton nmr techniques have been used to establish the same reactivity order for the reactions of $Co(chgH)_2py$ (47) with alkylcobaloximes, and thus a similar sensitivity to steric crowding about the α-carbon atom. In addition to the kinetic evidence in support of a bimolecular homolytic substitution process, inversion of configuration is observed in the transfer of optically active alkyl groups (47). Treatment of solutions of either the threo or erythro isomers of $PhCHDCHDCo(chgH)_2py$, stable to racemization in the absence of $Co^{II}(chgH)_2py$, with catalytic quantities of $Co^{II}(chgH)_2py$ results in the formation of racemic mixtures. This racemization is consistent with an inversion of configuration about the α-carbon atom expected from a bimolecular homolytic displacement, S_H2 mechanism. Finally, prolonged, multiple exchanges of the ω-hexenyl complex fails to produce any detectable cyclopentylmethyl or cyclohexyl complexes, expected if free radical or carbonium ion intermediates are involved.

The first apparent S_H2 reaction of an organic radical at the saturated α-carbon atom of benzyl(pyridine)cobaloxime, $PhCH_2Co(dmgH)_2py$, was reported in 1977 (48). Benzylcobaloxime is cleaved by $BrCCl_3$ in chloroform solution to afford $BrCo(dmgH)_2py$ and a 50/50 mixture of $PhCh_2CCl_3$ and

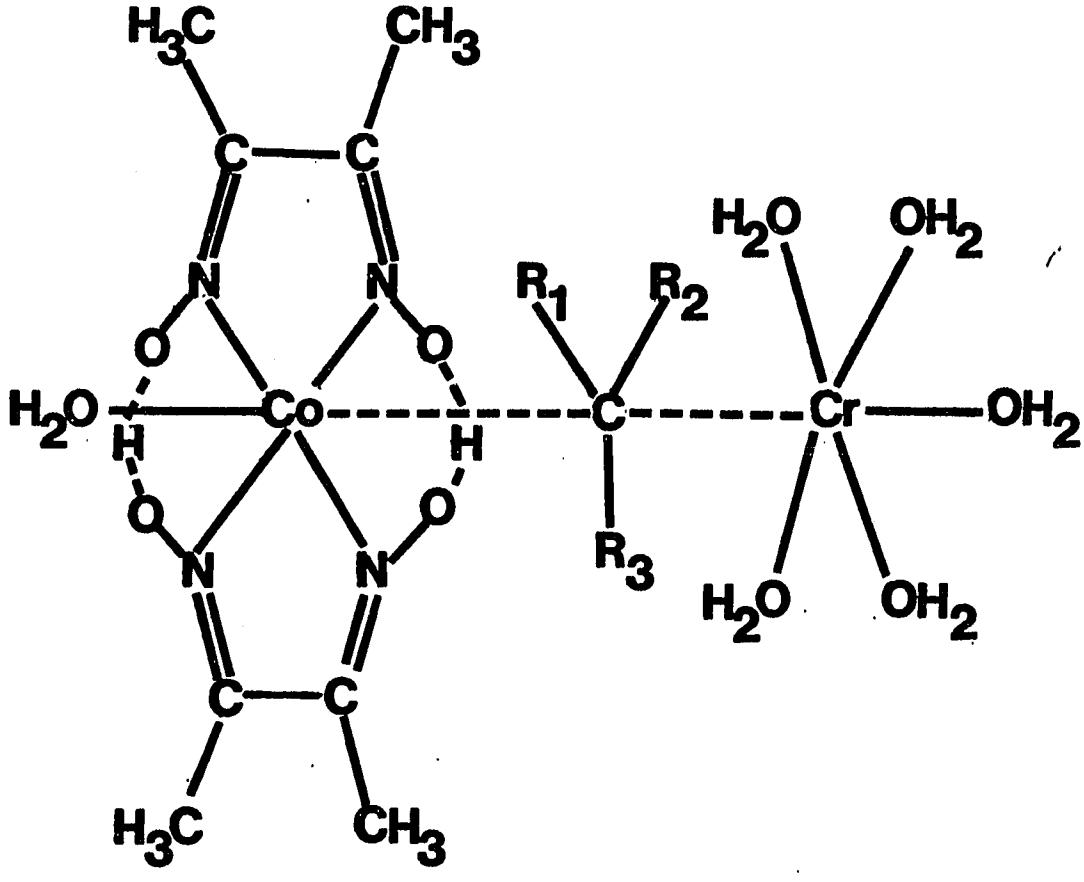

Figure I-2. A representation of the transition state for bimolecular homolytic substitution at the saturated α-carbon of alkylcobaloximes by $Cr^{2+}(aq)$

$PhCH_2Br$. Substitution of imidazole for pyridine as the axial base results in a nearly quantitative (>85%) yield of $PhCH_2CCl_3$ while substitution of electronegative groups on the phenyl ring results in a shift toward greater yields of $ArCH_2Br$ at the expense of $ArCH_2CCl_3$. The formation of $ArCH_2CCl_3$ was attributed to a chain reaction sequence,

$$Co(dmgH)_2py + BrCCl_3 \rightarrow BrCo(dmgH)_2py + \cdot CCl_3 \quad (30)$$

$$\cdot CCl_3 + ArCH_2Co(dmgH)_2py \rightarrow ArCH_2CCl_3 + Co(dmgH)_2py \quad (31)$$

with the key step involving S_H2 displacement at the α-carbon by $\cdot CCl_3$ in Equation 31. No bibenzyl and only traces of hexachloroethane, C_2Cl_6, were formed, precluding the formation of $ArCH_2CCl_3$ from radical cross-combination. The formation of benzyl bromide was attributed to a competing chain process involving a trans-bis(alkyl)cobalt(IV) species formed by coordination of $\cdot CCl_3$ radical to the axial position subsequent to loss of axial base.

$$ArCH_2Co^{III}(dmgH)_2py \rightleftarrows ArCH_2Co^{III}(dmgH)_2 + py \quad (32)$$

$$ArCH_2Co^{III}(dmgH)_2 + \cdot CCl_3 \rightleftarrows ArCH_2Co^{IV}(dmgH)_2CCl_3 \quad (33)$$

$$ArCH_2Co^{IV}(dmgH)_2CCl_3 \rightarrow Cl_3CCo^{III}(dmgH)_2 + ArCH_2\cdot \quad (34)$$

$$Cl_3CCo^{III}(dmgH)_2 + py \rightleftarrows Cl_3CCo^{III}(dmgH)_2py \quad (35)$$

$$ArCH_2\cdot + BrCCl_3 \rightarrow ArCH_2Br + \cdot CCl_3 \quad (36)$$

A similar result is observed for the reaction of arenesulphonyl radicals with selected organocobaloximes (49, 50).

The assignment of an S_H2 mechanism to reaction 31, as well as the reactions with arenesulphonyl radicals, was made primarily upon the products obtained. As the foregoing discussion has sought to establish, mechanistic assignments based solely on the products of reaction can be subject to a great deal of ambiguity. A mechanism involving first addition of the radical, followed by reductive elimination to give the hydrocarbon product would be indistinguishable from a concerted displacement, S_H2 mechanism, based solely upon the products of reaction. This ambiguity as well as the scarcity of authentic S_H2 reactions involving saturated sp^3 hybridized carbon provided an incentive to approach the problem from a kinetic perspective. The kinetic behavior of a family of alkylcobaloximes, of varying degree of steric crowding about the α-carbon atom, toward aliphatic free radicals would be expected to aid in an unambiguous mechanistic assignment. Based on the analysis of this kinetic behavior, it is concluded that some problems arise in trying to interpret the data in terms of an S_H2 mechanism. The reaction may better be described by prior addition of the radical to the cobaloxime, possibly preceded by electron transfer, followed by reductive elimination to afford the observed products.

EXPERIMENTAL

Materials

Cobaloximes

$H[Co(dmgH)_2Cl_2]$ Hydrogen dichlorobis(dimethylglyoximato)-cobaltate(1-) was prepared by the procedure of Babko and Korotun (51, 52). Dimethylglyoxime ($dmgH_2$) (33.0 g, 0.284 mole) and cobalt(II) chloride ($CoCl_2 \cdot 6H_2O$) (30.0 g, 0.142 mole) were dissolved in 500 mL of acetone and vigorously stirred for 4.5 hours. The green crystals, produced in approximately 83% yield, were collected by suction filtration, washed with water, ethanol, and dried with ether.

$ClCo(dmgH)_2OH_2$ Chloro(aquo)cobaloxime was prepared by controlled hydrolysis, Equation 37, of the dichloro complex according to the method of Costa, Tauzher, and Puxeddu (53).

$$Co(dmgH)_2Cl_2^- + H_2O \rightarrow ClCo(dmgH)_2OH_2 + Cl^- \qquad (37)$$

$C_6H_5CH_2Co(dmgH)_2OH_2$ Owing to the difficulty encountered in purifying the aquo derivatives of alkyl(aquo)cobaloximes, benzyl(aquo)-cobaloxime was prepared by a modification of the method of Schrauzer (54). In particular, rather than starting from a slurry of dimethylglyoxime and cobalt(II)chloride, purified $ClCo(dmgH)_2OH_2$ was reduced to cobalt(I) by borohydride. This procedure results in a very pure product, free of dimethylglyoxime or other contaminants.

Chloro(aquo)cobaloxime (5.00 g, 0.0146 mole) was dissolved in 200 mL of deaerated 0.1M NaOH in methanol and the deep-red solution further deaerated for 15 minutes with a vigorous stream of Cr^{2+}-scrubbed nitrogen.

Sodium borohydride (0.55 g, 0.0146 mole) was added. The formation of $Co(dmgH)_2^-$ became evident within several seconds. Benzylbromide (1.70 mL, 0.0146 mole) was injected, whereupon, the solution immediately turned deep red. The volume was reduced by rotary evaporation until deep-red crystals formed. After cooling in ice the crystals obtained, in approximately 50% yield, were collected by suction filtration, washed with a small volume of ice-cold water, followed by copious quantities of hexanes. The resulting compound was air dried in the dark.

Alternatively, the pyridine adduct, $PhCH_2Co(dmgH)_2py$, was isolated by the addition of an excess of pyridine to the reaction mixture. The pyridine adduct was converted to the aquo adduct by dissolution in a minimum volume of CH_2Cl_2. This solution was shaken with 2 equivalents of $HClO_4$, in the form of 6M $HClO_4$, and the resulting pyridinium perchlorate filtered. Vigorous shaking of the $CH_2Cl_2/HClO_4$ mixture with water resulted in the precipitation of $PhCH_2Co(dmgH)_2OH_2$, in approximately 50% yield, as dark reddish crystals. The product was isolated and treated as above.

$RCo(dmgH)_2OH_2$, where R = CH_3, CH_3CH_2, and $(CH_3)_2CH$ The alkylcobaloximes, prepared by borohydride reduction according to the method of Schrauzer (54) or, alternatively, by base assisted disproportionation according to the method of Yamazaki and Hohokabe (55), were donated by Dr. Andreja Bakac and Mr. Jwu-Ting Chen.

Organochromium reagents

$(H_2O)_5CrCH(CH_3)OC_2H_5^{2+}$ Solutions of α-ethoxyethyl(pentaaquo)-chromium(III) ion were prepared from diethyl ether, hydrogen peroxide, and

aqueous Cr(II) perchlorate, by the method of Schmidt, Swinehart, and Taube (56), according to Equations 38-40.

$$Cr^{2+} + H_2O_2 \rightarrow CrOH^{2+} + \cdot OH \quad (38)$$

$$\cdot OH + CH_3CH_2OC_2H_5 \rightarrow H_2O + \cdot CH(CH_3)OC_2H_5 \quad (39)$$

$$Cr^{2+} + \cdot CH(CH_3)OC_2H_5 \rightarrow CrCH(CH_3)OC_2H_5^{2+} \quad (40)$$

The organochromium complex was purified by anaerobic ion-exchange chromatography on Sephadex C-25 cation exchange resin in the Na^+ ion form. The ion-exchange column was maintained at 0^oC throughout the separation, to suppress homolytic and solvolytic decomposition, using a recirculating bath filled with ice-water. The organochromium complex was eluted as a yellow-brown band with 0.25M $NaClO_4$ containing 0.01M $HClO_4$. Solutions were kept frozen at all times when not in use to suppress decomposition.

$\underline{(H_2O)_5CrC(CH_3)_2OH^{2+}}$ Solutions of 2-hydroxy-2-propyl(pentaaquo)-chromium(III) ion were prepared by a modification of the above procedure (15, 56) substituting 2-propanol for diethyl ether, Equations 41-43.

$$Cr^{2+} + H_2O_2 \rightarrow CrOH^{2+} + \cdot OH \quad (41)$$

$$\cdot OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)\dot{C}OH \quad (42)$$

$$Cr^{2+} + \cdot C(CH_3)_2OH \rightarrow CrC(CH_3)_2OH^{2+} \quad (43)$$

Owing to its short lifetime in solution (15) this organochromium complex was prepared in <u>situ</u> and used immediately without prior purification. It should be noted however, that previous workers have already encountered this problem and studied reactions of their complexes in the unseparated

reaction solution (10, 15, 26-28, 56, 57). It has also been shown that the rates of reaction of $CrCH_2OH^{2+}$, where purification is possible, toward acidolysis, Cu^{2+} or Fe^{3+} (56, 58) are identical regardless of whether the complex is purified by ion-exchange chromatography or not.

$\underline{(H_2O)_5CrCH(CH_3)_2^{2+}}$ Solutions of isopropyl(pentaaquo)chromium(III) were prepared from Cr(II) and 2,3-dimethyl-2-butyl hydroperoxide, Equations 44-46, and purified according to literature procedures (59, 60).

$$Cr^{2+}(aq) + (CH_3)_2CHC(CH_3)_2OOH \rightarrow CrOH^{2+} + (CH_3)_2CHC(CH_3)_2O\cdot \quad (44)$$

$$(CH_3)_2CHC(CH_3)_2O\cdot \rightarrow \cdot CH(CH_3)_2 + (CH_3)_2CO \quad (45)$$

$$Cr^{2+}(aq) + \cdot CH(CH_3)_2 \rightarrow CrCH(CH_3)_2^{2+} \quad (46)$$

$\underline{(H_2O)_5CrCH_2Ph^{2+}}$ Solutions of benzyl(pentaaquo)chromium(III) were prepared from benzylbromide and aqueous chromium perchlorate in acetone according to the method of Kochi and Davis (61). This method involves halogen atom abstraction by Cr(II) followed by trapping of the benzyl radical formed by an additional mole of Cr(II).

$$Cr^{2+} + PhCH_2Br \rightarrow CrBr^{2+} + PhCH_2\cdot \quad (47)$$

$$PhCH_2\cdot + Cr^{2+} \rightarrow CrCH_2Ph^{2+} \quad (48)$$

The organochromium complex produced was purified by anaerobic ion-exchange chromatography on Sephadex C-25 cation-exchange resin in the Na^+ ion form. Benzyl(pentaaquo)chromium(III) ion was eluted with 0.25M $NaClO_4$, maintained at pH 2 with $HClO_4$, as a yellow-brown band. The column was maintained at

$0^{o}C$ throughout the elution using a recirculating ice-water bath. Solutions of the purified organochromium were kept frozen when not in use to retard decomposition.

Miscellaneous reagents

$[Co(en)_3](ClO_4)_3$ Tris(ethylenediamine)cobalt(III) perchlorate was prepared by addition of 70% $HClO_4$ to an aqueous solution of tris-(ethylenediamine)cobalt(III)chloride (62). Crystallization occurred upon cooling, and the needles were filtered and washed with ethanol and dried with diethyl ether.

$[Co(NH_3)_5F](ClO_4)_2$ The perchlorate salt was obtained from the nitrate salt by dissolution in water, adding 70% $HClO_4$, and cooling in ice.

H_2O_2 Reagent grade, 30% (Fisher), was used as received. The molarity of dilute solutions was determined by reaction with excess iodide ion followed by thiosulfate titration of the liberated iodine.

Organic reagents Methanol (Fisher), ethanol (Fisher), 2-propanol (Fisher), anhydrous diethyl ether (Fisher), ethylene (Matheson), dimethyl sulfoxide (Fisher), acetic acid (Allied), cyclopentane (Aldrich), and tert-butylhydroperoxide (Aldrich) were reagent grade chemicals and used as received.

2,3,3-Trimethyl-2-butyl hydroperoxide The hydroperoxide was prepared from the corresponding alcohol (Chemical Samples Co.) according to the method of Collins and Benjamin (63).

2,3-Dimethyl-2-butyl hydroperoxide The hydroperoxide was prepared from the corresponding alcohol (Chemical Samples Co.) according to the method of Ryan (60, and references therein).

$HClO_4$ and $LiClO_4$ Aqueous solutions of perchloric acid were prepared by dilution of 70% $HClO_4$ and titrated with standardized NaOH to a phenolphthalein endpoint. Lithium perchlorate was prepared by addition of Li_2CO_3 to 70% $HClO_4$, until no more CO_2 was evolved. The solution was evaporated until crystals of $LiClO_4$ formed, which were collected and recrystallized from water until no longer acidic. An aqueous solution was analyzed for the molarity of Li^+ by addition of an aliquot to a Dowex 50W-X8 cation exchange column in the H^+ form, and titrating the displaced acid with standardized NaOH to a phenolphthalein endpoint. Silver nitrate was used to verify the absence of chloride ion.

$[Cr(H_2O)_6](ClO_4)_2$ Solutions of Cr(II) in aqueous perchloric acid were prepared by reduction of standardized solutions of Cr(III) perchlorate, in aqueous perchloric acid, over amalgamated zinc. To increase the useful lifetime of these solutions, after reduction was complete, the solutions were transferred, by anaerobic techniques, from the amalgam.

Nitrogen. Nitrogen (Air Products) was purified of traces of O_2 by passage through two $Cr^{2+}(aq)$ scrubbing towers, followed by distilled water.

Methods

Analyses and characterizations

Reagents The organochromium(III) species were characterized by their uv-visible spectra. The 2-hydroxy-2-propyl complex, $(H_2O)_5CrC(CH_3)_2OH^{2+}$, exhibits characteristic absorption maxima at 407 nm (ε 700 M^{-1} cm^{-1}) and 311 nm (ε 2500 M^{-1} cm^{-1}) (64). The characteristic

maxima for the complex derived from diethyl ether, $(H_2O)_5CrCH(CH_3)OC_2H_5^{2+}$, occur, at slightly higher energy, at 396 nm (ε 468 M^{-1} cm^{-1}) and 290 nm (ε 2270 M^{-1} cm^{-1}) (56, 57, 64), and $(H_2O)_5CrCH_2Ph^{2+}$ exhibits three characteristic maxima at 356 nm (ε 2200 M^{-1} cm^{-1}), 295 nm (ε 6970 M^{-1} cm^{-1}) and 273 nm (ε 7670 M^{-1} cm^{-1}) (22, 61).

The organocobaloximes were characterized by elemental analysis, proton nmr, and their characteristic uv-visible absorption spectra. Table I-1 contains elemental analyses for the four organocobaloximes and Table I-2 shows the respective nmr and spectrophotometric data.

Table I-1. Elemental analyses for the alkylcobaloximes

R		% Co	% C	% H	% N
CH_3	(calc)	18.29	33.52	5.90	17.38
	(found)	18.24	33.01	5.95	17.20
CH_3CH_2	(calc)	17.53	35.70	6.25	16.66
	(found)	17.40	35.16	6.30	16.70
$(CH_3)_2CH$	(calc)	16.83	37.70	6.57	15.99
	(found)	16.70	37.00	6.51	15.85
$C_6H_5CH_2$	(calc)	14.76	45.21	5.78	14.06
	(found)	14.49	44.92	5.83	13.95

The inorganic reagents, $Co(NH_3)_5F^{2+}$ and $Co(en)_3^{3+}$, were characterized by their uv-visible spectra, λ/nm (ε/M^{-1} cm^{-1}): $Co(NH_3)_5F^{2+}$, 511 (45), 404 (7), 352 (38), 293 (7); $Co(en)_3^{3+}$, 465 (87), 387 (9), 338 (78), and 287 (5).

Table I-2. NMR and uv-visible spectrophotometric data for alkyl(aquo)-cobaloximes

R	NMR[a]		uv-vis[b,c]
CH_3	0.80	(s, CH_3)	444(1260)
	2.13	(s, dmg CH_3)	392(1790)
CH_3CH_2	2.20	(s, dmg CH_3)	454(1460)
	0.38	(t, CH_3)	399(1870)
	1.85	(q, CH_2)	
$(CH_3)_2CH$	2.23	(s, dmg CH_3)	467(1370)
	0.20	(d, CH_3)	405(1940)
	2.23	(m, CH)	
$C_6H_5CH_2$	2.22	(s, dmg CH_3)	468(954)
	6.96	(s, C_6H_5)	363 (5330)
	2.85	(s, CH_2)	

[a] In CD_3OD, δ in ppm relative to $Si(CH_3)_4$.

[b] λ/nm ($\varepsilon/M^{-1}\ cm^{-1}$).

[c] In 1.0M $HClO_4$, μ = 1.0M. The spectra vary with $[H^+]$ owing to a reversible protonation equilibrium.

% Co analysis

The cobalt content of the cobaloximes was determined as follows. An accurately weighed sample (~20 mg) was digested with fuming $HClO_4$ to yield $Co^{2+}(aq)$. In the presence of an excess of NH_4SCN in 50% acetone/H_2O, the absorbance of the $Co(SCN)_4^{2-}$ complex at 623 nm was determined; the concentration of $Co(SCN)_4^{2-}$ was calculated using $\varepsilon = 1842\ M^{-1}\ cm^{-1}$.

Product analyses

Organic product analysis The organic products from the reactions of benzyl(aquo)cobaloxime and the various aliphatic radicals studied, as well as the product obtained from isopropyl(aquo)cobaloxime and the 2-hydroxy-2-propyl radical, were identified by GC-MS methods. After completion of the reaction, the organic products were extracted into CH_2Cl_2, 9:1 (v/v) diethyl ether/pentane, or cyclopentane depending on the identity of the product. The organic phase was concentrated to approximately 2 mL, syringed into a 5 mL volumetric flask, and diluted to volume with the appropriate solvent.

Gas chromatographic separation of the products was carried out on a Varian 3920B instrument equipped with an FFAP packed column with an FID detector using a linear temperature program. Positive identification of the organic products was obtained by comparison of the retention time and mass spectrum to those of an authentic sample.

Quantitative estimates of the yield of the coupling products were obtained by comparison of peak areas of the sample and an authentic sample extracted from the same medium as the reaction mixture.

Inorganic product analysis The quantity of $Co^{2+}(aq)$ produced during selected competition runs was determined spectrophotometrically as the $Co(SCN)_4^{2-}$ complex in 50% acetone/H_2O. In a typical experiment, 10.0 mL of reaction mixture was added to 12.5 mL of acetone containing ∿2 grams of NH_4SCN and the volume adjusted to 25.0 mL with distilled water. The absorbance was measured at 623 nm (ε = 1842 M^{-1} cm^{-1}). To correct for minor absorption contributions from the organocobaloximes and product ions, appropriate blanks were used containing the cobaloximes and $Cr^{3+}(aq)$.

Rate determinations

The kinetics of the reaction of the organocobaloximes with 2-hydroxy-2-propyl and α-ethoxyethyl radicals were determined in solutions of 1.0M ionic strength maintained with $HClO_4$-$LiClO_4$. The reactions were followed by monitoring the decrease in absorbance of the organocobaloxime. Experiments were conducted with the rigorous exclusion of air in 5.00 cm quartz cells. Temperature control was achieved by immersing the reaction cell in a small water bath, equipped with quartz windows, positioned in the light beam of the Cary Model 219 spectrophotometer, and the water it contained was held at the desired temperature by circulation of water through an external jacket. Reactions were initiated by injecting a deaerated solution of appropriate organochromium(III) reagent.

DESIGN OF COMPETITION EXPERIMENTS

As mentioned briefly in the general introduction, three methods of competition kinetics exist based upon homolysis of CrR^{2+} complexes. The first of these, applicable to situations where the substrate is unreactive toward $Cr^{2+}(aq)$ on the time scale of the homolysis reaction, involves the competition between a measured excess of $Cr^{2+}(aq)$ and the substrate for the radical in question. This situation is illustrated by Equations 10 and 11.

$$CrR^{2+} \rightleftarrows Cr^{2+}(aq) + \cdot R \qquad (10)$$

$$\cdot R + S \rightarrow \text{Products} \qquad (11)$$

The second method, to be described here in detail, is applicable to cases where the substrates react with $Cr^{2+}(aq)$. Central to this method is homolysis of the CrR^{2+} complexes in the presence of two substrates which react competitively with the radical in question, Equations 10, 13 11a, and 11b.

$$CrR^{2+} \xrightarrow{k_H} Cr^{2+}(aq) + \cdot R \qquad (10)$$

$$Cr^{2+}(aq) + S \xrightarrow{\text{fast}} Cr(III)\ \text{Products} \qquad (13)$$

$$\cdot R \xrightarrow{S'} P_1 \qquad (11a)$$

$$\cdot R \xrightarrow{S''} P_2 \qquad (11b)$$

The kinetic analysis is based upon the quantitative determination of the products with due allowance being made for the contribution, if any, to the products or consumption of the substrate made by the reactions of

$Cr^{2+}(aq)$. The product analysis yields the ratio of the rate constants for the independent reactions of the two substrates with the radical. Independent knowledge of the rate constant for one substrate allows calculation of that for the other.

The third method, to be discussed in detail on pages 33-40, consists of a specialized modification of the second method. This method consists of promotion of the homolysis of benzylchromium in the presence of H_2O_2 and an organic substrate. The $Cr^{2+}(aq)$ produced from homolysis of the benzylchromium cation reacts rapidly with hydrogen peroxide to form hydroxyl radicals which in turn react with the organic substrate to give an organic carbon-centered radical. This situation is illustrated for 2-propanol by Equations 10a, 12a, and 13.

$$CrCH_2Ph^{2+} \rightarrow Cr^{2+}(aq) + \cdot CH_2Ph \qquad (10a)$$

$$Cr^{2+} + H_2O_2 \rightarrow CrOH^{2+} + \cdot OH \qquad (12a)$$

$$\cdot OH + (CH_3)_2CHOH \rightarrow H_2O + \cdot C(CH_3)_2OH \qquad (13)$$

As in method 2, the organic radical produced reacts competitively with two scavengers. This method is applicable to cases where one or both of the scavengers reacts with $Cr^{2+}(aq)$ too rapidly to be handled by method 1 but slowly enough not to interfere with reaction 12a. In addition, neither scavenger can be reactive toward the benzyl radical produced. It is methods 2 and 3 which are useful here for competition experiments involving the organocobaloximes.

·$CH(CH_3)OC_2H_5$ Radical

The inorganic complex $Co(NH_3)_5F^{2+}$ was used to compete with the alkylcobaloximes for the α-ethoxyethyl radical produced from homolysis of the $CrCH(CH_3)OC_2H_5^{2+}$ complex. The complex $Co(NH_3)_5F^{2+}$ was chosen because it meets several important requirements. First, and most importantly, the rate constant for reaction of $Co(NH_3)_5F^{2+}$ with the ·$CH(CH_3)OC_2H_5$ radical has been independently determined[1] and is of an appropriate magnitude to compete successfully with the alkylcobaloximes. This stipulation rules out use of the other halopentaamminecobalt(III) complexes, $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5Cl^{2+}$, whose rate constants for reaction with the ·$CH(CH_3)OC_2H_5$ radical are independently known (4) but are much too high to allow proper competition with the cobaloximes. Secondly, $Co(NH_3)_5F^{2+}$ is known to react rapidly with $Cr^{2+}(aq)$, $k = 9 \times 10^5\ M^{-1}\ s^{-1}$, 25.0°C, μ = 1.0M (65), thereby promoting homolysis without the unnecessary addition of yet another reagent. In addition, the products of this reaction are kinetically inert CrF^{2+} and $Co^{2+}(aq)$ (65). Finally, $Co(NH_3)_5F^{2+}$ lacks intense absorptions in the visible region of the spectrum which would complicate the data analysis.

Homolysis of the $CrCH(CH_3)OC_2H_5^{2+}$ complex (15) in the presence of mixtures of $Co(NH_3)_5F^{2+}$ and an alkylcobaloxime, and the fate of the $Cr^{2+}(aq)$ and the organic radical produced are represented in Equations 49-53.

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[1]This determination constitutes the subject of Part II of this thesis.

$$CrCH(CH_3)OC_2H_5^{2+} \rightarrow Cr^{2+}(aq) + \cdot CH(CH_3)OC_2H_5 \quad (49)$$

$$Cr^{2+}(aq) + Co(NH_3)_5F^{2+} \xrightarrow{(+5H^+)} CrF^{2+} + Co^{2+}(aq) + 5NH_4^+ \quad (50)$$

$$\cdot CH(CH_3)OC_2H_5 \begin{cases} \xrightarrow{Co(NH_3)_5F^{2+},\ (+H_2O,\ +4H^+)} CH_3CHO + CH_3CH_2OH + Co^{2+}(aq) + F^- + 5NH_4^+ \\ \xrightarrow[RCo(dmgH)_2OH_2,\ (+5H^+)]{} RCH(CH_3)OC_2H_5 \ (\underset{\sim}{A}) + Co^{II}(dmgH)_2OH_2 \end{cases} \quad (51)\ (52)$$

$$Co^{II}(dmgH_2)OH_2 \xrightarrow{v.\ fast} Co^{2+}(aq) + 2dmgH_2 \quad (53)$$

Since the acid hydrolysis of $Co^{II}(dmgH)_2OH_2$ is known to be extremely rapid in strongly acidic solution (66a, b), the ultimate products of the reaction between the α-ethoxyethyl radical and the alkylcobaloxime are $Co^{2+}(aq)$, the coupled ether ($\underset{\sim}{A}$), and free dimethylglyoxime, all virtually transparent in the visible region of the spectrum.

The ratio of the rate constants for reaction of the radical with $Co(NH_3)_5F^{2+}$ and the cobaloxime can be obtained from analysis of the rate ratio, Equation 54.

$$\frac{d[A]/dt}{d[F^-]/dt} = \frac{k_{52}[RCo(dmgH)_2OH_2]}{k_{51}[Co(NH_3)_5F^{2+}]} \quad (54)$$

Experiments were carried out with $[Co(NH_3)_5F^{2+}]_0$ and $[RCo(dmgH)_2OH_2]_0 >> [CrCH(CH_3)OC_2H_5^{2+}]_0$ such that neither substrate concentration changes appreciably with time. Integration of the rate ratio of Equation 54 with these as boundary conditions yields,

$$\frac{[A]_\infty}{[F^-]_\infty} = \frac{k_{52}[RCo(dmgH)_2OH_2]_{ave}}{k_{51}[Co(NH_3)_5F^{2+}]_{ave}} . \quad (55)$$

The products, F^- and A, are not directly measured quantities and it is necessary to recast Equation 55 in terms of the directly measured quantities $[CrCH(CH_3)OC_2H_5^{2+}]_0$, $[RCo(dmgH)_2OH_2]_0$, and $[RCo(dmgH)_2\ OH_2]_\infty$.

The amount of the radical which reacts with the cobaloxime, $[A]_\infty$, is very accurately determined from the observed absorbance change. Since the contribution to this absorbance change from $Co(NH_3)_5F^{2+}$ is negligible, the observed absorbance change is directly related to the change in organocobaloxime according to Equation 56.

$$\Delta[RCo(dmgH)_2OH_2] = [A]_\infty = \Delta D/\varepsilon_{cobaloxime}(pathlength) \quad (56)$$

Acidolysis is negligible relative to homolysis for the $CrCH(CH_3)OC_2H_5^{2+}$ complex (15, 64), therefore, the total available radical must be equal to the initial organochromium(III) complex concentration.

$$[CH(CH_3)OC_2H_5]_T = [CrCH(CH_3)OC_2H_5^{2+}]_0 = \Delta[RCo(dmgH)_2OH_2] + [F^-]_\infty \quad (57)$$

Rearranging Equation 57 results in an expression for $[F^-]_\infty$ in terms of directly measured quantities,

$$[F^-]_\infty = [CrCH(CH_3)OC_2H_5^{2+}]_0 - \Delta[RCo(dmgH)_2OH_2]. \quad (58)$$

Substitution of Equations 56 and 58 into Equation 55 affords the final expression, Equation 59, entirely in terms of directly measured quantities.

$$\frac{[A]_\infty}{[F^-]_\infty} = \frac{\Delta[RCo(dmgH)_2OH_2]}{\{[CrCH(CH_3)OC_2H_5^{2+}] - \Delta[RCo(dmgH)_2OH_2]\}} =$$

$$\frac{k_{52}[RCo(dmgH)_2OH_2]_{ave}}{k_{51}[Co(NH_3)_5F^{2+}]_{ave}} \qquad (59)$$

Due considerations must be made in calculating $[Co(NH_3)_5F^{2+}]_{ave}$ for the quantitative consumption by $Cr^{2+}(aq)$, Equation 50. Thus, $[Co(NH_3)_5F^{2+}]_{ave} = [Co(NH_3)_5F^{2+}]_0 - \frac{1}{2}\{\Delta[RCo(dmgH)_2OH_2] + [CrCH(CH_3)OC_2H_5^{2+}]_0\}$ and $[RCo(dmgH)_2OH_2]_{ave} = [RCo(dmgH)_2OH_2]_0 - \frac{1}{2}\Delta[RCo(dmgH)_2OH_2]$.

In the case of benzylaquocobaloxime, absorbance changes were monitored at either 404 nm, a minimum for $Co(NH_3)_5F^{2+}$, or 468 nm, a maximum for the cobaloxime. In order to obtain the maximum sensitivity, absorbance changes for methyl, ethyl and isopropyl(aquo)cobaloximes were monitored at 404 nm.

$\cdot C(CH_3)_2OH$ Radical

Unlike the clean situation encountered for the study of the α-ethoxyethyl radical obtained directly from the homolysis of the $CrCH(CH_3)OC_2H_5^{2+}$ complex, kinetic competition experiments based upon homolysis of the $CrC(CH_3)_2OH^{2+}$ complex are complicated by the presence of at least one additional reaction which consumes a variable portion of the free radical. Indeed, analysis of the organic products from the reaction of the 2-hydroxy-2-propyl radical, obtained from homolysis of $CrC(CH_3)_2OH^{2+}$ (15), with benzylcobaloxime indicated not only the coupled alcohol product, $PhCH_2C(CH_3)_2OH$, but also significant quantities of

pinacol, $HO(CH_3)_2CC(CH_3)_2OH$. The self-reaction between a pair of $\cdot C(CH_3)_2OH$ radicals results only in disproportionation products, 2-propanol and acetone (67). In addition, under the conditions employed in these experiments, namely organocobaloxime and organochromium concentrations on the order of 10^{-3}M, the steady-state concentration of the radicals was too low to allow radical self-reaction to compete with the reaction between the radical and benzylcobaloxime. Thus, the detection of pinacol requires a pathway other than radical self-reaction. One such pathway involves a reaction with the parent organochromium ion analogous to the coupling reaction with the cobaloxime.

$$\cdot C(CH_3)_2OH + CrC(CH_3)_2OH^{2+} \rightarrow Cr^{2+}(aq) + \text{Pinacol} \qquad (60)$$

Thus it was necessary to develop a system to generate quantitatively, and at low concentration, $\cdot C(CH_3)_2OH$ radical without directly involving the $CrC(CH_3)_2OH^{2+}$ complex.

Homolysis of an alkylchromium(III) complex, CrR^{2+}, results not only in the generation of an alkyl radical, but also generates an equivalent concentration of $Cr^{2+}(aq)$ ions. If the proper organochromium complex is chosen such that the radical produced proves unreactive toward the cobaloxime and the competing substrate, this generation of $Cr^{2+}(aq)$ can be profitably utilized to produce another aliphatic free radical.

Benzylchromium(III), $CrCH_2Ph^{2+}$, is one such organochromium complex which produces a radical completely unreactive toward the organocobaloximes studied. Nohr and Espenson (22) have shown the benzyl radical to be completely unreactive toward the $Co(NH_3)_5Cl^{2+}$ and $Co(en)_3^{3+}$ complexes.

Experiments involving homolysis of $CrCH_2Ph^{2+}$ in the presence of $Co(NH_3)_5Cl^{2+}$ and benzylcobaloxime, $PhCH_2(dmgH)_2OH_2$, were used to establish the unreactivity of $\cdot CH_2Ph$ radical toward $PhCH_2Co(dmgH)_2OH_2$. No detectable change in the spectrum of the cobaloxime was observed. In addition, analysis of the $Co^{2+}(aq)$ produced, indicated only 1 mole of $Co^{2+}(aq)$ was produced for each mole of $CrCH_2Ph^{2+}$ which underwent homolysis, consistent with reaction 61. Had any reaction between benzyl radical and

$$Cr^{2+} + Co(NH_3)_5Cl^{2+} \xrightarrow{(+5H^+)} CrCl^{2+} + Co^{2+}(aq) + 5NH_4^+ \qquad (61)$$

the cobaloxime occurred, additional $Co^{2+}(aq)$ would have been formed.

Homolysis of $CrCH_2Ph^{2+}$ (22) in the presence of moderate excesses of H_2O_2 and an organic solute, in this case 2-propanol, were used to generate an additional aliphatic free radical.

$$CrCH_2Ph^{2+} \rightarrow Cr^{2+} + \cdot CH_2Ph \qquad (62)$$

$$2\cdot CH_2Ph \rightarrow PhCH_2CH_2Ph \qquad (63)$$

$$Cr^{2+}(aq) + H_2O_2 \rightarrow CrOH^{2+} + \cdot OH \qquad (64)$$

$$\cdot OH + HC(CH_3)_2OH \rightarrow H_2O + \cdot C(CH_3)_2OH \qquad (65)$$

Careful consideration of the rate constants for reactions 64 and 65, will show that it is very easy to guarantee that every mole of $Cr^{2+}(aq)$ produced in reaction 62 ultimately leads to a mole of $\cdot C(CH_3)_2OH$ radical. Hydrogen peroxide reacts rapidly with $Cr^{2+}(aq)$, $k_{64} = 7.06 \times 10^4\ M^{-1}\ s^{-1}$ (68), to yield hydroxyl radicals which react at nearly the diffusion controlled limit with 2-propanol, $k_{65} = 2.2 \times 10^9\ M^{-1}\ s^{-1}$ (69), to

produce $\cdot C(CH_3)_2OH$ (85%) and $\cdot CH_2CH(CH_3)OH$ (13.5%) (70). Thus, only 3-5 fold excesses of H_2O_2 are necessary to insure that reaction 64 is fast relative to homolysis of $CrCH_2Ph^{2+}$, $k_{62} = 2.62 \times 10^{-3}\ s^{-1}$ (22). Higher concentrations of H_2O_2 must be avoided, at least for the slower reacting cobaloximes, due to a competing chain reaction involving H_2O_2 (71).

$$H_2O_2 + \cdot C(CH_3)_2OH \rightarrow \cdot OH + (CH_3)_2CO + H_2O \qquad (66)$$

In light of the very rapid hydrogen atom abstraction from 2-propanol by $\cdot OH$ radical, Equation 65, only modest concentrations ($\geq$0.5M) of 2-propanol are necessary to insure quantitative yields of $\cdot C(CH_3)_2OH$ radical. As presented in the discussion, the β radical produced via hydrogen atom abstraction from 2-propanol by hydroxyl radicals is competitively converted into α radical according to Equation 67, and does not interfer

$$\cdot CH_2CH(CH_3)OH + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH + \cdot C(CH_3)_2OH \qquad (67)$$

in the kinetic analysis.

If the homolysis of benzylchromium ion (22) is promoted with H_2O_2 and 2-propanol in the presence of an organocobaloxime and an appropriate competitor, the rate constant for reaction of the $\cdot C(CH_3)_2OH$ radical with the cobaloxime may be determined from an analysis of the products obtained. Unlike competition experiments involving homolysis of $CrCH(CH_3)OC_2H_5^{2+}$, where it was desirable to use a competitor which reacted rapidly with $Cr^{2+}(aq)$ to insure promotion of homolysis, it is imperative in the benzylchromium system that the competitor chosen <u>not</u> react at an appreciable rate with $Cr^{2+}(aq)$. The inorganic complex $Co(en)_3^{3+}$

represents a good choice as a competitor for $\cdot C(CH_3)_2OH$ radical. Its reaction with $Cr^{2+}(aq)$, Equation 67, is exceedingly slow, $k_{67} \simeq 2 \times 10^{-5}$ M^{-1} s^{-1} (72). In addition, the rate constant for reduction by $\cdot C(CH_3)_2OH$

$$Cr^{2+}(aq) + Co(en)_3^{3+} \xrightarrow{(+3H^+)} Cr^{3+}(aq) + Co^{2+}(aq) + 3enH^+ \qquad (67)$$

radical, Equation 68 has been independently determined in strongly acidic

$$\cdot C(CH_3)_2OH + Co(en)_3^{3+} \xrightarrow{(+2H^+)} Co^{2+}(aq) + (CH_3)_2CO + 3enH^+ \qquad (68)$$

solution (10), and finally, $Co(en)_3^{3+}$, like $Co(NH_3)_5F^{2+}$, lacks intense visible absorption bands which would complicate the data analysis. Thus, the scheme for the kinetic competition experiments involving $\cdot C(CH_3)_2OH$ radical is represented by Equations 62 through 65 and 68 through 70.

$$CrCH_2Ph^{2+} \rightarrow Cr^{2+}(aq) + \cdot CH_2Ph \qquad (62)$$

$$2 \cdot CH_2Ph \rightarrow PhCH_2CH_2Ph \qquad (63)$$

$$Cr^{2+}(aq) + H_2O_2 \rightarrow CrOH^{2+} + \cdot OH \qquad (64)$$

$$\cdot OH + HC(CH_3)_2OH \rightarrow H_2O + \cdot C(CH_3)_2OH \qquad (65)$$

$$\cdot C(CH_3)_2OH \begin{cases} \xrightarrow{Co(en)_3^{3+}\ (+2H^+)} (CH_3)_2CO + Co^{2+}(aq) + 3enH^+ & (68) \\ \xrightarrow[RCo(dmgH)_2OH_2]{} RC(CH_3)_2OH + Co^{II}(dmgH)_2OH_2 & (69) \end{cases}$$

$$Co^{II}(dmgH)_2OH_2 + 2H^+ \rightarrow Co^{2+}(aq) + 2dmgH_2 \qquad (70)$$

To determine the rate constant for reaction 69, analysis of the rate ratio, Equation 71, is necessary.

$$\frac{d[\text{acetone}]/dt}{d[B]/dt} = \frac{k_{68}[Co(en)_3^{3+}]}{k_{69}[RCo(dmgH)_2OH_2]} \tag{71}$$

At this point in the discussion, it is helpful to consider separately the case where R = benzyl. The rate constant for the reaction of the radical with benzylcobaloxime, as detailed in the results section, is nearly two orders of magnitude larger than that for reduction of $Co(en)_3^{3+}$ by the 2-hydroxy-2-propyl radical. This necessitated carrying out experiments at high concentrations of $Co(en)_3^{3+}$ relative to the benzylcobaloxime concentration in order to attain a balanced competition. Thus, the concentration of $Co(en)_3^{3+}$ remained very nearly constant while the cobaloxime concentration changed appreciably with time. To account for this change in concentration with time the quantity $\{[RCo(dmgH)_2OH_2]_0 - [B]_t\}$ must be substituted for the simple term in the denominator of the right side of Equation 71.

$$\frac{d[\text{acetone}]/dt}{d[B]/dt} = \frac{k_{68}[Co(en)_3^{3+}]}{k_{69}\{[RCo(dmgH)_2OH_2]_0 - [B]t\}} \tag{72}$$

Integration of Equation 72 affords the complex product expression of Equation 73.

$$\frac{[\text{acetone}]_\infty}{\ln\left\{\frac{[RCo(dmgH)_2OH_2]_0}{[RCo(dmgH)_2OH_2]_0 - [B]_\infty}\right\}} = \frac{k_{68}}{k_{69}}[Co(en)_3^{3+}]_0 \tag{73}$$

As in the expression derived for the α-ethoxyethyl radical competition experiment, $[\text{acetone}]_\infty$ and $[B]_\infty$ are not directly measured quantities and

it is necessary to recast Equation 73 in terms of the measured quantities $[CrCH_2Ph^{2+}]_0$, $[RCo(dmgH)_2OH_2]_0$, and $[RCo(dmgH)_2OH_2]_\infty$.

Acidolysis of $CrCH_2Ph^{2+}$ is unimportant relative to homolysis (22) as it was in the case of the $CrCH(CH_3)OC_2H_5^{2+}$ complex. Thus, in strict analogy to the derivation of Equation 59,

$$[B]_\infty = \Delta[RCo(dmgH)_2OH_2] \tag{74}$$

and

$$[\text{acetone}]_\infty = \Delta[Co(en)_3^{3+}] = [CrCH_2Ph^{2+}]_0 - \Delta[RCo(dmgH_2)_2OH_2]. \tag{75}$$

Substitution of these quantities into Equation 73 affords

$$Y = \frac{\Delta[Co(en)_3^{3+}]}{\ln\left\{\dfrac{[RCo(dmgH)_2OH_2]_0}{[RCo(dmgH)_2OH_2]_0 - \Delta[RCo(dmgH)_2OH_2]}\right\}} = \frac{k_{68}}{k_{69}}[Co(en)_3^{3+}]_0 \tag{76}$$

Absorbance changes were monitored at 360 nm, a very intense maximum for benzyl(aquo)cobaloxime, or 387 nm, a minimum for the $Co(en)_3^{3+}$ complex.

For the other alkylcobaloximes, the rate constant for reaction 69 proved to be small enough to permit competition experiments to be carried out where neither competitor concentration changed appreciably throughout the run. In the limit of constant cobaloxime concentration, Equation 76 becomes

$$\frac{\Delta[RCo(dmgH)_2OH_2]}{\Delta[Co(en)_3^{3+}]} = \frac{k_{69}}{k_{68}}\frac{[RCo(dmgH)_2OH_2]_{ave}}{[Co(en)_3^{3+}]_{ave}} \tag{77}$$

where $[RCo(dmgH_2)OH_2]_{ave} = [RCo(dmgH_2)OH_2]_0 - \frac{1}{2}\Delta[RCo(dmgH)_2OH_2]$ and similarly, $[Co(en)_3^{3+}]_{ave} = [Co(en)_3^{3+}]_0 - \frac{1}{2}\Delta[Co(en)_3^{3+}]$.

Owing to the less intense absorptions of the alkylcobaloximes relative to benzyl(aquo)cobaloxime, absorbance changes were monitored at 387 nm, a minimum for the $Co(en)_3^{3+}$ complex, $\varepsilon = 9\ M^{-1}\ cm^{-1}$, and within 10 nm of a maximum of the alkylcobaloximes.

RESULTS

Reactions of the $\cdot CH(CH_3)OC_2H_5$ Radical with Organocobaloximes

Benzyl(aquo)cobaloxime, $PhCH_2Co(dmgH)_2OH_2$

Organic product Consistent with Equation 78, the only detectable organic product from the reaction of the $\cdot CH(CH_3)OC_2H_5$ radical with benzyl(aquo)cobaloxime was 2-ethoxy-1-phenylpropane.

$$\cdot CH(CH_3)OC_2H_5 + PhCH_2Co(dmgH)_2OH_2 \rightarrow PhCH_2CH(CH_3)OC_2H_5 + Co^{II}(dmgH)_2OH_2 \quad (78)$$

Although no authentic sample of the ether was available, the mass spectrum, Figure I-3, is fully consistent with the formulation of the product as 2-ethoxy-1-phenylpropane. The parent ion peak at m/e 164, while not large, is clearly visible. The presence of an oxygen atom can be deduced from the strong peak at m/e 73, corresponding to carbon-carbon bond cleavage β to the oxygen atom. The strong peaks at m/e 91 and 65

$$PhCH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle +}{CH}}-O-CH_2-CH_3 \rightarrow PhCH_2\cdot + \underset{\displaystyle CH_3}{CH}=\overset{\displaystyle +}{\dot{O}}-C_2H_5 \quad \text{m/e 73}$$

are indicative of the presence of the benzyl substituent.

$$PhCH_2\underset{\displaystyle CH_3}{\overset{\displaystyle +}{CH}}-O-CH_2CH_3 \rightarrow \underset{\text{m/e 91}}{C_7H_7^{+}\cdot} + \cdot CH(CH_3)OC_2H_5$$

$$C_7H_7^{+}\cdot \rightarrow \underset{\text{m/e 65}}{C_5H_5^{+}\cdot} + HC\equiv CH$$

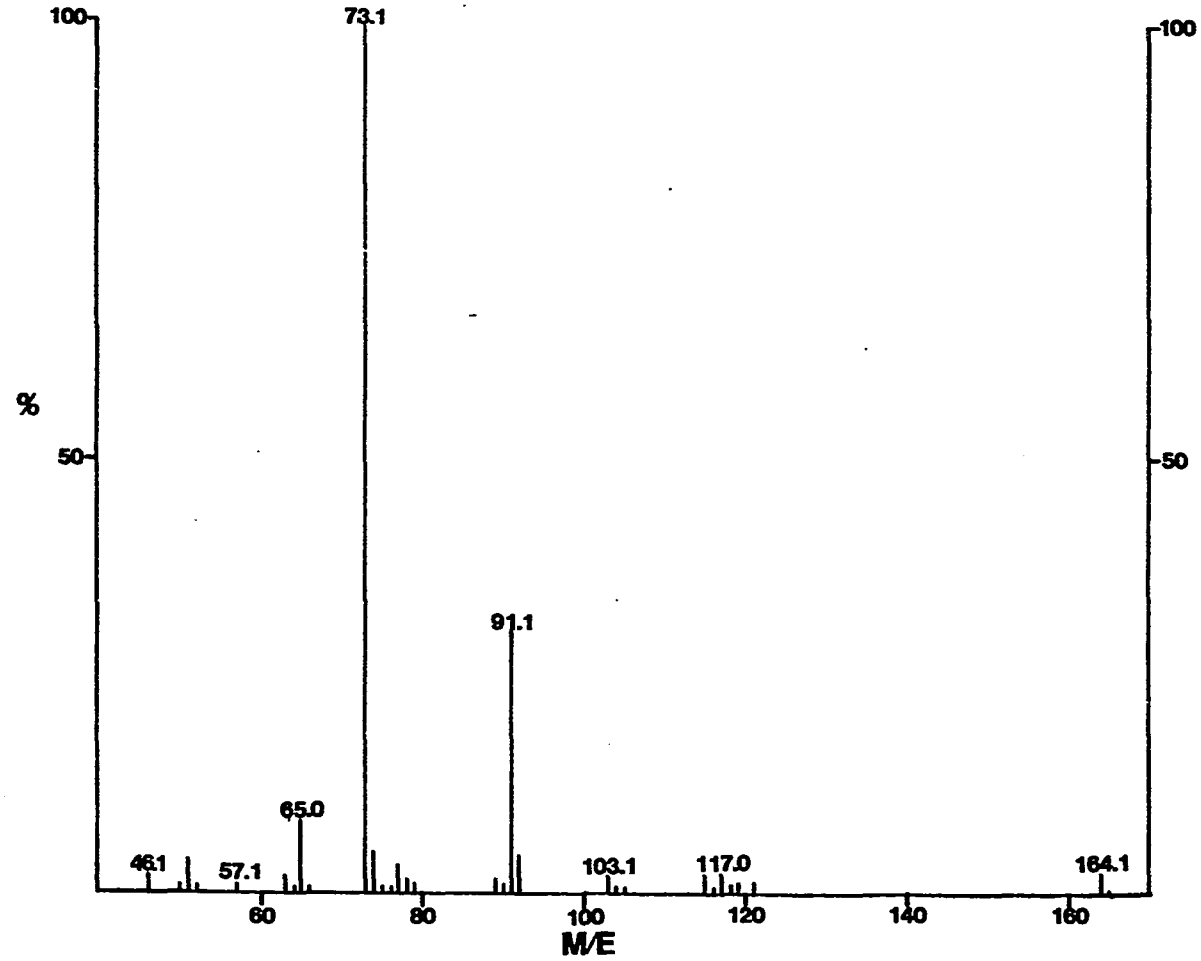


Figure I-3. Mass spectrum of 2-ethoxy-1-phenyl-propane

Kinetics Competition experiments were carried out, over the acid range 1.0M to 0.15M, at 25.0°C and 1.0M ionic strength maintained with $HClO_4$-$LiClO_4$. Purified $CrCH(CH_3)OC_2H_5^{2+}$ stock solutions were used in every run. The cobaloxime concentration was varied from 6.00×10^{-5}M to 2.00×10^{-4}M and the competing substrate, $Co(NH_3)_5F^{2+}$, was varied over the range 6.00×10^{-5}M to 6.00×10^{-4}M. The data obtained are summarized in Table I-3. Figure I-4 represents a plot of the data obtained at 1.0M and 0.15M $[H^+]$ according to Equation 59.

$$\frac{\Delta[RCo(dmgH)_2OH_2]}{[F^-]_\infty} = \frac{k_{52}[RCo(dmgH)_2OH_2]_{ave}}{k_{51}[Co(NH_3)_5F^{2+}]_{ave}} \qquad (59)$$

The data do indeed describe a straight line. The small positive intercept, not anticipated from Equation 59 is believed to reflect a compilation of the random and systematic errors incurred in the product determinations and data manipulation, rather than a chemically significant process. From Equation 59, the slope of the plot at fixed acidity corresponds to the ratio of the rate constants for the competing substrates. Since the rate constant k_{51} is known, $k_{51} = 1.15 \times 10^6$ M^{-1} s^{-1}, k_{52} at fixed acidity may be determined from the slope.

$$\text{slope} = k_{52}/k_{51} = \frac{k_{R(Co)}}{k_{Co(NH_3)_5F^{2+}}}$$

where $R(Co) = PhCH_2Co(dmgH)_2OH_2$

Table I-4 lists the values of k_{52}^{app} as a function of $[H^+]$. The values of k_{52}^{app} as obtained from the slopes of the individual lines at fixed acidity

Table I-3. Data for the competition between $PhCH_2Co(dmgH)_2OH_2$, R'(Co), and $Co(NH_3)_5F^{2+}$, A_5CoF^{2+}, for the radical derived from homolysis of $CrCH(CH_3)OC_2H_5^{2+}$, $CrROR^{2+}$, Equation 59. μ = 1.0M, T = 25.0°C

$[CrROR^{2+}]_o$/M	$10^5[R'(Co)]_o$/M	$10^4[A_5CoF^{2+}]_o$/M	$10^5\Delta[R'(Co)]$/M	$10^5[F^-]_\infty$
2.00×10^{-5}	6.00	6.00	1.02	0.976
2.00×10^{-5}	6.00	24.0	0.60	1.40
2.00×10^{-5}	6.00	42.0	0.41	1.59
2.00×10^{-5}	6.00	15.0	0.67	1.33
4.00×10^{-5}	20.0	10.0	2.64	1.36
4.00×10^{-5}	20.0	30.0	1.78	2.22
4.00×10^{-5}	20.0	60.0	1.35	2.65
4.00×10^{-5}	20.0	10.0	2.77	1.23
2.00×10^{-5}	6.00	6.00	1.05	0.95
4.00×10^{-5}	20.0	10.0	2.66	1.34
2.00×10^{-5}	6.00	6.00	1.02	0.98
4.00×10^{-5}	20.0	10.0	2.58	1.42
2.00×10^{-5}	6.00	6.00	0.977	1.02
4.00×10^{-5}	20.0	10.0	2.39	1.61
2.00×10^{-5}	6.00	6.00	0.868	1.13

$\Delta[R'(Co)]/[F^-]_\infty$	$10^5[R'(Co)]_{av}$	$10^4[A_5CoF^{2+}]_{av}$	$\frac{[R'(Co)]_{av}}{[A_5CoF^{2+}]_{av}}$	$[H^+]/M$
1.05	5.49	5.85	0.0938	1.00
0.429	5.70	23.8	0.0239	1.00
0.258	5.79	41.8	0.0139	1.00
0.504	5.66	14.8	0.0382	1.00
1.94	18.7	9.73	0.192	1.00
0.802	19.1	29.7	0.0643	1.00
0.509	19.3	59.7	0.0323	1.00
2.25	18.6	9.39	0.191	0.75
1.11	5.48	5.53	0.0935	0.75
1.99	18.7	9.33	0.192	0.50
1.04	5.49	5.51	0.0938	0.50
1.82	18.7	9.29	0.192	0.25
0.958	5.51	5.49	0.0942	0.25
1.48	18.8	9.20	0.193	0.15
0.768	5.57	5.44	0.0953	0.15

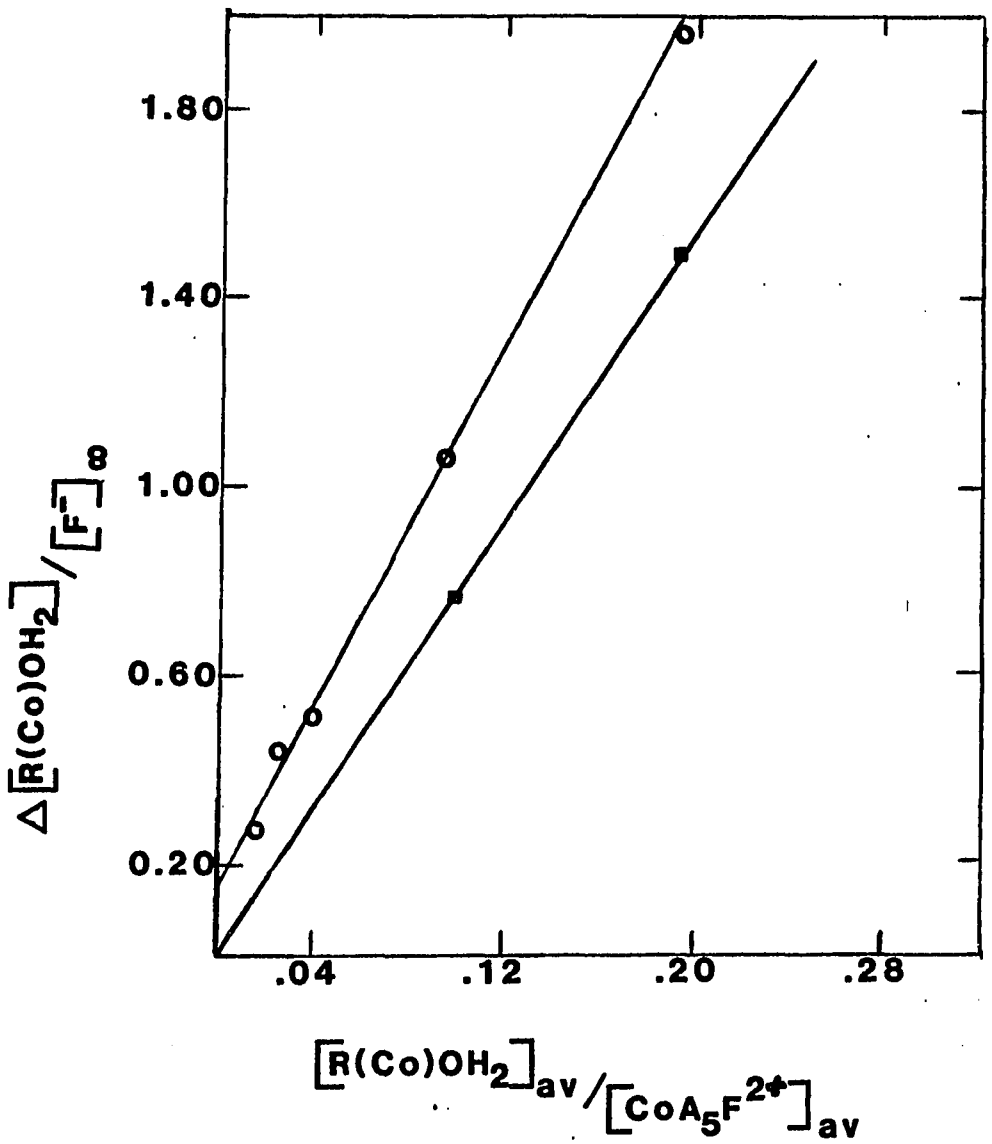


Figure I-4. Analysis of data for kinetic competition of $\cdot CH(CH_3)OC_2H_5$ for reaction with $PhCH_2Co(dmgH)_2OH_2$ (Equation 52) and $Co(NH_3)_5F^{2+}$. Data are plotted according to Equation 59 ($[H^+]$: 1.00M, circles; 0.150M, squares)

Table I-4. k_{52}^{app} as a function of $[H^+]$

$[H^+]/M$	$k_{R'(Co)}^{app}/k_{Co(NH_3)_5F^{2+}}$	$10^{-7}(k_{R'(Co)}^{app})/M^{-1}\ s^{-1}$
1.00	13.94	1.60
0.75	11.78	1.35
0.75	11.87	1.37
0.50	10.36	1.19
0.50	11.09	1.28
0.25	9.48	1.09
0.25	10.19	1.17
0.15	7.67	0.882
0.15	8.08	0.929

are plotted vs $[H^+]$ in Figure I-5. The pH dependence indicated in Figure I-5 can easily be explained considering the known protonation equilibrium of benzyl(aquo)cobaloxime.

Alkylcobaloximes are known to undergo a rapid and reversible equilibrium reaction with H^+ (73-78). In the equilibrium, one of the two hydrogen bound O-H....O moieties is converted to two separate OH groups. The equilibrium is symbolized as:

$$RCo(dmgH)_2OH_2 + H^+ \overset{K_H}{\rightleftharpoons} RCo(dmg_2H_3)OH_2^+.$$

Values of K_H typically lie in the range 1-10 M^{-1} for various alkyl and aryl groups (67, 73, 75, 77). If both the protonated and unprotonated

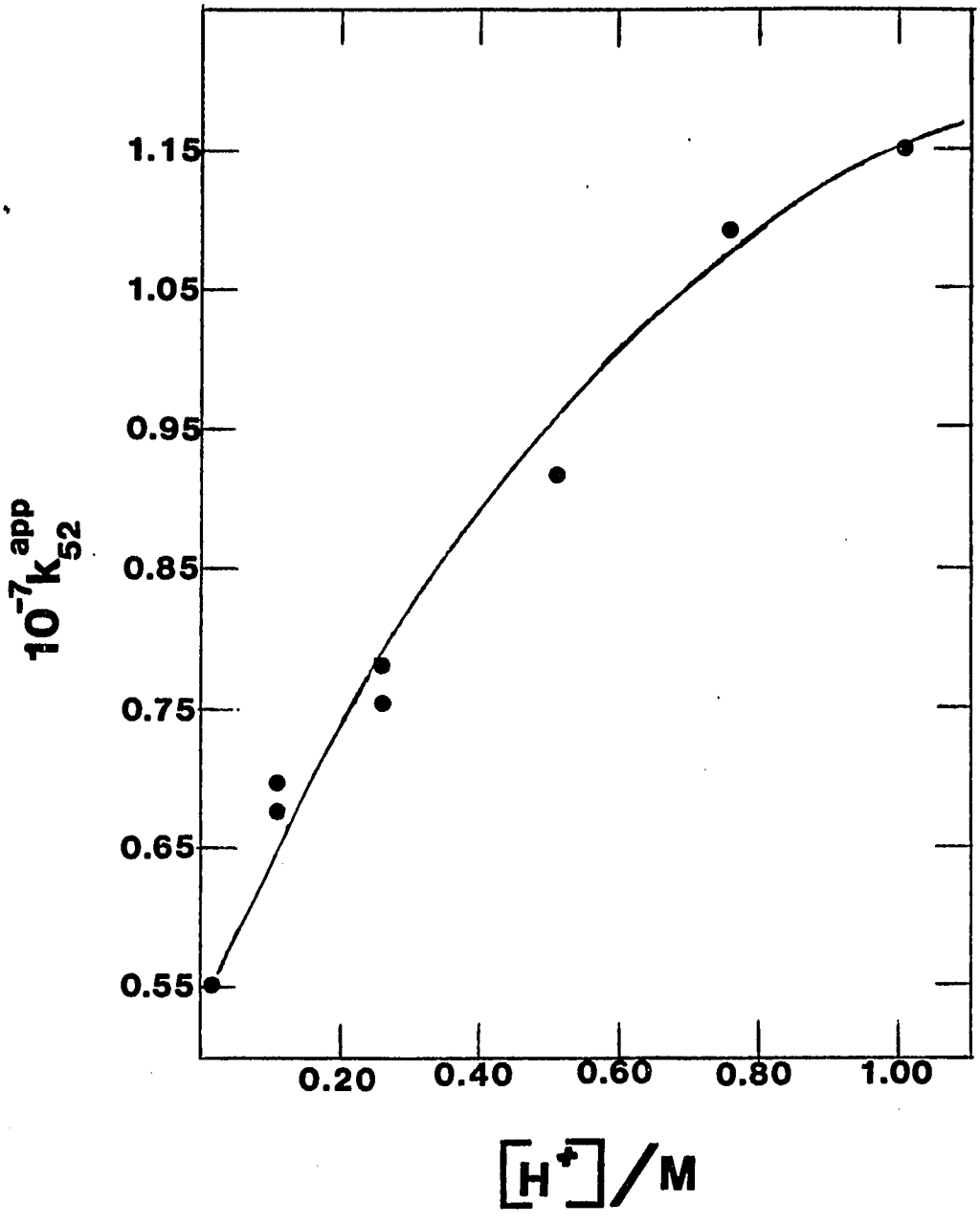


Figure I-5. Plot of k_{52}^{app} vs $[H^+]$ for the reaction of $\cdot CH(CH_3)OC_2H_5$ radical with $PhCH_2Co(dmgH)_2OH_2$, Equation 52

forms of the alkylcobaloxime react with the $\cdot CH(CH_3)OC_2H_5$ radical (= ·R in Equation 52), a plausible mechanism which is consistent with the observed dependence of k_{52}^{app} on $[H^+]$, Figure I-5, is given in Equations 79, 52a, 52b, 53a, and 53b.

$$PhCH_2Co(dmgH)_2OH_2 + H^+ \overset{K_H}{\rightleftharpoons} PhCH_2Co(dmg_2H_3)OH_2^+ \quad (79)$$

$$PhCH_2Co(dmg_2H_3)OH_2^+ + \cdot R \xrightarrow{k_a} PhCH_2R + Co(dmg_2H_3)OH_2^{1+} \quad (52a)$$

$$PhCH_2Co(dmgH)_2OH_2 + \cdot R \xrightarrow{k_b} PhCH_2R + Co(dmgH)_2OH_2 \quad (52b)$$

$$Co(dmg_2H_3)OH_2^+ + H^+ \xrightarrow{fast} Co^{2+}(aq) + 2dmgH_2 \quad (53a)$$

$$Co(dmgH)_2OH_2 + 2H^+ \xrightarrow{fast} Co^{2+}(aq) + 2dmgH_2 \quad (53b)$$

Protonation of the oxime bridge position is attended by slight but nonetheless significant changes in the uv-visible spectrum of the alkylcobaloxime, which can be used to evaluate the protonation constant K_H. Abley, Dockal, and Halpern (75) have determined the protonation constant for benzyl(aquo)cobaloxime in aqueous perchloric acid. In addition, as detailed in a later section, the value of K_H was redetermined in aqueous acidic 1.0M 2-propanol. The value obtained, $K_H = 2.6 \pm 0.3\ M^{-1}$, lies within the experimental error of the previously determined value of $2.4 \pm 0.3\ M^{-1}$ (75).

The sequence of equations for the reaction of $\cdot CH(CH_3)OC_2H_5$ radical with the protonated and unprotonated forms of the alkylcobaloxime leads to Equation 80. An excellent correction of the kinetic data to a plot

$$k_{52}^{app} = \frac{k_{52b} + k_{52a}K_H[H^+]}{1 + K_H[H^+]} \qquad \text{where } K_H = 2.6\ M^{-1} \quad (80)$$

of $k_{52}^{app}(1 + K_H[H^+])$ vs $[H^+]$, with $K_H = 2.6\ M^{-1}$, is shown in Figure I-6. A nonlinear least squares computer analysis of the data resulted in the following values:

$$k_{52b} = (5.9 \pm 0.7) \times 10^6\ M^{-1}\ s^{-1}$$

$$k_{52}^a = (1.9 \pm 0.1) \times 10^7\ M^{-1}\ s^{-1}$$

Other alkylcobaloximes, $RCo(dmgH)_2OH_2$ (R = CH_3, CH_2CH_3, and $i\text{-}C_3H_7$)

Kinetic results Competition experiments were conducted for methyl, ethyl, and isopropylcobaloximes, at 25.0°C and 1.0M ionic strength, in a manner strictly analogous to that employed for the study of benzyl(aquo)cobaloxime. Data were obtained at two acid concentrations, 1.0M and 0.01M. The organocobaloxime concentrations were varied over the range 1.50×10^{-4}M to 2.50×10^{-4}M, and that of the competing reagent, $Co(NH_3)_5F^{2+}$, was varied from 7.50×10^{-4}M to 4.00×10^{-3}M. The data obtained at 1.0 and 0.01M H^+ are summarized in Tables I-5 and I-6, respectively. A nonlinear least-squares computer analysis was used to fit the data to Equation 59. The data obtained for the three alkyl and

$$\frac{\Delta[RCo(dmgH)_2OH_2]}{\Delta[Co(en)_3^{3+}]} = \frac{k_{52}[RCo(dmgH)_2OH_2]_{ave}}{k_{51}[Co(NH_3)_5F^{2+}]_{ave}} \qquad (59)$$

benzylcobaloximes at 1.0M H^+ are displayed in Figure I-7.

Since the protonated alkylcobaloximes represent only a few percent of the total organocobaloxime at 0.01M H^+, the value of k_{52}^{app} obtained at 0.01M H^+ corresponds to the rate constant for reaction of the unprotonated cobaloxime, k_{52b}.

$$k_{0.01M}^{app} \simeq k_{52b}$$

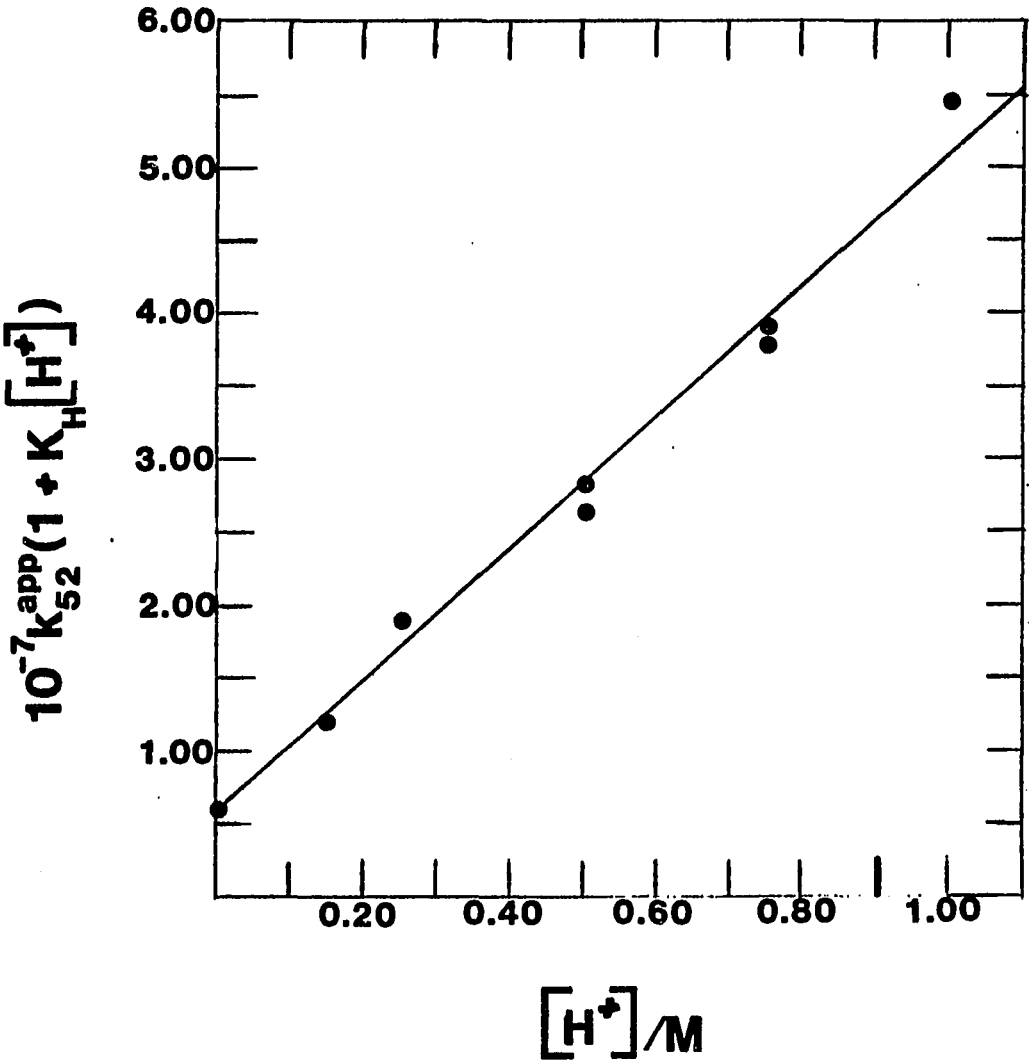


Figure I-6. Plot of $k_{52}^{app}(1 + K_H[H^+])$ vs $[H^+]$

Table I-5. Data for the competition between $Co(NH_3)_5F^{2+}$ and $RCo(dmgH)_2OH_2$ for $\cdot CH(CH_3)OCH_2CH_3$ radical. $[H^+]$ = 1.0M, μ = 1.0M

R	$10^6\Delta[R(Co)]$	$10^5[F^-]_\infty$	$10^4[R(Co)]_{ave}$	$10^3[CoA_5F^{2+}]_{ave}$	$\frac{\Delta[R(Co)]}{[F^-]_\infty}$	$\frac{[R(Co)]_{ave}}{[CoA_5F^{2+}]_{ave}}$
CH_3	9.18	2.28	1.45	0.723	0.404	0.202
	7.30	2.47	1.46	1.02	0.296	0.143
	7.08	2.49	1.46	1.47	0.285	0.0993
	5.25	2.68	1.47	2.99	0.194	0.0492
	4.37	2.76	1.48	4.00	0.159	0.0370
CH_3CH_2	6.25	2.48	1.47	0.722	0.250	0.203
	4.51	2.65	1.48	1.47	0.170	0.101
	3.70	2.73	1.48	2.22	0.136	0.0667
	3.10	2.79	1.48	3.72	0.111	0.0398
$i\text{-}C_3H_7$	4.50	2.65	1.48	0.721	0.170	0.205
	3.44	2.76	1.48	1.47	0.123	0.101
	2.97	2.80	1.49	2.22	0.107	0.0669
	2.75	2.83	1.49	2.97	0.095	0.0500
	2.28	2.87	1.49	3.72	0.080	0.0401

Table I-6. Data for the competition between $Co(NH_3)_5F^{2+}$ and $RCo(dmgH)_2OH_2$ for $\cdot CH(CH_3)OCH_2CH_3$ radical. $[H^+]$ = 0.01M, μ = 1.0M

R	$10^6\Delta[R(Co)]$	$10^5[F^-]_\infty$	$10^4[R(Co)]_{ave}$	$10^3[CoA_5F^{2+}]_{ave}$	$\frac{\Delta[R(Co)]}{[F^-]_\infty}$	$\frac{[R(Co)]_{ave}}{[CoA_5F^{2+}]_{ave}}$
CH_3	2.91	2.81	1.49	3.72	0.104	0.0401
	3.78	2.72	2.48	3.72	0.139	0.0667
	5.00	2.60	1.48	1.47	0.192	0.101
	6.69	2.43	1.47	0.722	0.275	0.204
	9.88	2.11	2.45	0.724	0.468	0.338
CH_3CH_2	7.21	2.38	2.46	0.723	0.303	0.340
	4.52	2.65	1.48	1.47	0.171	0.101
	4.35	2.67	2.48	3.72	0.163	0.0667
	3.51	2.75	1.48	3.72	0.128	0.0400
$i\text{-}C_3H_7$	5.71	2.43	2.47	0.768	0.235	0.322
	4.30	2.57	1.48	0.767	0.167	0.193
	2.90	2.81	1.49	1.47	0.103	0.101
	2.48	2.85	1.49	2.22	0.0870	0.0671

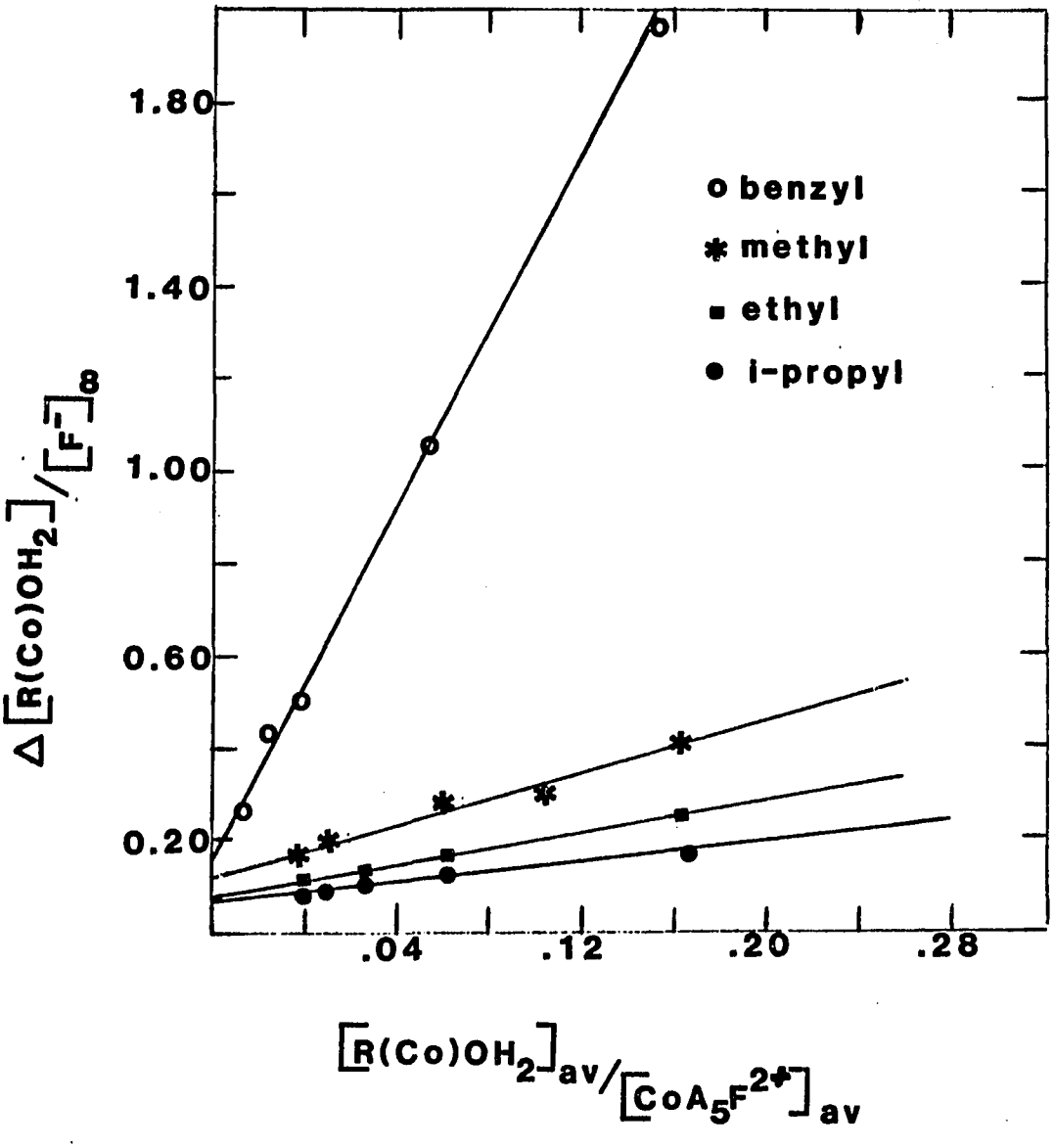


Figure I-7. Analysis of data obtained at 1.0M H^+ for kinetic competition between $RCo(dmgH)_2OH$, where R = CH_3, CH_2CH_3, $CH(CH_3)_2$, and $PhCH_2$ (Equation 52), and $Co(NH_3)_5F^{2+}$ for $\cdot CH(CH_3)OC_2H_5$ radical. Data are plotted according to Equation 59

With the values of k_{52}^{app} at 1.0M H^+, obtained from plots of the data according to Equation 59, k_{52b}, and K_H known for the particular alkylcobaloxime, (alkyl, K_H; methyl, 3.2 ± 0.2 M^{-1}, ethyl 3.4 ± 0.2 M^{-1}, and isopropyl, 4.2 ± 0.3 M^{-1} (73)) Equation 80 was solved for k_{52a}. Table I-7 lists the rate constants for the reaction of the acid form (k_{52a}) and the base form (k_{52b}) of methyl, ethyl, and isopropylcobaloximes with $\cdot CH(CH_3)OC_2H_5$ radical. For comparison, the rate constants for the two forms of benzylcobaloxime are also included in Table I-7. The interpretation and significance of the lack of steric effects will be presented in the discussion.

Table I-7. Rate constants for the reaction of $\cdot CH(CH_3)OC_2H_5$ radical with the acid and base forms of $RCo(dmgH)_2OH_2$, where R = CH_3, CH_2CH_3, $CH(CH_3)_2$, and $PhCH_2$

R	$10^{-6}k_a/M^{-1}\ s^{-1}$	$10^{-6}k_b/M^{-1}\ s^{-1}$
$PhCH_2$	19 ± 1	5.9 ± 0.7
CH_3	1.7	1.3
CH_2CH_3	1.0	0.66
$CH(CH_3)_2$	0.60	0.60

Reactions of the $\cdot C(CH_3)_2OH$ Radical with Organocobaloximes

Benzyl(aquo)cobaloxime, $PhCH_2Co(dmgH)_2OH_2$

Organic product Based upon the mass spectral fragmentation pattern, Figure I-8, and the gas chromatographic retention time, the

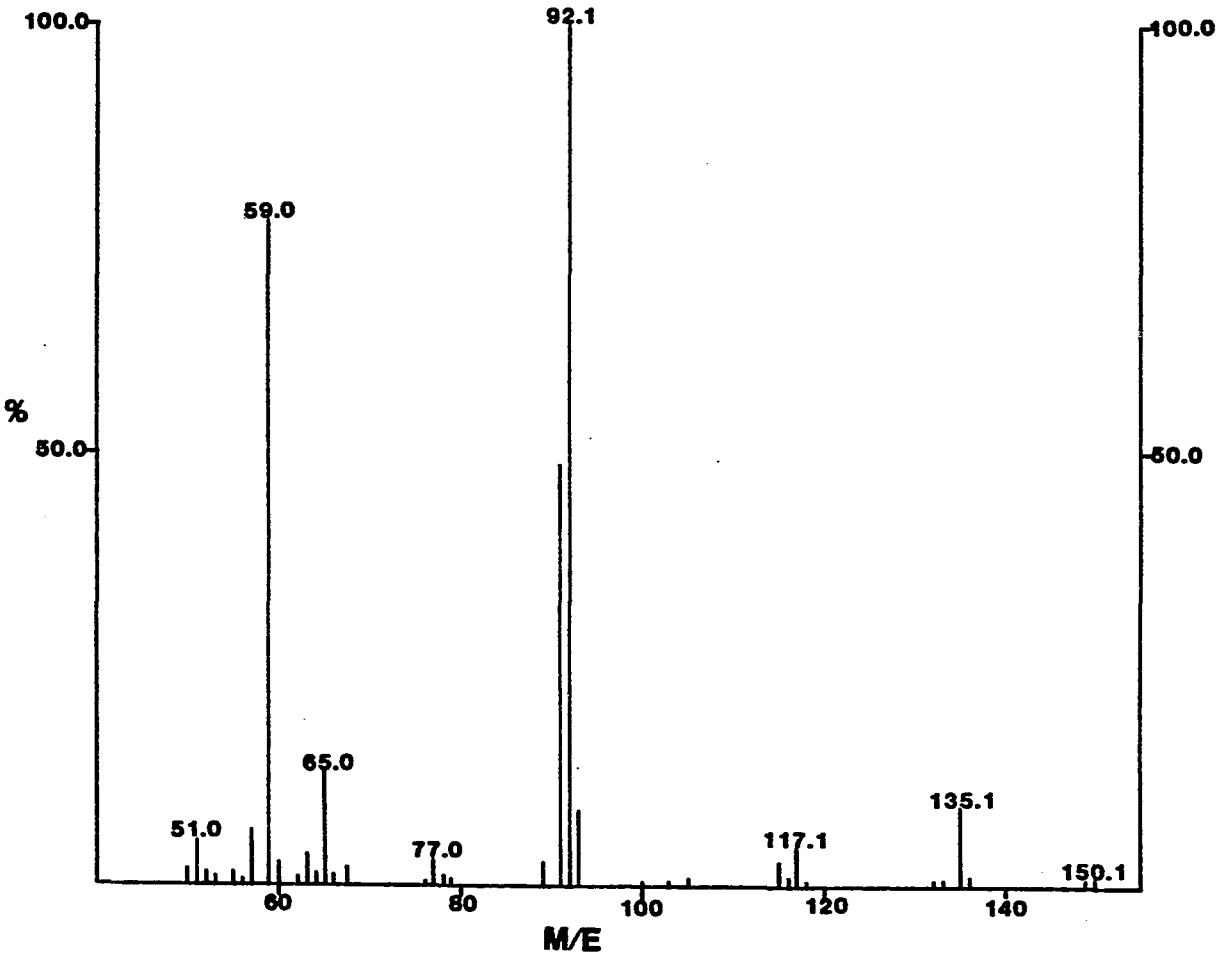


Figure I-8. Mass spectrum of 2-methyl-1-phenyl-2-propanol

product of the reaction between $\cdot C(CH_3)_2OH$ radical and benzylcobaloxime was identified as 2-methyl-1-phenyl-2-propanol, $PhCH_2C(CH_3)_2OH$.

$$\cdot C(CH_3)_2OH + PhCH_2Co(dmgH)_2OH_2 \rightarrow PhCH_2C(CH_3)_2OH + Co(dmgH)_2OH_2 \quad (81)$$

2-Methyl-1-phenyl-2-propanol proved isolable in greater than 90% yield when the $\cdot C(CH_3)_2OH$ radical was generated via homolysis of the benzylchromium(III) ion in the presence of H_2O_2 and 2-propanol. The sole aromatic product observed when the $\cdot C(CH_3)_2OH$ radical was generated in this fashion in the absence of benzylcobaloxime was 1,2-diphenylethane, the dimer of benzyl radical. This indicates the only source of $PhCH_2C(CH_3)_2OH$ is reaction 81 and the $\cdot C(CH_3)_2OH$ radical does not react with $CrCH_2Ph^{2+}$ to produce the alcohol. As indicated earlier, when the radical was generated directly from $CrC(CH_3)_2OH^{2+}$, the yield of $PhCH_2C(CH_3)_2OH$ decreased significantly and an additional peak with a retention time corresponding to pinacol, $HO(CH_3)_2CC(CH_3)_2OH$, was observed in the gc trace. Quantitative analyses of the yield of pinacol were not fruitful due to the difficulty encountered in removing pinacol from the aqueous solution and the poor resolution between the solvent (CH_2Cl_2) peak and that of pinacol. Pinacol, as discussed previously, may arise from attack by the radical upon the parent organochromium complex.

$$\cdot C(CH_3)_2OH + CrC(CH_3)_2OH^{2+} \rightarrow Cr^{2+}(aq) + HO(CH_3)_2CC(CH_3)_2OH \quad (60)$$

Kinetics As discussed previously, competition experiments employing $CrC(CH_3)_2OH^{2+}$ as the direct source of the $\cdot C(CH_3)_2OH$ radical were complicated by the presence of an extra reaction pathway, possibly

described by Equation 60, which consumed a portion of the free radical. Thus, competition experiments were performed using homolysis of $CrCH_2Ph^{2+}$ (22) in the presence of H_2O_2 and 2-propanol as the source of the $\cdot C(CH_3)_2OH$ radical.

Competition experiments were carried out under rigorously oxygen-free conditions at 25.0°C with $[CrCH_2Ph^{2+}]_0 = 2.00 \times 10^{-5}M$, $[PhCH_2Co(dmgH)_2OH_2]_0 = 6.00 \times 10^{-5}M$, and $[H_2O_2] = 3.00 \times 10^{-4}M$. The ionic strength was maintained constant at 1.0M with $HClO_4$-$LiClO_4$. Purified $CrCH_2Ph^{2+}$ stock solutions were used in every run. Yields of $Co^{2+}(aq)$ determined after reaction in selected runs indicated quantitative formation of $Co^{2+}(aq)$, i.e. $[Co^{2+}]_\infty = [CrCH_2Ph^{2+}]_0$. This supports the argument that the $\cdot C(CH_3)_2OH$ radical formed either reacts with the organocobaloxime or with $Co(en)_3^{3+}$ and that little is "wasted" in unproductive side-reactions. The data obtained are summarized in Tables I-8 and I-9. A plot of the data obtained at 1.0M and 0.010M H^+ according to Equation 76 is represented in Figure I-9.

$$Y = \frac{\Delta[Co(en)_3^{3+}]}{\ln\left\{\frac{[RCo(dmgH)_2OH_2]_0}{[RCo(dmgH)_2OH_2]_0 - \Delta[RCo(dmgH)_2OH_2]}\right\}} = \frac{k_{68}}{k_{69}}[Co(en)_3^{3+}]_0 \qquad (76)$$

The reduction of $Co(en)_3^{3+}$ in strongly acidic solution has been independently studied (10). The rate constant, $k_{68} = 1.7 \times 10^5\ M^{-1}\ s^{-1}$, at 1.0M ionic strength and 25.0°C has been shown to be independent of hydrogen ion concentration in the region pH 0-3. Thus, as was the case for the study of the $\cdot CH(CH_3)OC_2H_5$ radical, the pH dependence must arise from the protonation equilibrium of the cobaloxime. Equations 69a and 69b

Table I-8. Data for the competition between $PhCH_2Co(dmgH)_2OH_2$ and $Co(en)_3^{3+}$ for $\cdot C(CH_3)_2OH$ radical. μ = 1.0M, T = 25.0°C

10^5 [$PhCH_2Co(dmgH)_2OH_2$] / M	$10^5[PhCH_2Co(dmgH)_2OH_2]_0$ / M	$10^3[Co(en)_3^{3+}]_0$ / M	$[H^+]$ / M	10^5Y[a] / M
1.90, 2.00	6.00	0	1.00	0
1.55	6.00	0.600	1.00	1.17
1.52	6.00	1.20	1.00	1.64
1.32	6.00	1.50	1.00	2.34
1.03	6.00	3.60	1.00	5.17
0.879	6.00	4.39	1.00	6.44
0.844	6.00	5.20	1.00	7.64
0.749	6.00	5.85	1.00	8.63
2.00	6.00	0	0.10	0
1.59	6.00	0.600	0.10	1.35
1.25	6.00	1.20	0.10	3.21
0.860	6.00	3.00	0.10	7.38

[a]The quantity Y is defined as in Equation 76.

Table I-9. Data for the competition between $Co(en)_3^{3+}$ and $PhCH_2Co(dmgH)_2OH_2$ for $\cdot C(CH_3)_2OH$ radical as a function of $[H^+]$. $[Co(en)_3^{3+}]_0 = 3.00 \times 10^{-3}M$, $[PhCH_2Co(dmgH)_2OH_2]_0 = 6.00 \times 10^{-5}M$. Ionic strength maintained at 1.0M with $LiClO_4$

$10^6\Delta[PhCH_2Co(dmgH)_2OH_2]/M$	$10^5[CrCH_2Ph^{2+}]_0/M$	$[H^+]/M$	$10^5Y^a/M$
9.87	1.80	1.00	4.43
10.0	1.85	0.75	4.65
9.21	1.85	0.50	5.56
7.98	1.76	0.25	6.73
8.27	1.83	0.25	6.51
6.86	1.60	0.10	7.51
5.35	1.25	0.10	7.29
7.56	1.75	0.01	9.25

[a]The quantity Y is defined as in Equation 76.

represent the reactions of the protonated and unprotonated forms of the cobaloxime with the $\cdot C(CH_3)_2OH$ radical, $\cdot ROH$, respectively.

$$\cdot ROH + PhCH_2Co(dmg_2H_3)OH_2^+ \rightarrow PhCH_2ROH + Co(dmg_2H_3)OH_2^+ \quad (69a)$$

$$\cdot ROH + PhCH_2Co(dmgH)_2OH_2 \rightarrow PhCH_2ROH + Co(dmgH)_2OH_2 \quad (69b)$$

To determine the values of k_{69a} and k_{69b} the data obtained at fixed reactant concentrations as a function of $[H^+]$, Table I-9, were treated as follows:

Equation 76 predicts Y = 0 at $[Co(en)_3^{3+}]_0 = 0$, thus one point at each acidity was used to determine the quantity m defined by Equation 82.

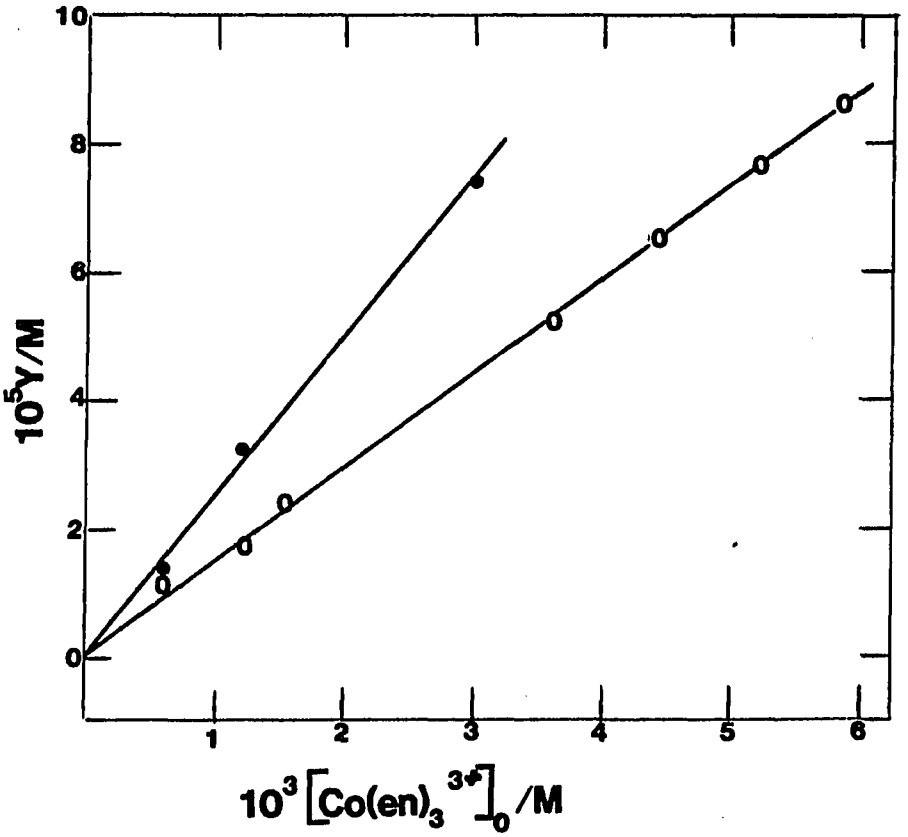


Figure I-9. Analysis of data for kinetic competition of $\cdot C(CH_3)_2OH$ for reaction with $PhCH_2Co(dmgH)_2OH_2$ (Equation 69) and $Co(en)_3^{3+}$. Data are plotted according to Equation 76 ($[H^+]$: 1.00M, open circles; 0.10M, filled circles)

$$m = Y[Co(en)_3^{3+}]_0 = \frac{k_{68}}{\frac{k_{69b} + k_{69a}K_H[H^+]}{1 + K_H[H^+]}} \quad (82)$$

Since k_{68} is known (10), values of k_{69}^{app} were obtained from Equation 83.

$$k_{68}/m = k_{69}^{app} = \frac{k_{69b} + k_{69a}K_H[H^+]}{1 + K_H[H^+]} \quad (83)$$

Table I-10 summarizes the data obtained as a function of $[H^+]$.

Table I-10. k_{69}^{app} as a function of $[H^+]$

$10^5 Y^a/M$	$Y^a/[Co(en)_3^{3+}]_0$	$10^{-6}k_{69}^{app}/M^{-1}\ s^{-1}$	$[H^+]/M$
4.43	0.0148	11.52	1.00
4.65	0.0155	10.94	0.75
5.56	0.0186	9.14	0.50
6.73	0.0225	7.55	0.25
6.51	0.0218	7.81	0.25
7.51	0.0251	6.77	0.10
7.29	0.0244	6.98	0.10
9.25	0.0307	5.53	0.01

[a]The quantity Y is defined as in Equation 76.

In order to determine k_{69a} and k_{69b} it was necessary to accurately determine K_H for benzylcobaloxime in aqueous solutions containing 1.0M 2-propanol. This determination is presented in a later section; however,

the value obtained, $K_H = 2.6 \pm 0.3\ M^{-1}$ is within the experimental error of the value determined in purely aqueous solution (75).

Figure I-10 illustrates a plot of the data obtained for the competition between $PhCH_2Co(dmgH)_2OH_2$ and $Co(en)_3^{3+}$ for the $\cdot C(CH_3)_2OH$ radical as a function of $[H^+]$, Table I-10, according to Equation 84 ($K_H = 2.6\ M^{-1}$).

$$k_{69}^{app}(1 + K_H[H^+]) = k_{69b} + k_{69a}K_H[H^+] \qquad (84)$$

A nonlinear least-squares computer analysis of the data of Table I-10, according to Equation 83,

$$k_{69}^{app} = \frac{k_{69b} + k_{69a}K_H[H^+]}{1 + K_H[H^+]} \qquad (83)$$

with $K_H = 2.6\ M^{-1}$, resulted in the following values:

$$k_{69b} = (5.2 \pm 0.2) \times 10^6\ M^{-1}\ s^{-1}$$

$$k_{69a} = (1.28 \pm 0.06) \times 10^7\ M^{-1}\ s^{-1}$$

Other alkylcobaloximes, $RCo(dmgH)_2OH_2$ (R = CH_3, CH_2CH_3, and i-C_3H_7)

Product of reaction with $(CH_3)_2CHCo(dmgH)_2OH_2$ Based upon the mass spectral fragmentation pattern, Figure I-11, and the gas chromatographic retention time, the product of the reaction between $\cdot C(CH_3)_2OH$ radical and isopropyl(aquo)cobaloxime was identified as 2,3-dimethyl-2-butanol.

$$\cdot C(CH_3)_2OH + (CH_3)_2CHCo(dmgH)_2OH_2 \rightarrow H(CH_3)_2CC(CH_3)_2OH + Co(dmgH)_2OH_2 \qquad (85)$$

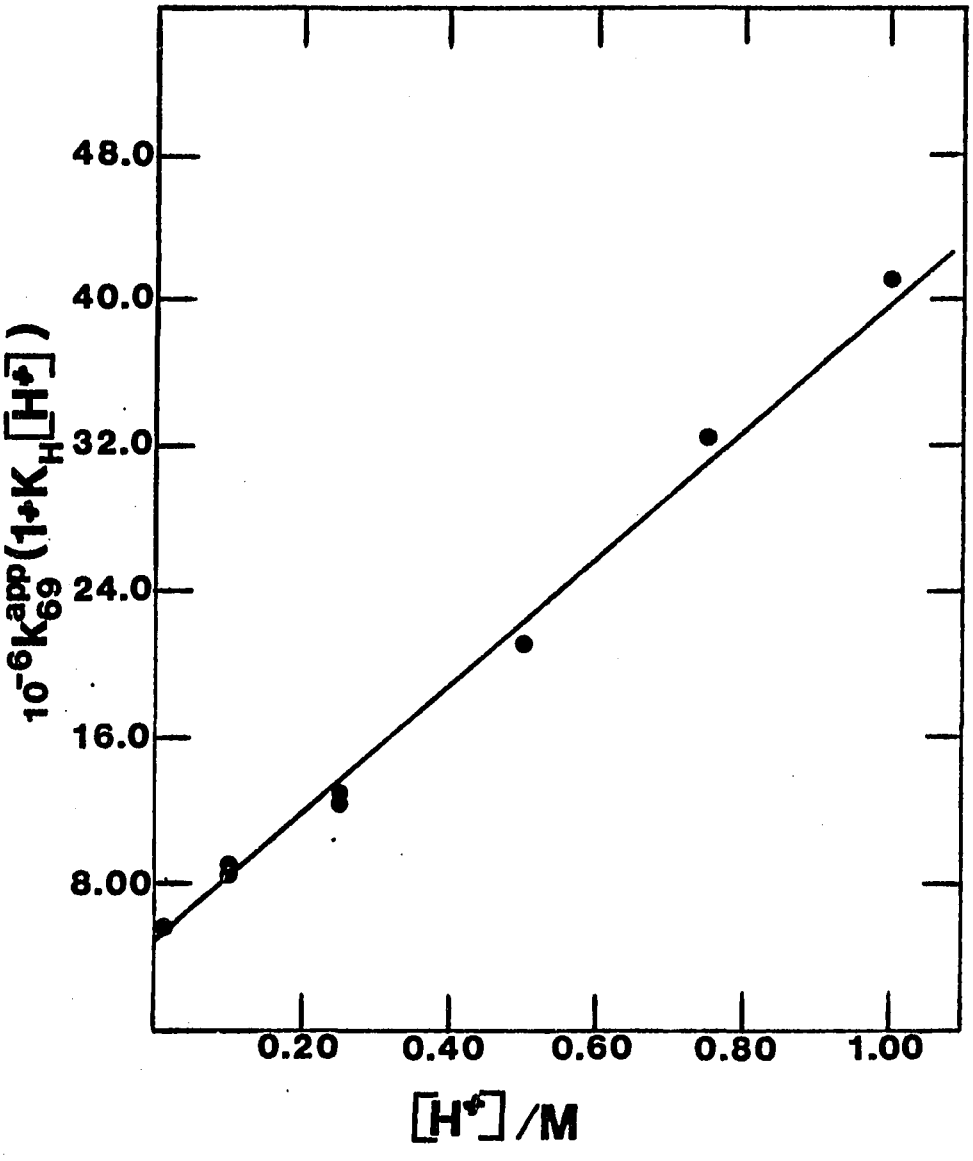


Figure I-10. Analysis of the data obtained from the competition for $\cdot C(CH_3)_2OH$ radical between $PhCH_2Co(dmgH)_2OH_2$ and $Co(en)_3^{3+}$ as a function of $[H^+]$, Table I-10, according to Equation 84

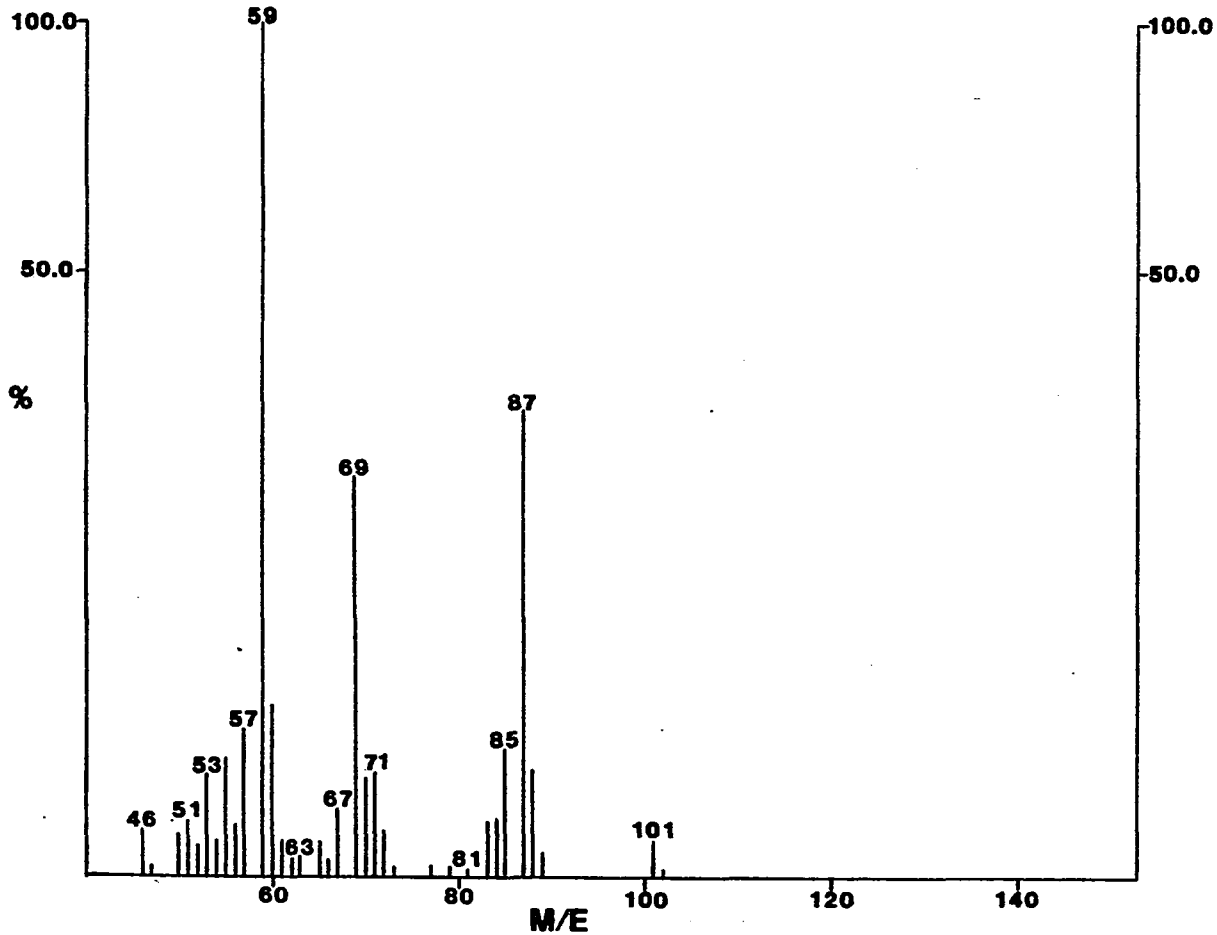


Figure I-11. Mass spectrum of 2,3-dimethyl-2-butanol

2,3-Dimethyl-2-butanol, like all low molecular weight alcohols, proved very difficult to extract from water. Based upon a comparison of the peak areas of an authentic sample of 2,3-dimethyl-2-butanol extracted into CH_2Cl_2 vs an unextracted sample, extraction with CH_2Cl_2 is only ∿30% efficient. Attempts to find a better extractant proved futile. Nonetheless, even with poor extraction efficiency, the yield of 2,3-dimethyl-2-butanol estimated from comparison of the peak height of an extracted standard sample with that of the product alcohol was fully consistent with the yield expected from the observed spectrophotometric change.

Kinetics The rate constants associated with the reactions of methyl, ethyl, and isopropylcobaloximes with the $\cdot C(CH_3)_2OH$ radical are of similar magnitude to that for reduction of $Co(en)_3^{3+}$ in strongly acidic solution. This allowed competition experiments to be carried out under conditions where the concentrations of neither competitor changed appreciably throughout the run. Thus, Equation 77 was used to treat the data obtained.

$$\frac{\Delta[RCo(dmgH)_2OH_2]}{\Delta[Co(en)_3^{3+}]} = \frac{k_{69}\,[RCo(dmgH)_2OH_2]_{ave}}{k_{68}\,[Co(en)_3^{3+}]_{ave}} \qquad (77)$$

The rate constants k_{69} and k_{68} refer to the reactions of the alkylcobaloximes and $Co(en)_3^{3+}$ with the $\cdot C(CH_3)_2OH$ radical, respectively.

$$\cdot C(CH_3)_2OH + RCo(dmgH)_2OH_2 \rightarrow RC(CH_3)_2OH + Co(dmgH)_2OH_2 \qquad (69)$$

$$\cdot C(CH_3)_2OH + Co(en)_3^{3+} \xrightarrow{(+2H^+)} Co^{2+}(aq) + (CH_3)_2CO + 3enH^+ \qquad (68)$$

Competition experiments were carried out at 25.0°C with the rigorous exclusion of oxygen. The ionic strength was maintained constant at 1.0M with $LiClO_4$-$HClO_4$. In all experiments, the initial concentration of $CrCH_2Ph^{2+}$ was less than 4.60×10^{-5}M. The initial concentration of H_2O_2 was set at three times that of the organochromium. Higher concentrations of H_2O_2 were avoided owing to a possible chain reaction involving reaction of the radical with H_2O_2.

$$\cdot C(CH_3)_2OH + H_2O_2 \rightarrow \cdot OH + H_2O + (CH_3)_2CO$$

Although this reaction is slow, $k = 5 \times 10^5\ M^{-1}\ s^{-1}$ (71), compared to other reactions of the $\cdot C(CH_3)_2OH$ radical, it was fast enough to interfere with the competition experiments.

The data obtained are summarized in Table I-11. Figure I-12 represents a plot of the data obtained at 1.0M H^+. Values of k_{69}^{app} were calculated from the slopes of the lines obtained from plots of data according to Equation 77.

In strict analogy to the data treatment for benzylcobaloxime, the rate constant k_{69a} pertains to the reaction of the protonated (acid) form of the cobaloxime,

$$\cdot C(CH_3)_2OH + RCo(dmg_2H_3)OH_2^+ \rightarrow RC(CH_3)_2OH + Co(dmg_2H_3)OH_2^+ \qquad (69a)$$

while k_{69b} pertains to the reaction of the unprotonated (base) form.

$$\cdot C(CH_3)_2OH + RCo(dmgH)_2OH_2 \rightarrow RC(CH_3)_2OH + Co(dmgH)_2OH_2 \qquad (69b)$$

For ethyl and isopropylcobaloximes, the value of k_{69}^{app} at 0.01M H^+ was equated with k_{69b} and used to calculate k_{69a} from Equation 86.

Table I-11. Data obtained from the competition for the $\cdot C(CH_3)_2OH$ radical between $Co(en)_3^{3+}$ and $RCo(dmgH)_2OH_2$; R(Co), where R = methyl, ethyl and isopropyl. T = 25.0°C, μ = 1.0M[a]

R	$[H^+]$	$10^5\Delta[R(Co)]$	$10^5\Delta[Co(en)_3^{3+}]$
CH_3	1.00	2.13	1.62
	1.00	1.37	2.38
	0.10	1.97	2.03
	0.10	1.23	2.77
CH_3CH_2	1.00	1.50	1.80
	1.00	1.08	1.56
	1.00	1.15	2.00
	1.00	1.13	2.44
	0.01	1.54	2.16
	0.01	1.10	2.90
$i\text{-}C_3H_7$	1.00	1.14	1.86
	1.00	1.02	1.98
	1.00	1.48	2.52
	1.00	1.12	2.88
	1.00	0.787	3.21
	1.00	0.800	3.20
	1.00	1.06	3.50
	1.00	0.631	3.37
	1.00	0.00	4.00
	0.01	0.876	2.12
	0.01	0.818	3.18
	0.01	0.611	3.49

[a]Ionic strength maintained with $LiClO_4$.

$10^4[R(Co)]_{ave}$	$10^3[Co(en)_3^{3+}]_{ave}$	$\frac{\Delta[R(Co)]}{\Delta[Co(en)_3^{3+}]}$	$\frac{[R(Co)]_{ave}}{[Co(en)_3^{3+}]_{ave}}$
1.96	0.997	1.315	0.196
1.97	2.00	0.575	0.0985
1.90	0.990	0.970	0.192
1.94	1.99	0.444	0.0975
1.93	0.991	0.833	0.195
1.95	1.24	0.692	0.157
1.94	1.49	0.575	0.130
1.44	1.49	0.463	0.0966
1.92	0.985	0.710	0.195
1.95	1.98	0.379	0.0986
1.94	0.970	0.602	0.200
1.95	0.990	0.515	0.197
1.93	0.990	0.587	0.195
1.94	1.49	0.389	0.130
1.96	1.98	0.246	0.0988
1.46	1.48	0.250	0.0986
1.95	1.98	0.303	0.0984
1.97	2.98	0.187	0.0661
0.00	1.50	0.00	0.00
1.96	0.989	0.413	0.198
1.96	1.99	0.257	0.0985
1.47	2.23	0.175	0.0658

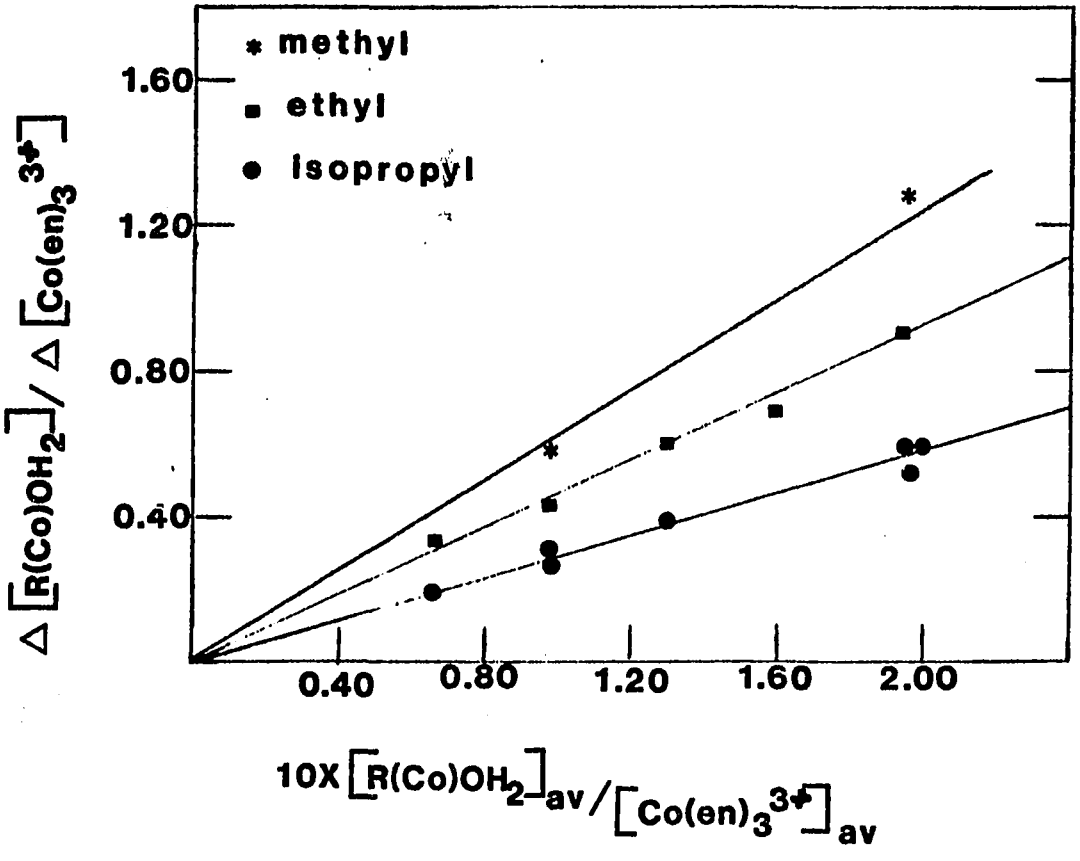


Figure I-12. Plot of the data at 1.0M H^+, from Table I-11, according to Equation 77

$$k_{69a} = \frac{k_{69}^{1.0M\ H^+}(1 + K_H) - k_{69b}}{K_H} \qquad (86)$$

For methylcobaloxime, the values of k_{69a} and k_{69b} were calculated from the experimentally determined values of k_{69}^{app} at 1.0M and 0.1ØM H^+ by solution of the system of two simultaneous equations in k_{69a} and k_{69b} obtained from Equation 87.

$$k_{69}^{app} = \frac{k_{69b} + k_{69a}K_H[H^+]}{1 + K_H[H^+]} \qquad (87)$$

Table I-12 lists the rate constants for the reaction of the acid form (k_{69a}) and the base form (k_{69b}) of methyl, ethyl, and isopropylcobaloximes with $\cdot C(CH_3)_2OH$ radical. For comparison, the rate constants for the two forms of benzylcobaloxime are also included in Table I-12.

Table I-12. Rate constants for the reaction of $\cdot C(CH_3)_2OH$ radical with the protonated and unprotonated forms of $RCo(dmgH)_2OH_2$, where R = CH_3, CH_2CH_3, $CH(CH_3)_2$, and $PhCH_2$

R	$10^{-6}\ k_a/M^{-1}\ s^{-1}$	$10^{-6}\ k_b/M^{-1}\ s^{-1}$
$PhCH_2$	12.8 ± 0.60	5.2 ± 0.2
CH_3	1.2	0.71
CH_2CH_3	0.79	0.64
$CH(CH_3)_2$	0.49	0.41

Products of the Coupling Reactions Between Selected Free Radicals and Benzyl(aquo)cobaloxime

As discussed previously, homolysis of benzylchromium (22) in the presence of H_2O_2 and a suitable organic substrate can be utilized to chemically generate desired radicals. The only constraints placed upon the substrate are modest water solubility, >0.01M, and clean reaction with either ·OH radical or $Cr^{2+}(aq)$ to produce one or at most two carbon centered radicals.

Table I-13 indicates the coupling reactions observed, and kinetically studied, between $\cdot C(CH_3)_2OH$ and $\cdot CH(CH_3)OC_2H_5$ radicals are apparently quite general in nature. Of all the radicals investigated, only $\cdot CH_2Ph$ and meta-chlorophenyl radicals proved unreactive toward benzylcobaloxime.

The unreactivity of benzyl radical toward benzylcobaloxime was not altogether unexpected since $\cdot CH_2Ph$ radical is unreactive toward inorganic cobalt(III) oxidants, such as $Co(NH_3)_5Br^{2+}$ (22). The unreactivity of meta-chlorophenyl radical, although not completely understood, must be related to the electronic nature of the radical. The odd electron of the phenyl radical is localized in an sp^2 orbital, and hence is a σ radical. All the other radicals studied are π radical, with the lone electron occupying the p_z orbital.

It is interesting to note, when the substrate used was ethanol, both products, stemming from the reaction of the α and β radicals, were identified. Hydroxyl radical reacts with ethanol to produce 84.3% $\cdot CH(CH_3)OH$ radical and 13.2% $\cdot CH_2CH_2OH$ radical (70).

Table I-13. Products obtained from the coupling reactions of selected free radicals with benzylcobaloxime

Substrate	Radical(s)	Product(s)	Characterization method(s)
CH_3OH	$\cdot CH_2OH$	$PhCH_2CH_2OH$	G[a]
CH_3CH_2OH	$\cdot CH(CH_3)OH$	$PhCH_2CH(CH_3)OH$	G, M[b] (Figure I-13)
	$\cdot CH_2CH_2OH$	$PhCH_2CH_2CH_2OH$	G, M (Figure I-14)
C_2H_4[c]	$\cdot CH_2CH_2OH$	$PhCH_2CH_2CH_2OH$	G, M (Figure I-14)
$(CH_3)_2CHOH$	$\cdot C(CH_3)_2OH$	$PhCH_2C(CH_3)_2OH$[d]	G, M (Figure I-8)
$CH_3CH_2OC_2H_5$	$\cdot CH(CH_3)OC_2H_5$	$PhCH_2CH(CH_3)OC_2H_5$	G, M (Figure I-3)
$(CH_3)_3COOH$[e]	$\cdot CH_3$	$PhCH_2CH_3$	G
DMSO[f]	$\cdot CH_3$	$PhCH_2CH_3$	G
$(CH_3)_2CHC(CH_3)_2OOH$[e]	$\cdot CH(CH_3)_2$	$PhCH_2CH(CH_3)_2$[g]	G
$(CH_3)_3CC(CH_3)_2OOH$[e]	$\cdot C(CH_3)_3$	$PhCH_2C(CH_3)_3$	G, M (Figure I-15)
$\underline{c}$-C_5H_{10}	$\underline{c}$-$C_5H_9\cdot$	$PhCH_2$-$\underline{c}$-C_5H_9	G, M (Figure I-16)
$CH_3C(O)OH$	$\cdot CH_2C(O)OH$	$PhCH_2CH_2C(O)OH$[h]	G
$CrCH_2Ph^{2+}$	$\cdot CH_2Ph$	no reaction	
meta-ClPhC(O)OOH	meta-chlorophenyl	no reaction	

[a]G = gas chromatographic retention time.

[b]M = mass spectrum.

[c]Hydroxyl radical addition to the double bond of ethylene occurs exclusively.

[d]Product identified from direct homolysis of $CrC(CH_3)_2OH^{2+}$ as well as from the kinetic competition solutions $[PhCH_2Co(dmgH)_2OH_2] = 6 \times 10^{-5}M$.

[e]Hydrogen peroxide is unnecessary when substrates are hydroperoxides. Chromium(II) reacts to initially produce an alkoxy radical. An alkyl radical is formed by subsequent rapid β-scission of the alkoxy radical.

[f]Hydroxyl radical addition to $(CH_3)_2SO$ followed by β-elimination of methyl radical.

[g]$PhCH_2CH(CH_3)_2$ was also produced by the reaction of $\cdot CH(CH_3)_2$, obtained from direct homolysis of $CrC(CH_3)_2^{2+}$ (60), with benzylcobaloxime.

[h]Chromatographed as the methyl ester, $PhCH_2CH_2C(O)OCH_3$.

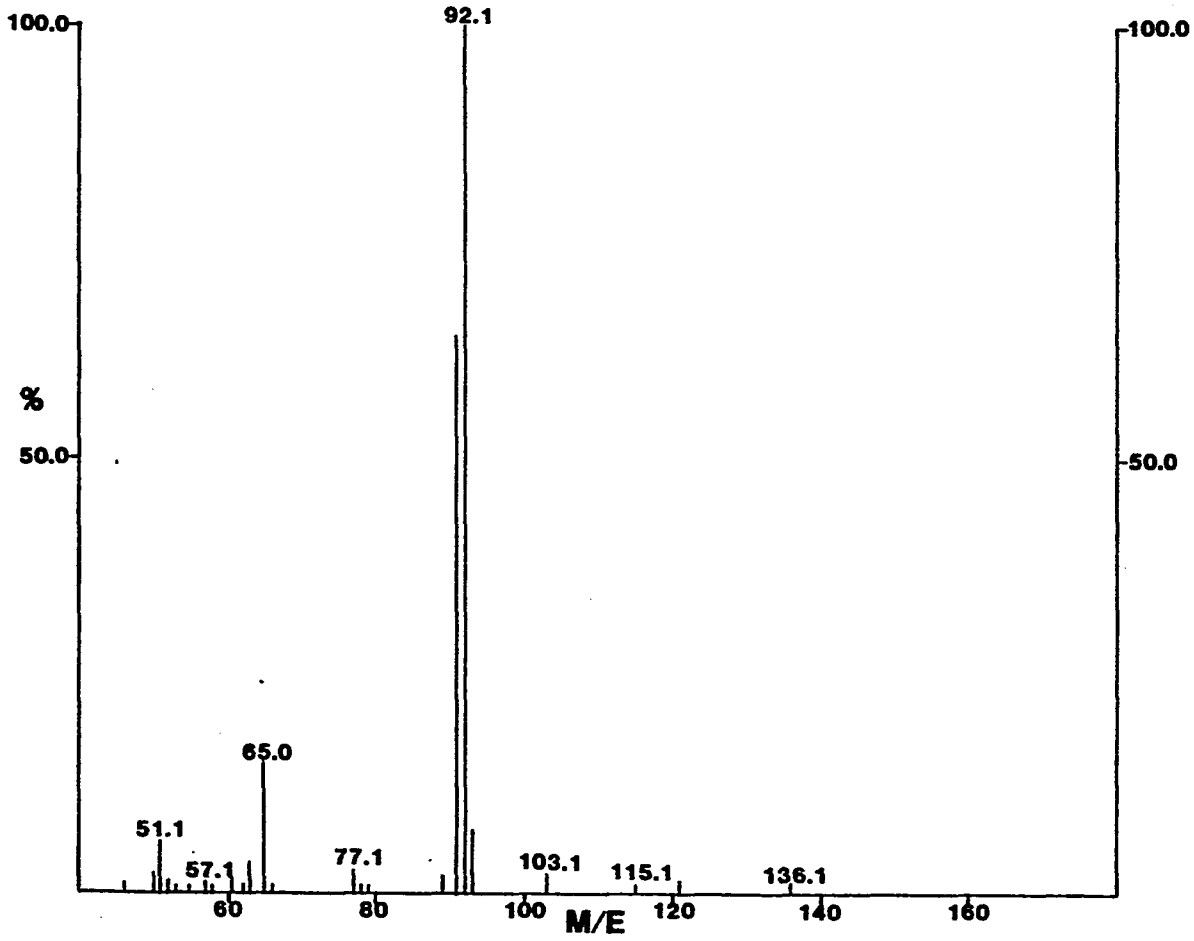


Figure I-13. Mass spectrum of 1-phenyl-2-propanol

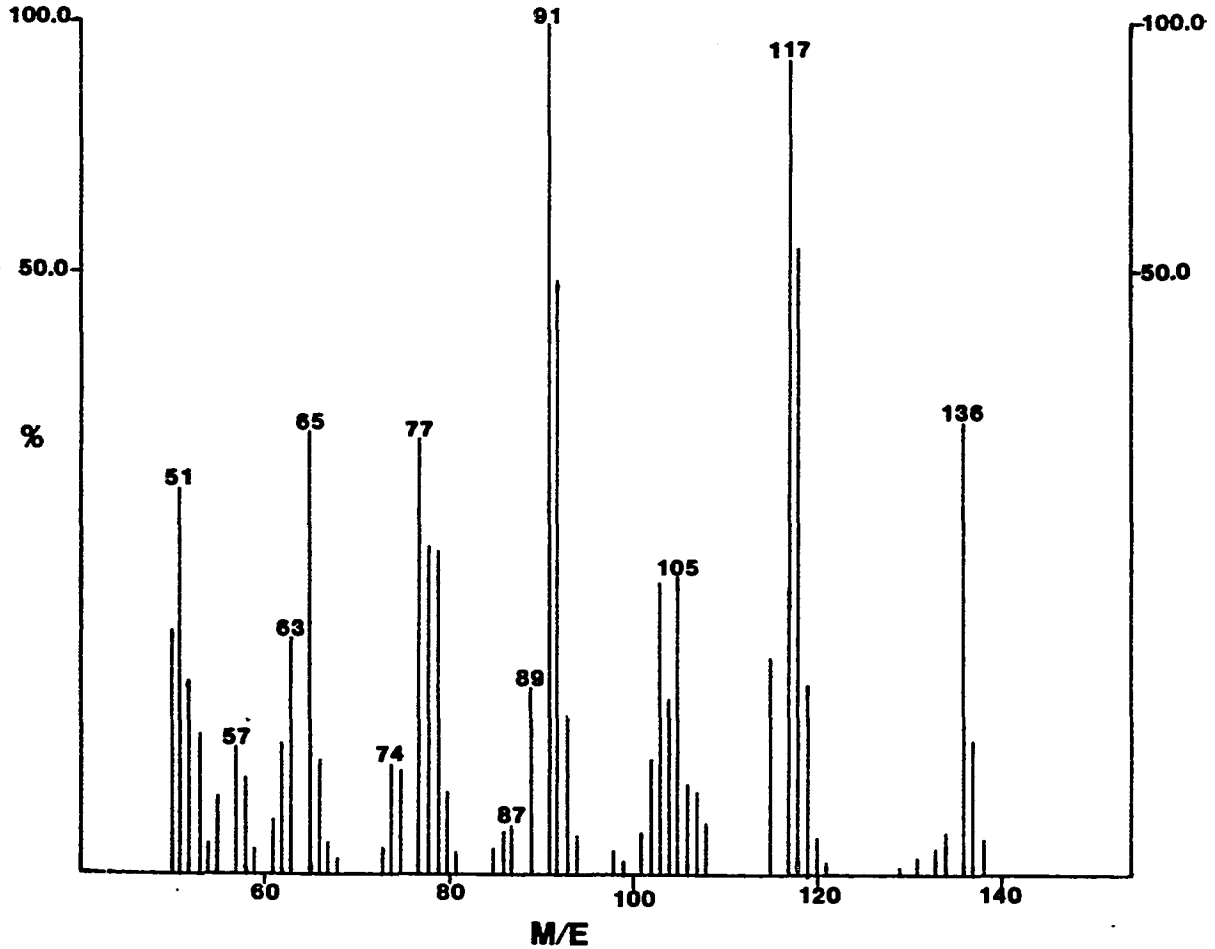


Figure I-14. Mass spectrum of 3-phenyl-1-propanol

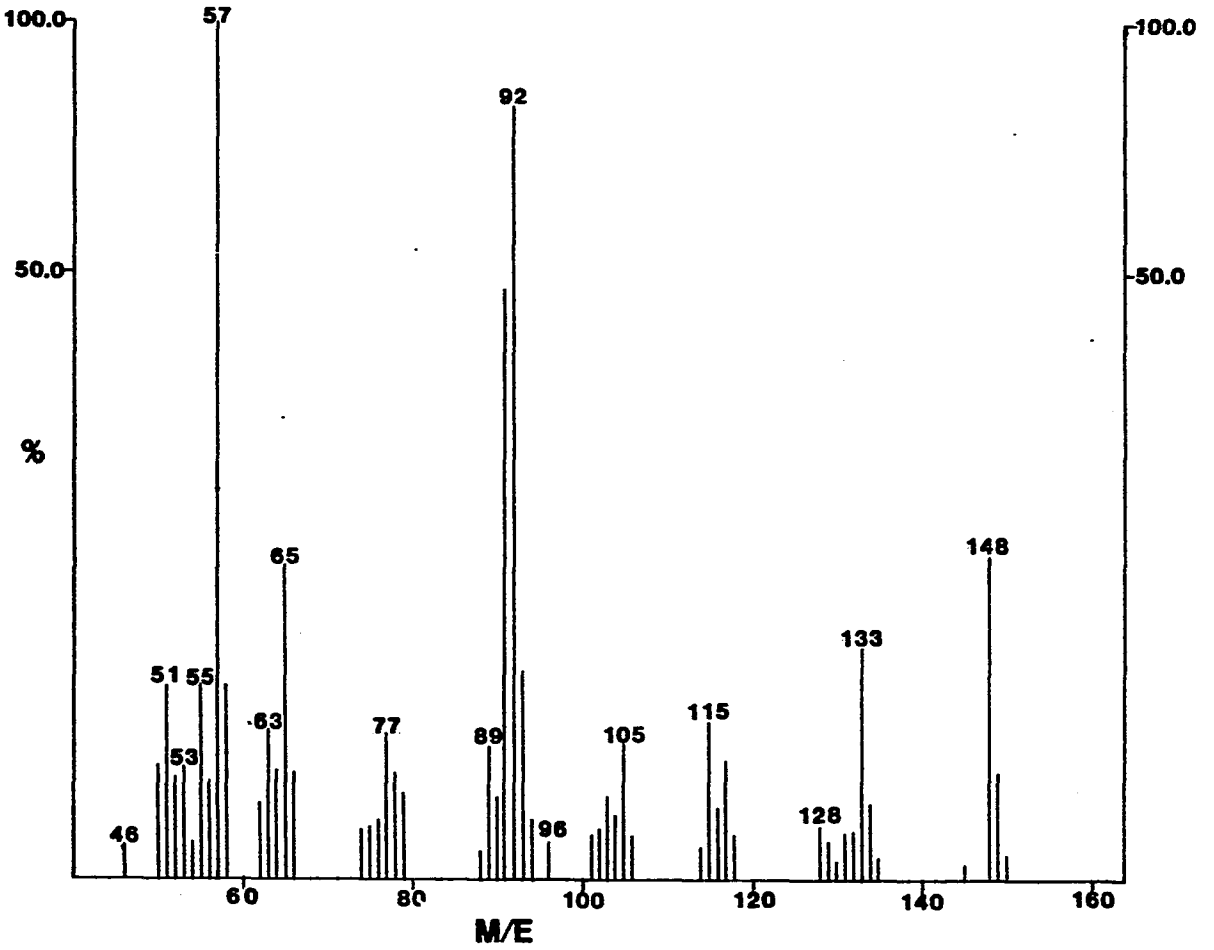


Figure I-15. Mass spectrum of neopentylbenzene, $PhCH_2C(CH_3)_3$

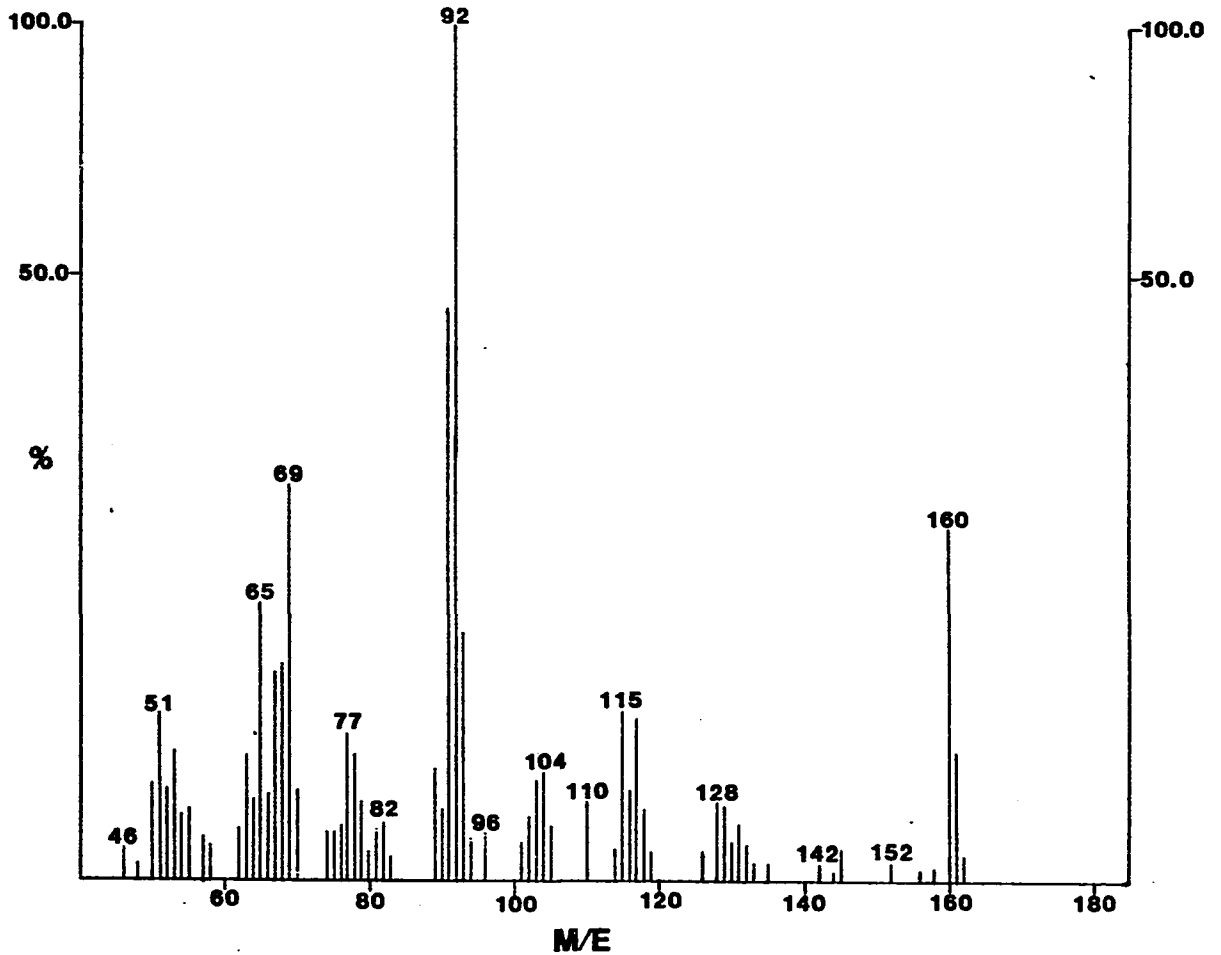


Figure I-16. Mass spectrum of phenylcyclopentylmethane

$$\cdot OH + CH_3CH_2OH \rightarrow H_2O + \cdot CH(CH_3)OH$$

$$\cdot OH + CH_3CH_2OH \rightarrow H_2O + \cdot CH_2CH_2OH$$

Analysis of the gas chromatographic peak areas of the two products obtained indicated isolation in a 7:1 ratio (α/β), in agreement with the calculated ratio of 6.4:1.

Preparation of a Large Sample of 2-Methyl-1-phenyl-2-propanol

The reaction of $\cdot C(CH_3)_2OH$ radical with benzylcobaloxime to produce 2-methyl-1-phenyl-2-propanol, $PhCH_2C(CH_3)_2OH$, is efficient, not only on the kinetic competition scale, but also at much higher concentrations. Experiments conducted at the 10^{-4}M and 10^{-3}M benzylcobaloxime level established the fact that 2-methyl-1-phenyl-2-propanol is the sole organic product from the reaction of $\cdot C(CH_3)_2OH$ radical and benzylcobaloxime. Yields obtained from gc analyses of hexane extracts were in absolute agreement with those calculated from the uv-visible absorption changes. Thus, the efficiency of this reaction was such as to permit the preparation of 2-methyl-1-phenyl-2-propanol on the gram scale.

A suspension of approximately 4 grams (0.01 mole) of $PhCH_2Co(dmgH)_2OH_2$ was prepared in 250 mL of 1.0M 2-propanol and 2.0M in perchloric acid. At this acidity, greater than 90% of the organocobaloxime dissolved. While protecting the solution from light, 10.0 mL of 30% H_2O_2 (0.10 mole) was added. After thorough deaeration with Chromous-scrubbed nitrogen, 500 mL of 0.105M Cr^{2+} (1.0M $HClO_4$) was added dropwise with extremely vigorous stirring. After the addition of Cr^{2+}(aq) was completed, the uv-visible spectrum indicated approximately 90% of the

cobaloxime had been consumed. The organic product was extracted into 300 mL of hexanes. Nearly all of the hexane was removed by atmospheric evaporation leaving approximately 1½ mL of nearly pure alcohol. The $PhCH_2C(CH_3)_2OH$ was purified by preparatory gas chromatography on a 6' x ¼" 5% FFAP packed column at 175°C. The isolated product (1.0 mL) exhibited mass spectrum, nmr, and gas chromatographic retention time identical to those of an authentic sample.

Protonation Constant K_H for Benzylcobaloxime

In order to accurately determine k_{69a} and k_{69b} it was necessary to accurately determine K_H for benzylcobaloxime. The previously determined value of K_H (75) was obtained from the kinetic effect of the protonation equilibrium, Equation 79, upon the reaction of benzylcobaloxime with Hg(II) and Tl(III). In addition, competition experiments involving the

$$PhCH_2Co(dmgH)_2OH_2 + H^+ \overset{K_H}{\rightleftharpoons} PhCH_2Co(dmg_2H_3)OH_2^+ \qquad (79)$$

2-hydroxy-2-propyl radical must of necessity be done in solutions containing appreciable concentrations of 2-propanol. In light of possible medium effects, it was necessary to redetermine K_H in the presence of 1.5M 2-propanol.

The protonation of one of the oxime bridge positions, Equation 79, is attended by slight, yet nonetheless significant, changes in the uv-visible spectrum of the cobaloxime. For a system containing two absorbing species, symbolized R(Co) and $R(Co)^+$, related by Equation 79, the observed extinction coefficient, ε_{obs}, is related to the concentrations of the two absorbing species according to Equation 88,

$$\varepsilon_{obs}[R(Co)]_T = \varepsilon_1[R(Co)] + \varepsilon_2[R(Co)^+] \quad (88)$$

where $[R(Co)]_T = [R(Co)] + [R(Co)^+]$, $\varepsilon_{obs} = Deq/\ell[R(Co)]_T$. Substitution of $[R(Co)] = [R(Co)]_T - [R(Co)^+]$ into Equation 88 yields,

$$\varepsilon_{obs}[R(Co)]_T = \varepsilon_1\{[R(Co)]_T - [R(Co)^+]\} + \varepsilon_2[R(Co)] \quad (89)$$

Expansion and rearrangement of Equation 89 affords Equation 90.

$$(\varepsilon_{obs} - \varepsilon_1)[R(Co)]_T = (\varepsilon_2 - \varepsilon_1)[R(Co)^+] \quad (90)$$

Inversion of both sides of Equation 90 yields Equation 91.

$$(\varepsilon_{obs} - \varepsilon_1)^{-1} = (\varepsilon_2 - \varepsilon_1)^{-1}[R(Co)]_T/[R(CO)^+] \quad (91)$$

Since $[R(Co)]_T = [R(Co)] + [R(Co)^+]$, substitution into Equation 91 affords,

$$(\varepsilon_{obs} - \varepsilon_1)^{-1} = (\varepsilon_2 - \varepsilon_1)^{-1}\{1 + [R(Co)]/[R(Co)^+]\} \quad (92)$$

With the protonation equilibrium defined as in Equation 79, Equation 92 can be rearranged to give,

$$(\varepsilon_{obs} - \varepsilon_1)^{-1} = (\varepsilon_2 - \varepsilon_1)^{-1}\{1 + K_H^{-1}[H^+]^{-1}\}. \quad (93)$$

Table I-14 lists the data obtained from a spectrophotometric titration of $PhCH_2Co(dmgH)_2OH_2$ with $HClO_4$ at 440 nm. Figure I-17 illustrates a plot of the data according to Equation 93. The ratio of intercept to slope affords $K_H = 2.6 \pm 0.3\ M^{-1}$. From a comparison of this value of K_H with the previously determined value of $2.4 \pm 0.3\ M^{-1}$ (75), it may be concluded that modest concentrations of 2-propanol exert no effect upon the equilibrium represented by Equation 79.

Table I-14. Data obtained for the equilibrium of Equation 79

ε_{obs}[a]/M^{-1} cm^{-1}	$(\varepsilon_{obs}-\varepsilon_1)$[b]	$(\varepsilon_{obs}-\varepsilon_1)^{-1}$/M cm	$[H^+]$/M	$[H^+]^{-1}$/M^{-1}
1102	293	3.41×10^{-3}	1.00	1.00
1053	244	4.10×10^{-3}	0.75	1.33
1026	217	4.61×10^{-3}	0.50	2.00
980	171	5.85×10^{-3}	0.25	4.00
895	86	1.16×10^{-2}	0.10	10.0
855	46	2.17×10^{-2}	0.05	20.0

[a] λ400nm T = 25.0°C, μ = 1.00 M [2-propanol] = 1.50 M.

[b] ε_1 = 809 M^{-1} cm^{-1}.

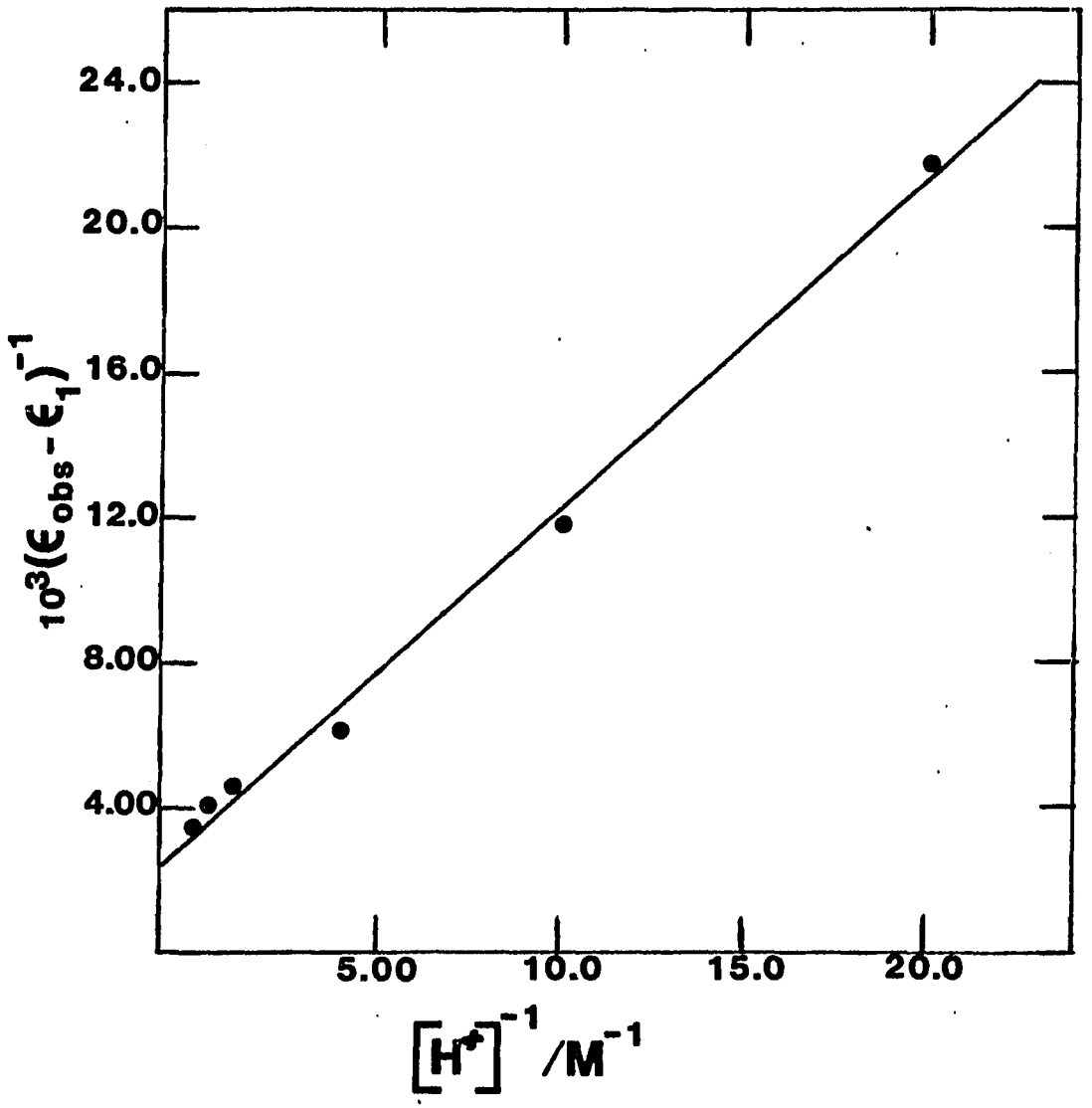


Figure I-17. Plot of the data obtained for the acid-base equilibrium of $PhCH_2Co(dmgH)_2OH_2$ according to Equation 93

DISCUSSION

The results presented above have established several experimental facts concerning the reaction of alkylcobaloximes with selected aliphatic free radicals. First, the reaction involves highly specific carbon-carbon bond formation with concomitant one-electron reduction of the metal center. In all cases, the organic product produced results from coupling of the α-carbon atom of the alkyl moiety with the free radical. In no case was rearrangement of any sort observed. From the

$$\cdot R' + R_1R_2R_3CCo(dmgH)_2OH_2 \rightarrow R_1R_2R_3CR' + Co(dmgH)_2OH_2 \qquad (94)$$

wealth of radicals studied, as well as their varied nature, this reaction appears to be quite general. Secondly, these reactions proceed with quite good yield, provided they are carried only to low conversions of the organocobaloximes, less than some 40% in the case of benzyl(aquo)-cobaloxime. Quantitative analyses of the organic products have established a 1:1 correspondence with the yield calculated from the spectrophotometric change. Isolated yields of greater than 90%, based upon the amount of organocobalt complex destroyed, were common. In addition, $Co^{2+}(aq)$ yields indicate little, if any, of the free radicals are "wasted" in unproductive side reactions. Finally, the various competition experiments have established the reaction to be a bimolecular process, first order in the free radical and first order in the organocobaloxime. Table I-15 summarizes the kinetic parameters obtained for the reaction of the protonated and unprotonated forms of the organocobaloximes with $\cdot C(CH_3)_2OH$ and $\cdot CH(CH_3)OC_2H_5$ radicals.

Table I-15. Rate constants[a] ($10^{-6}k/M^{-1}\ s^{-1}$) for the reaction of $RCo(dmg_2H_3)OH_2^+$ (k_a) and $RCo(dmgH)_2OH_2$ (k_b) with $\cdot C(CH_3)_2OH$ and $\cdot CH(CH_3)OC_2H_5$ radicals

·R	$\cdot C(CH_3)_2OH$		$\cdot CH(CH_3)OC_2H_5$	
	k_a	k_b	k_a	k_b
$PhCH_2$-	12.8 ± 0.60	5.2 ± 0.2	19 ± 1	5.9 ± 0.7
CH_3-	1.2	0.71	1.7	1.3
CH_3CH_2-	0.79	0.64	1.1	0.66
$(CH_3)_2HC$-	0.49	0.41	0.60	0.60

[a] $T = 25.0^oC$, $\mu = 1.0M$ ($LiClO_4$-$HClO_4$).

As can be seen from the data of Table I-15, protonation of one of the hydrogen bonded O-H...O units of the $(dmgH)_2$ pseudo-macrocycle consistently results in a minor enhancement in the reactivity of the organocobaloxime.

Protonation of one of the oxime bridges of the organocobaloxime typically results in either a minor enhancement in reactivity upon protonation or, alternatively, a very stark effect with only the unprotonated form being reactive. Reactions which exhibit the former type of effect are characterized by reduction of the metal center. Examples include the reaction of Cr^{2+}(aq) with organocobaloximes (45) and the decomposition of α-phenylethyl(aquo)cobaloxime in acidic solution (66b). The latter type of effect is observed for electrophillic substitution reactions, typical examples being the reactions of Hg^{2+} and Tl^{3+} (75).

The reactions of aliphatic free radicals with organocobaloximes also involve a formal reduction of the metal center, and thus would be expected to exhibit a slight enhancement in reactivity upon protonation of the organocobaloxime. The effects observed are completely consistent with those predicted by the general trends.

Mechanistic Alternatives

Several mechanisms for the reaction between aliphatic free radicals and the organocobaloximes may be proposed:

i) Rate limiting homolysis of the cobalt-carbon bond, followed by rapid coupling of the two radical fragments.

$$RCo(dmgH)_2OH_2 \rightarrow \cdot R + Co(dmgH)_2OH_2$$

$$\cdot R + \cdot R' \rightarrow RR'$$

ii) a "redox" sequence involving rate limiting electron transfer from the radical to the organocobaloxime forming a transient "reduced cobaloxime", followed by loss of the alkyl moiety as a carbanion and coupling of the two alkyl fragments.

$$RCo(dmgH)_2OH_2 + \cdot R' \rightarrow [RCo(dmgH)_2OH_2^-] + {}^+R'$$

$$\downarrow \rightarrow R^- + Co(dmgH)_2OH_2$$

$$R^- + {}^+R' \rightarrow RR'$$

An alternative formulation involving rate limiting electron transfer from the radical to one of the nitrogens of the oxime, followed by rapid collapse to an N-alkylated intermediate with reductive elimination leading to products must also be considered.

iii) A bimolecular homolytic substitution (S_H2) mechanism at the saturated α-carbon atom of the organocobaloxime by the attacking radical.

iv) An addition-elimination sequence involving either a seven-coordinate bis(alkyl)cobalt(IV) species with a trans oxime configuration, a six-coordinate bis(alkyl)cobalt(IV) species having both the organic groups as well as the oxime moeities in a cis configuration, or a pathway involving addition of the incoming radical to one of the four nitrogen atoms of the $(dmgH)_2$ pseudo-macrocycle, followed by reductive elimination to form the observed products.

Of the mechanistic pathways indicated, only the addition-elimination sequence appears to adequately conform to the experimental observations. The first pathway, involving rate limiting homolysis of the organocobaloxime can be ruled out for several reasons. First, the organocobaloximes studied do not appear to undergo homolysis at any appreciable rate, being reasonably stable in acidic aqueous solution in the absence of the radical precursor, when protected from light. Considering the acid sensitivity of $Co(dmgH)_2OH_2$ (66a, b), if homolysis were to occur it would be drawn to completion in the strongly acidic solutions employed, resulting in bleaching of the uv-visible absorptions with formation of $Co^{2+}(aq)$ and free dimethylglyoxime. Even the most unstable organocobaloxime employed in this study, $PhCH_2Co(dmgH)_2OH_2$, failed to produce any detectable $Co^{2+}(aq)$ over a period of several hours in the absence of light and the radical precursors. Secondly, rate limiting homolysis of the organocobaloxime would exhibit first-order dependence only on the cobaloxime, not the bimolecular dependence observed experimentally.

Finally, the products obtained are inconsistent with those expected from coupling of two free radicals, ·R and ·R'. Significant quantities of the products obtained from the self-reactions of the two radicals would be expected as well as the cross-coupling product. Thus, in the case of benzylcobaloxime, significant quantities of bibenzyl would be expected. Product analyses of reactions involving direct homolysis of the $CrCH(CH_3)OC_2H_5^{2+}$ and $CrC(CH_3)_2OH^{2+}$ complexes as the radical source, indicated no detectable bibenzyl.

Electron transfer mechanisms

The second pathway, while consistent with the bimolecular nature of the reactions observed, may also be ruled out. Combination of the carbocation and carbanion to form the observed product must compete with solvolysis of the organic fragments. Thus, significant quantities of alcohol and hydrocarbon would also be expected. In the extensive product

$$R^+ + H_2O \rightarrow ROH + H^+$$

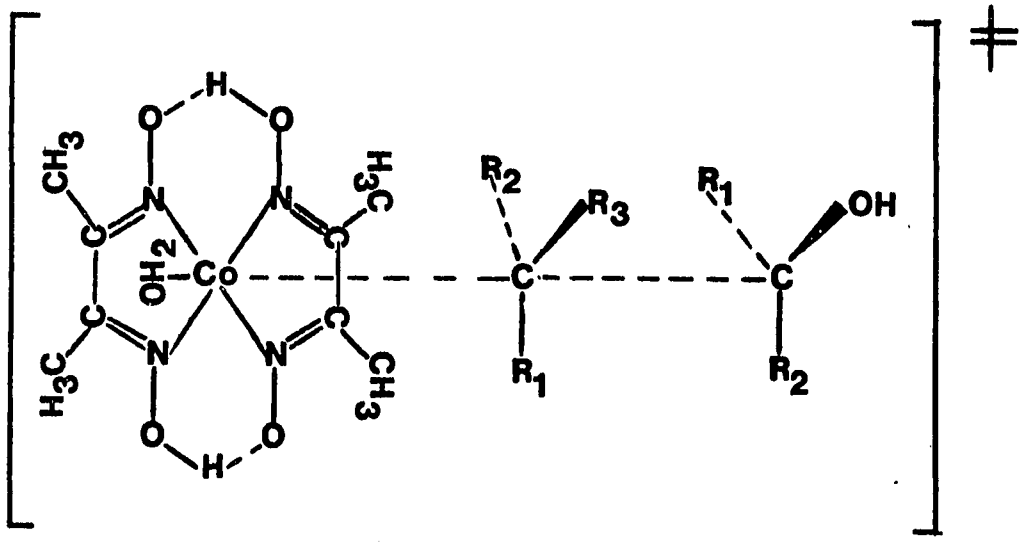
$$R'^- + H_2O \rightarrow R'H + OH^-$$

study of the reactions of benzyl(aquo)cobaloxime with various free radicals, Table I-14, toluene, corresponding to solvolysis of the benzyl anion, was never observed. In all cases the only observed product was the coupling product RR'. Cage collapse of the oxidized radical and the reduced nitrogen of one of the dimethylglyoxime units to form an N-alkylated intermediate might account for the lack of solvolysis products. Neither mechanistic alternative is, however, consistent with the kinetic insensitivity of the reaction to the identity of the attacking radical.

Any mechanism dependent upon electron transfer to form oxidized and reduced intermediates would be expected to exhibit marked sensitivity toward the redox potentials of the incoming radical as well as the respective organocobaloxime. This, however, is clearly not observed experimentally. Although only qualitative observations have been made concerning the reactivity of benzylcobaloxime toward a family of free radicals, it appears that the ease of reaction to form the coupling product is virtually independent of radical identity, while the oxidation potentials of the various radicals investigated vary over a wide range. In addition, the nearly equal reactivity of methyl and ethylcobaloximes appears inconsistent with a redox mechanism. Although the reduction potentials for methyl and ethylcobaloximes are unknown, Costa et al. have investigated the reduction potentials of other B_{12} model compounds (79). The results of these studies indicate that the methyl derivatives are better oxidants with $E_{\frac{1}{2}}$ values approximately 0.2 volts less negative than the ethyl derivatives. A difference in rate constants of around 10^2 would be more in keeping with this potential difference.

Bimolecular homolytic substitution

The reaction of trichloromethyl radical with benzyl(pyridine)-cobaloxime has been proposed to proceed via an S_H2 mechanism with a direct bimolecular homolytic substitution at the saturated α-carbon atom of the cobaloxime by $\cdot CCl_3$ radical (48). Such a direct bimolecular homolytic substitution, the transition state for which is of the form,



appears highly unlikely, for the radicals studied here, in light of the lack of steric effects observed. Espenson and Shveima have studied the reaction of $Cr^{2+}(aq)$ with organocobaloximes (45), a reaction inferred to involve direct bimolecular homolytic substitution at the saturated α-carbon on the basis of the observed steric effects. The rate constants obtained exhibit a marked sensitivity to increasing steric bulk, not only on the α-carbon but also on the β-carbon as well. Thus, the cobaloximes follow the reactivity order expected of a bimolecular substitution, methyl>>ethyl>n-propyl>isopropyl>neopentyl. The 10^5 fold reduction in rate constant from methylcobaloxime, $k = 24\ M^{-1}\ s^{-1}$ (25.0°C), to the isopropyl derivative, $k = 1.08 \times 10^{-4}\ M^{-1}\ s^{-1}$ (25.0°C), should be compared to the slightly more than two fold reduction observed in this study. Similar effects have been observed in the alkyl transfer reactions of alkylcobaloximes with Co(II) complexes of cyclohexanedionedioxime (chgH), Equation 95 (47).

$$RCo(dmgH)_2py + Co(chgH)_2py \rightleftarrows Co(dmgH)_2py + RCo(chgH)_2py \quad (95)$$

These reactions are also inferred on the basis of the steric effects to proceed via direct bimolecular homolytic substitution at the saturated α-carbon atom of the alkylcobaloxime by the incoming cobalt(II) complex. As expected, methylcobaloxime exhibits the greatest reactivity, $k = 50\ M^{-1}\ s^{-1}$ (0°C), while the isopropyl complex, even at 28°C reacts nearly 10^4 times more slowly, $k = 5.9 \times 10^{-3}\ M^{-1}\ s^{-1}$ (28.0°C).

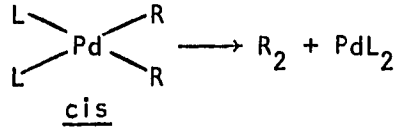
Addition-elimination mechanisms

Of the addition-elimination pathways presented above, that involving addition of the radical to one of the nitrogen-carbon double bonds of the $(dmgH)_2$ pseudo-macrocycle followed by reductive elimination to products appears to be most plausible in light of the very minor effects observed for increasing steric bulk of the alkyl moiety. Reductive elimination to form RR' must occur via an intermediate with the alkyl moeities cis with regard to each other. Not only is it difficult to envisage formation of RR' from an intermediate with the alkyl fragments trans across the $(dmgH)_2$ pseudo-macrocycle, but work involving the decomposition of trans $R_2Co(IV)(dpnH)^+$ and $R_2Co(IV)(tim)^{2+}$ species[2] (80) has shown the sole mode of decomposition of these trans compounds to be loss of one alkyl fragment to form a stable mono(alkyl)cobalt(III) complex, Equation 96. It is not possible to synthesize cis or trans

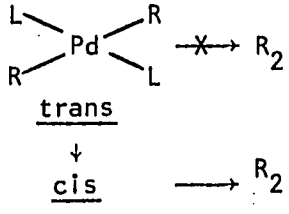
[2]The chelates dpnH and tim differ from $(dmgH)_2$ in the replacement of one and both of the O-H...O moieties with $-CH_2CH_2CH_2-$ groups, respectively. Unlike complexes of dmgH, trans-bis(alkyl)cobalt(III) complexes of dpnH and tim have been isolated.

$$R_2Co(IV)(chelate)^{n+} \rightarrow \cdot R + RCo(III)(chelate)^{n+} \qquad (96)$$

bis(alkyl)cobalt(III) complexes of dimethylglyoxime, however, Lau, Huffman and Kochi (81) have prepared cis-bis(alkyl)iron(II) complexes of the formula $R_2Fe(bipy)_2$. Although these complexes are stable in the 3+ oxidation state, oxidation to Fe(IV) species, either chemically or electrolytically, results in smooth and rapid two-electron reductive elimination to $Fe(bipy)_2^{2+}$ and R_2 (81). Lastly, Gillie and Stille have shown 1,1 reductive elimination to occur only from the cis isomer of bis(alkyl)bis(phosphine)palladium(II), L_2PdR_2, compounds (82).

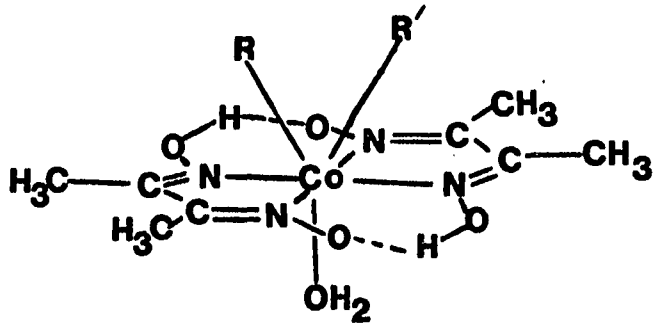


The trans isomer slowly undergoes isomerization to the cis isomer prior to reductive elimination.

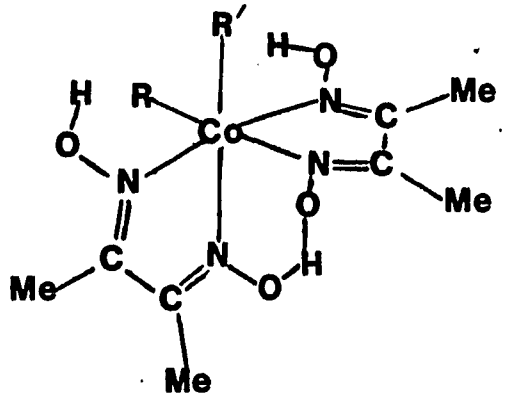


In those cases where isomerization is prohibited by use of a chelating phosphine, reductive elimination does not occur.

The requirement of reductive elimination from an intermediate with both organic fragments on the same side of the $(dmgH)_2$ pseudo-macrocycle makes a seven-coordinate bis(alkyl) intermediate of the form



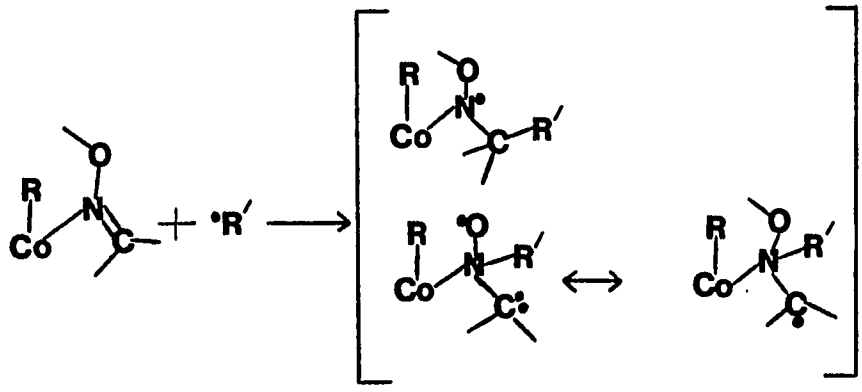
highly unlikely in view of the lack of sensitivity toward increasing steric bulk of both the alkyl group of the organocobaloxime and the incoming radical. The remaining two mechanistic pathways, a six-coordinate cis-bis(dimethylglyoximato) intermediate formed by displacement of one of the nitrogen atoms by the incoming radical to the position



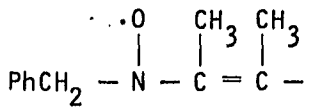
trans to the original alkyl moeity, and addition of the radical to one of the carbon-nitrogen double bonds of the pseudo-macrocycle, are difficult to distinguish. However, the latter pathway appears to better conform to the available data.

Only one cis-dimethylglyoxime complex of cobalt has been reported to date (83). Reaction of several alkyl(pyridine)cobaloximes with an excess of trifluoroacetic acid in chloroform gave the cis-cobaloxime(II) complex: di-trifluoroacetyoxybis(butane-2,3-dione dioxime)cobalt(II) (83). From the conditions necessary to isolate the cis complex, as well as the experimental observations, it is clear that protonation of both oxime hydrogen bridges of the trans complex is necessary to produce the cis geometry. In view of these results, one would expect the protonated form of the organocobaloxime to exhibit greatly enhanced reactivity relative to the unprotonated form toward aliphatic free radicals if the reaction involves a cis dimethylglyoxime intermediate. This is in strong contrast to the nearly equal reactivity of the two forms. One must conclude that either this pathway is unimportant for these reactions or protonation of the oxime bridge is of much less importance than expected.

Addition of the incoming aliphatic radical to one of the carbon-nitrogen double bonds of the $(dmgH)_2$ pseudo-macrocycle can in principle occur at either the carbon or nitrogen ends of the double bonds.



Giannotti and Merle have identified an apparent nitroxide radical of the form



obtained by anaerobic photolysis of benzyl(pyridine)cobaloxime in methylene chloride (84). This same sort of interaction with the nitrogen atoms of the $(dmgH)_2$ pseudo-macrocycle may also be involved in the dioxygen insertion reactions of alkylcobaloximes. Optically active alkylcobaloximes have been shown to insert O_2 while retaining their optical activity (85), in strong contrast to other oxygen insertion reactions which proceed by a free radical mechanism where complete loss of optical activity occurs (86). Addition at the nitrogen atom may be preferential due to formation of a radical which is stabilized by interaction with the cobalt atom. This sort of preferential stabilization of a radical center β to a metal atom has been observed by Russell and Hershberger in the substitution reactions of vinyl mercurials by free radicals (87). Kochi and Nugent have observed similar effects for hydrogen atom abstraction from mercury alkyls by the trichloromethyl radical (88).

Addition of the radical to the double bond on the side of the pseudo-macrocycle trans to the alkyl moiety would produce an intermediate unable to reductively eliminate to form RR'. Thus, in order to account for the fact that little or no radical is wasted in unproductive side-reactions, the addition must be reversible on the time scale of the reductive elimination or internal reduction of the metal center. Alternatively,

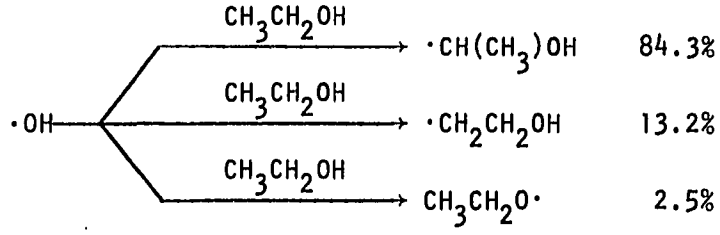
radical addition must occur preferentially on the side of the pseudo-macrocycle cis to the alkyl moiety, possibly owing to the increased electron density from the alkyl moiety.

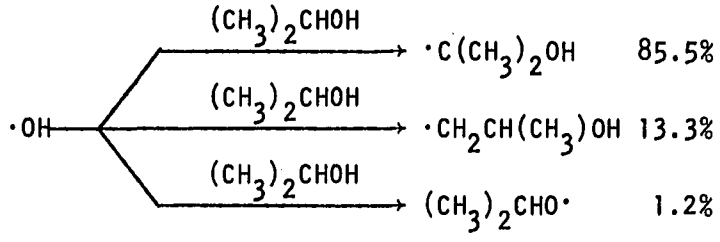
This mechanism involving radical addition to the carbon-nitrogen double bond is the most consistent with the experimental observations. Not only does it allow for the bimolecular formation of RR' without additional side products, it is much less subject to steric constraints. Models indicate that although the two alkyl moieties of the adduct are still close enough together to reductively eliminate, they are nonetheless subject to much less steric crowding than any other mechanistic alternative with the exception of the six-coordinate cis dimethylglyoxime intermediate discussed above.

In summary, a direct bimolecular homolytic substitution mechanism appears highly unlikely for the reactions of the radicals studied here. It remains uncertain whether trichloromethyl radical reacts with benzyl-(pyridine)cobaloxime in methylene chloride (48) by such a homolytic substitution mechanism. An addition-elimination sequence involving radical addition to the carbon-nitrogen double bond of the pseudo-macrocycle best conforms to the experimental observations presented here. An alternative mechanism involving displacement of one of the four nitrogens to form a transient cis-bis(alkyl)cobalt(IV) species with the dimethylglyoxime moeities cis to each other cannot, however, be ruled out with complete certainty.

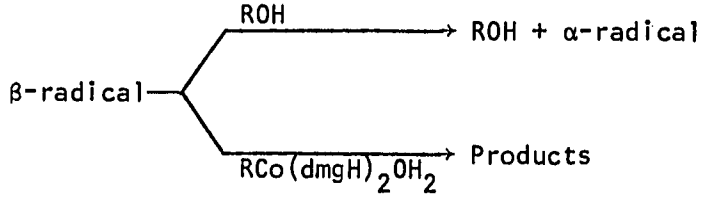
Fate of the β-radicals from 2-propanol and ethanol

Hydrogen atom abstraction from 2-propanol and ethanol by hydroxyl radicals generates ∿86% α-radical and ∿14% β-radical (70).





Analysis of the products from the reaction of the radicals produced from ethanol with benzyl cobaloxime indicates both radicals react with the organocobaloxime. However, only the product corresponding to the α-radical was isolated from experiments involving 2-propanol. The detection of β-product in the case of ethanol and the failure to detect β-product from 2-propanol can easily be understood in terms of a competition between the organocobaloxime and the organic substrate, either ethanol or 2-propanol, for the β-radical.



Burchill and Ginns have determined the rate constant for reaction of $\cdot CH_2CH_2OH$ with ethanol, Equation 94, $k_{94} = 16\ M^{-1}\ s^{-1}$ (89), while the corresponding reaction of $\cdot CH_2CH(CH_3)OH$ radical with 2-propanol, Equation 95, has $k_{95} > 53\ M^{-1}\ s^{-1}$ (71).

$$\cdot CH_2CH_2OH + CH_3CH_2OH \rightarrow CH_3CH_2OH + \cdot CH(CH_3)OH \quad (94)$$

$$\cdot CH_2CH(CH_3)OH + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH + \cdot C(CH_3)_2OH \quad (95)$$

With alcohol concentrations of 1.0M and 1.5M, ethanol and 2-propanol respectively, the pseudo-first order rate constants for reaction of the β-radicals with their parent alcohols are 16 s^{-1} and 75 s^{-1}. Typical product analysis experiments with ethanol employed 1×10^{-3}M organocobaloxime, whereas, those involving 2-propanol, kinetic competition experiments, had organocobaloxime concentrations of 6×10^{-5}M. If the assumption is made that the β-radicals react with benzylcobaloxime with a rate constant of $10^6\ M^{-1}\ s^{-1}$, the pseudo-first order rate constant for the reaction of benzylcobaloxime with the β-radicals are $10^3\ s^{-1}$ and 60 s^{-1}, ethanol and 2-propanol respectively, under the conditions employed.

Thus, under the conditions employed in the two experiments, benzylcobaloxime competes effectively for the β-radical from ethanol and both products were detected, whereas, the β-radical from 2-propanol reacts preferentially with 2-propanol to form the α-radical and hence only α-products were obtained from 2-propanol.

A careful consideration of the rate constants involved argues that experiments with 0.1M 2-propanol and high organocobaloxime concentrations should afford both α and β products as was observed for ethanol.

Conclusions

A direct bimolecular homolytic substitution has been proposed to explain the products of the reaction between trichloromethyl radicals and benzyl(pyridine)cobaloxime in CH_2Cl_2 (48). This mechanistic assignment was based largely on the products obtained. As presented in the introduction, mechanistic assignments based solely on products can be very misleading in radical reactions. By the judicious choice of radical, competitor, and reaction conditions, it has been possible to study the kinetic behavior of a family of organocobaloximes toward aliphatic free radicals in aqueous solution with an aim toward elucidation of the mechanism operative. From this study, it must be concluded that such a direct bimolecular homolytic substitution at saturated carbon is highly unlikely in aqueous solution and that the reaction most likely involves an addition-elimination mechanism. This finding helps to further establish the rarity of S_H2 reactions at saturated sp^3 hybridized carbon.

PART II. REDUCTION OF FLUOROPENTAAMMINECOBALT(III), $Co(NH_3)_5F^{2+}$, BY 2-HYDROXY-2-PROPYL AND α-ETHOXYETHYL RADICALS

INTRODUCTION

The determination of the rate constants for the reactions of alkylcobaloximes with $\cdot CH(CH_3)OC_2H_5$ radical by competition with $Co(NH_3)_5F^{2+}$ for the radical, presented in PART I, provided the primary motivation for undertaking the determination of the rate constants for reduction of $Co(NH_3)_5F^{2+}$ by $\cdot C(CH_3)_2OH$ and $\cdot CH(CH_3)OC_2H_5$ radicals presented here. In addition, there is considerable interest in the mechanism by which aliphatic free radicals reduce cobalt(III) complexes. For instance, some doubt remains concerning the mechanism by which $Co(NH_3)_5X^{2+}$ complexes, where X = Cl, Br, I, and F, are reduced by $\cdot C(CH_3)_2OH$ and $\cdot CH(CH_3)OC_2H_5$ radicals. The data obtained to date (4) may be explained by either of two mechanisms, direct outer-sphere electron transfer, Equation 96, or a halide-bridged inner-sphere electron transfer, Equations 97 and 98.

$$\cdot C(CH_3)_2OH + Co(NH_3)_5X^{2+} \xrightarrow{(+4H^+)} Co^{2+} + 5NH_4^+ + (CH_3)_2CO + X^- \quad (96)$$

$$\cdot C(CH_3)_2OH + Co(NH_3)_5X^{2+} \xrightarrow{(+5H^+)} Co^{2+} + 5NH_4^+ + XC(CH_3)_2OH \quad (97)$$

$$XC(CH_3)_2OH \rightarrow X^- + H^+ + (CH_3)_2CO \quad (98)$$

The strong correlation of the rates of reduction with the redox potentials of the various halide complexes is consistent with either mechanism. In addition, mechanistic assignments have been complicated by the fact that the products obtained from either mechanism are identical, owing to the transient nature of the α-halo alcohols and ethers produced by an atom-transfer mechanism.

Several free radicals have been inferred to reduce $Co(NH_3)_5I^{2+}$ and $Co(NH_3)_5Br^{2+}$ via such an inner sphere (or atom-transfer) mechanism (90). The observation that the acetate radical anion, $\cdot CH_2CO_2^-$, reduces $Ru(NH_3)_5Br^{2+}$ and $Ru(NH_3)_5Cl^{2+}$ has been used to support an atom-transfer mechanism (2, 91), since this radical is a strong oxidizing agent and a weak reducing agent. In addition, the radicals $\cdot CH_2OH$, $\cdot CH(CH_3)OH$, $\cdot C(CH_3)_2OH$, and $\cdot CH(CH_3)OC_2H_5$ react with $Co(NH_3)_5CN^{2+}$ to yield intermediates with an absorption spectrum between 250 and 550 nm (4). Cohen and Meyerstein argue these intermediates involve attack of the cyanide group.

Recently, two thorough investigations of the reduction of $IrCl_6^{2-}$ by aliphatic free radicals have been reported (31, 32). The results of these studies indicate that reduction by alkyl and halo-alkyl radicals proceeds by an atom-transfer mechanism, whereas, α-hydroxy and α-alkoxy radicals react solely by outer-sphere electron transfer.

In addition to the mechanistic interest in the reduction of $Co(NH_3)_5X^{2+}$ complexes, an accurately determined value for the rate constant for reduction of $Co(NH_3)_5F^{2+}$ by $\cdot CH(CH_3)OC_2H_5$ would serve a valuable purpose. The determination of the rate constants for the reactions of alkylcobaloximes with $\cdot CH(CH_3)OC_2H_5$ radical, Equation 96, depends upon the competition for the free radical between the organo-

$$\cdot R + R'Co(dmgH)_2OH_2 \rightarrow RR' + Co(dmgH)_2OH_2 \qquad (99)$$

cobaloxime and a suitably chosen second reagent whose rate constant with the radical is known. It is also necessary that this reagent react rapidly with $Cr^{2+}(aq)$. The latter experiment exists because CrR^{2+}

complexes, species whose homolytic decomposition is promoted by selected oxidizing agents (15), serve as the source of free radicals in many of the experiments concerning Equation 96.

Likely competing reagents are the halo-pentaamminecobalt(III) complexes, $Co(NH_3)_5X^{2+}$. The chloro and bromo complexes, whose rate constants for reduction by $\cdot CH(CH_3)OC_2H_5$ radical have been previously determined by pulse radiolysis (4), proved too reactive to be useful in competition with the alkyl(aquo)cobaloximes.

A pulse radiolytically determined value for the rate constant for reduction of $Co(NH_3)_5F^{2+}$ by either $\cdot C(CH_3)_2OH$ or $\cdot CH(CH_3)OC_2H_5$ radical is lacking. It seemed likely, however, that these values are below $\sim 3 \times 10^6$ M^{-1} s^{-1} which is the approximate lower limit for any reaction between an aliphatic free radical and a cobalt(III) complex studied by pulse radiolysis. This lower limit results from a consideration of the radical detection limits, the rate constants for radical self-reaction, and the practical substrate concentration attainable. Hence a nonradiolytic method based upon competition kinetics was developed to determine the rate constants for reduction of $Co(NH_3)_5F^{2+}$ by $\cdot C(CH_3)_2OH$ and $\cdot CH(CH_3)OC_2H_5$ radicals.

The reduction of $Co(NH_3)_5F^{2+}$ by aliphatic radicals produces, in addition to organic products and ammonium ions, $Co^{2+}(aq)$ and fluoride ion. A very sensitive method for the spectrophotometric determination of fluoride ion in aqueous solution exists, based upon the extreme sensitivity of the Zr(IV)-SPADNS complex to fluoride ion (92). The advantages of this method over other possible methods of fluoride analysis

are the ease of the method and the virtual nonexistence of interference from common anions such as other halides, SO_4^{2-}, ClO_4^-, and NO_3^-.

Thus, it was decided to undertake the determination of the rate constants for reduction of $Co(NH_3)_5F^{2+}$ using carefully controlled competition experiments where the only source of fluoride ion was the reduction of $Co(NH_3)_5F^{2+}$ by $\cdot C(CH_3)_2OH$ and $\cdot CH(CH_3)OC_2H_5$ radicals.

EXPERIMENTAL

Materials

Organochromium(III) reagents

Aqueous solutions of 2-hydroxy-2-propyl(pentaaquo)chromium(III). $(H_2O)_5CrC(CH_3)_2OH^{2+}$, and α-ethoxyethyl(pentaaquo)chromium(III), $(H_2O)_5CrCH(CH_3)OC_2H_5^{2+}$, were prepared, purified, and handled as detailed in PART I, Experimental. The complex derived from 2-propanol was prepared in situ in the presence of a small but known excess of Cr^{2+} and used immediately. The small excess of $Cr^{2+}(aq)$ is necessary to retard decomposition prior to the initiation of homolysis by addition of the cobalt complexes.

Inorganic cobalt(III) reagents

$[Co(NH_3)_5F](ClO_4)_2$ The perchlorate salt was obtained from the nitrate salt as detailed in PART I, Experimental. Solid $[Co(NH_3)_5F](ClO_4)_2$ was found to contain a slight, but nonetheless appreciable, quantity of free fluoride ion. Repeated recrystallizations from perchloric acid and washing with copious quantities of 9:1 $MeOH/H_2O$ containing 0.01M $HClO_4$ were used to reduce this value as much as possible. The highest purity $[Co(NH_3)_5F](ClO_4)_2$ obtained contained ∿0.5% free fluoride ion, which was applied as a correction to the fluoride ion concentrations determined at the end of the reaction.

$[Co(NH_3)_5Cl](ClO_4)_2$ The perchlorate salt was obtained from the chloride compound by dissolution in water containing 0.01M $HClO_4$, adding 70% $HClO_4$, and cooling in ice (93, and references therein). The product

obtained was isolated by suction filtration, washed with ice-cold 0.01M $HClO_4$, ethanol and dried with ether.

$[Co(en)_3](ClO_4)_3$ Tris(ethylenediamine)cobalt(III) perchlorate was prepared from aqueous solutions of the chloride salt as detailed in PART I, Experimental.

Miscellaneous reagents

2-Propanol (Fisher), anhydrous diethyl ether (Fisher), and sodium fluoride (Baker) were reagent grade chemicals used as received.

$HClO_4$ and $LiClO_4$ Aqueous solutions of perchloric acid were prepared by dilution of 70% $HClO_4$ and titrated with standardized NaOH to a phenolphthalein endpoint. Lithium perchlorate was prepared by addition of Li_2CO_3 to 70% $HClO_4$, until no more CO_2 was evolved. The solution was evaporated until crystals of $LiClO_4$ formed, which were collected and recrystallized from water until no longer acidic. An aqueous solution was analyzed for the molarity of Li^+ by addition of an aliquot to a Dowex 50W-X8 cation exchange column in the H^+ form, and titrating the displaced acid with NaOH. Silver nitrate was used to verify the absence of chloride ions.

Cr(II) perchlorate solutions Solutions of $Cr^{2+}(aq)$ in perchloric acid were prepared by reduction of standardized solutions of $Cr(ClO_4)_3$ in perchloric acid over amalgamated zinc. To increase the useful lifetime of these solutions, after reduction, the solutions were transferred by anaerobic techniques to remove them from the amalgam.

$ZrOCl_2 \cdot 8H_2O$ and sodium 2(p-sulfophenylazo)-1,8-dihydroxy-3,6-napthalene disulfonate (SPADNS) We gratefully acknowledge Dr. John D. Corbett for the gift of zirconyl chloride octahydrate and Dr. James S. Fritz for the sample of SPADNS.

Methods

Analyses and characterizations

Inorganic cobalt(III) complexes The inorganic reagents, $Co(NH_3)_5F^{2+}$, $Co(NH_3)_5Cl^{2+}$, and $Co(en)_3^{3+}$, were characterized by their uv-visible spectra, λ/nm ($\varepsilon/M^{-1}\ cm^{-1}$): $Co(NH_3)_5F^{2+}$, 511 (45), 404 (7), 352 (38), 293 (7); $Co(NH_3)_5Cl^{2+}$, 530 (47.3), 417 (9.3), 362 (45), 328 (34), 229 (17800); $Co(en)_3^{3+}$, 465 (87), 387 (9), 338 (78), and 287 (5).

Fluoride determination Concentrations of free fluoride ion at the end of the reaction were determined using the method of Belcher, et al. (92) based on the Zr(IV)-SPADNS complex. Zirconyl ions form colored complexes with SPADNS in hydrochloric acid media, which are monomolecular or bimolecular, depending on the acidity and the quantity of dye present. The absorption spectra of the two complexes are quite similar, and in the presence of excess dye, both complexes may be present. When fluoride ion is present in the solution, the zirconyl ion reacts preferentially with it, forming a colorless complex. This acts to withdraw zirconyl ion from the colored complex and results in a reduction of the total optical density of the system, Table II-1. This system involves complex equilibria in which acidity, zirconyl ion, SPADNS concentration, fluoride concentration, temperature, and interfering ion concentrations all contribute to the optical density. Therefore, no

Table II-1. Data for the preparation of the standard ΔD vs $[F^-]$ curve for the determination of fluoride ion by the Zr-SPADNS method[a]

$[F^-]/M$	ΔD[b]$/\lambda 570$ nm
0	0.967
3.50×10^{-7}	0.963
1.75×10^{-6}	0.935
4.40×10^{-6}	0.926
8.80×10^{-6}	0.892
1.75×10^{-5}	0.842
2.20×10^{-5}	0.773
3.50×10^{-5}	0.682
4.40×10^{-5}	0.595
6.72×10^{-5}	0.424
8.76×10^{-5}	0.322
1.10×10^{-4}	0.242
1.59×10^{-4}	0.172
2.20×10^{-4}	0.138
3.16×10^{-4}	0.123
3.98×10^{-4}	0.114
5.39×10^{-3}	0.107

[a]SPADNS = sodium 2(p-sulfophenylazo)-1,8-dihydroxy-3,6-napthalene disulfonate.

[b]ΔD calculated as $D_{sample} - D_{reference}$, where the reference cell contains free SPADNS. Pathlength = 2.0 cm.

simple stoichiometric relationship exists between the fluoride, zirconyl ion, and dye concentrations.

The method of Belcher, et al. (92) responds sensitively to fluoride ion concentration in the range 10^{-5} - 3 x 10^{-4}M, although the nonlinear response at higher concentrations required use of a calibration curve. The calibration curve, Figure II-1, was obtained at 570 nm using standard solutions of sodium fluoride contained in the same medium as the reaction solutions and carried through the same ion-exchange procedure to be detailed below.

The reactions were carried out under rigorously oxygen-free conditions at 25.0°C using lithium perchlorate to adjust the ionic strength to 1.0M. After reaction, a measured volume of the solution was passed through a column of Dowex 50W-X8 cation exchange resin in the H^+ form, with prior dilution at high $[H^+]$. Dilution avoids the elution of the metal complexes from the resin and eliminates any pH effect on the disulfonate ligand SPADNS and its complexation with Zr(IV). The ion exchange was necessary to remove $(H_2O)_5CrF^{2+}$ and excess $Co(NH_3)_2F^{2+}$, the presence of which leads to erroneously high fluoride concentrations. That these high values of fluoride ion are due to direct interference from the complex ions rather than hydrolysis to yield extra fluoride ion was confirmed by blank experiments. The fluoride ion, in the form of HF, was washed from the column using 0.01M $HClO_4$ which prevented hydrolysis of $(H_2O)_5CrF^{2+}$ and $Co(NH_3)_5F^{2+}$.

$Co^{2+}(aq)$ analysis The quantity of $Co^{2+}(aq)$ produced in the competition experiments was determined spectrophotometrically as the $Co(SCN)_4^{2-}$ complex in 50/50 volume % acetone/water. In a typical

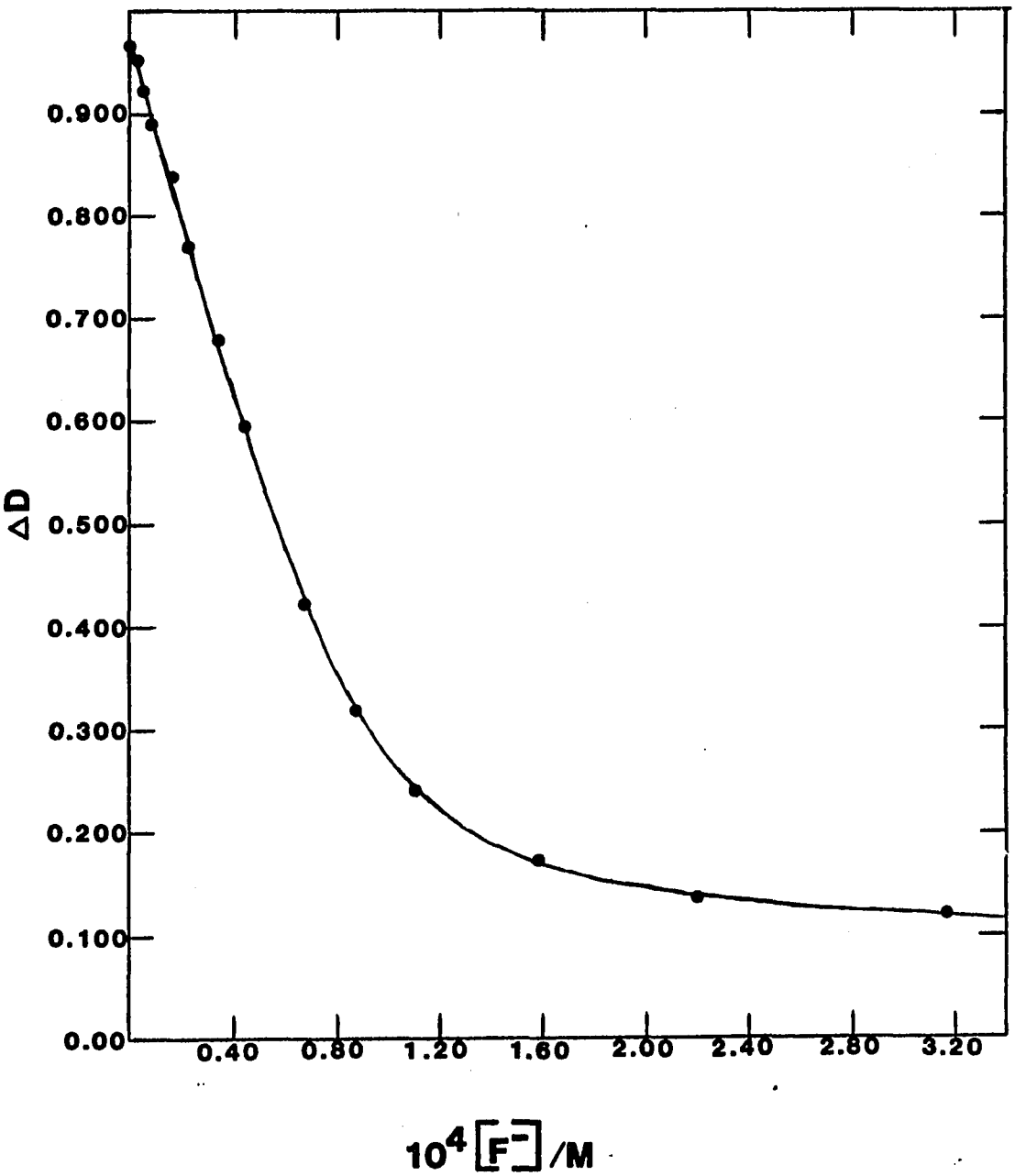


Figure II-1. Standard ΔD vs $[F^-]$ curve for the determination of $[F^-]$ by the Zr-SPADNS method. T = 25.0°C, 570 nm

experiment, 10.0 mL of reaction mixture were added to 12.5 mL of acetone containing ∿2 grams NH_4SCN and the volume adjusted to 25.0 mL with distilled water. Absorbance readings were measured at 623 nm (ε = 1842 M^{-1} cm^{-1}) in 5.00 cm quartz cells. In order to correct for possible contributions to the absorbance at 623 nm from the excess halopentaamminecobalt(III) and the product halochromium(III) ions, appropriate blanks were prepared containing known quantities of these ions.

Competition experiments

Competition experiments were conducted at 25.0°C, 1.0M ionic strength ($HClO_4$-$LiClO_4$), and either 0.10M or 0.50M $[H^+]$. In experiments involving $H_2O)_5CrCH(CH_3)OC_2H_5^{2+}$, the reaction was initiated by the injection of an aliquot of purified organochromium solution into thermostatted 5.00 cm quartz cells containing appropriate ratios of $Co(NH_3)_5F^{2+}$ to $Co(NH_3)_5Cl^{2+}$. The reaction was allowed to proceed for 60 minutes (10 half-lives) and the fluoride ion content analyzed. In the case of $(H_2O)_5CrC(CH_3)_2OH^{2+}$, its shorter lifetime in solution (15) necessitated injection of thermostatted mixtures of $Co(NH_3)_5F^{2+}$ and $Co(en)_3^{3+}$ into 5.00 cm quartz cells containing freshly prepared organochromium solution. The reaction was allowed to proceed for 60 seconds (greater than 10 half-lives) and the fluoride ion content analyzed.

Results

2-Hydroxy-2-propyl radical

The rate constant for reduction of $Co(NH_3)_5F^{2+}$ by $\cdot C(CH_3)_2OH$ radical was determined via competition with $Co(en)_3^{3+}$ whose rate constant for

reduction by $\cdot C(CH_3)_2OH$ radical is known (10). Homolysis of the $CrC(CH_3)_2OH^{2+}$ complex (15) in the presence of mixtures of $Co(NH_3)_5F^{2+}$ and $Co(en)_3^{3+}$, and the fate of the $Cr^{2+}(aq)$ and the organic radical produced are represented in Equations 100-103.

$$CrC(CH_3)_2OH^{2+} \rightarrow Cr^{2+} + \cdot C(CH_3)_2OH \qquad (100)$$

$$Cr^{2+} + Co(NH_3)_5F^{2+} \xrightarrow{(+5H^+)} CrF^{2+} + Co^{2+} + 5NH_4^+ \qquad (101)$$

$$\cdot C(CH_3)_2OH \xrightarrow{Co(en)_3^{3+}\ (+2H^+)} (CH_3)_2CO + Co^{2+} + 3enH^+ \qquad (102)$$

$$\cdot C(CH_3)_2OH \xrightarrow{Co(NH_3)_5F^{2+}\ (+4H^+)} (CH_3)_2CO + Co^{2+} + 5NH_4^+ + F^- \qquad (103)$$

The ratio of the rate constants for the reaction of the radical with $Co(NH_3)_5F^{2+}$ and $Co(en)_3^{3+}$ can be obtained from analysis of the rate ratio, Equation 104.

$$\frac{-d[Co(en)_3^{3+}]/dt}{d[F^-]/dt} = \frac{k_{102}[\cdot C(CH_3)_2OH][Co(en)_3^{3+}]}{k_{103}[\cdot C(CH_3)_2OH][Co(NH_3)_5F^{2+}]} \qquad (104)$$

Since CrF^{2+} is kinetically stable for the duration of these experiments, the sole source of free F^- is Reaction 103. Experiments were carried out with $[Co(en)_3^{3+}]_0$ and $[Co(NH_3)_5F^{2+}]_0 >> [CrC(CH_3)_2OH^{2+}]_0$ such that neither substrate concentration changed appreciably with time. Integration of the rate ratio of Equation 104 with these as boundary conditions yields,

$$\frac{\Delta Co(en)_3^{3+}}{[F^-]_\infty} = \frac{k_{102}[Co(en)_3^{3+}]_0}{k_{103}[Co(NH_3)_5F^{2+}]_0} . \qquad (105)$$

The change in concentration of $Co(en)_3^{3+}$ was taken to be the difference between the experimentally determined quantities, $[CrC(CH_3)_2OH^{2+}]_0$ - $[F^-]_\infty$. Determinations of the total $Co^{2+}(aq)$ yield in each run were used to establish the validity of this assumption. Substitution of this equality into Equation 105 and rearrangement affords an expression, Equation 106, which permits calculation of the desired rate constant ratio.

$$\frac{k_{102}}{k_{103}} = \left\{ \frac{[CrC(CH_3)_2OH^{2+}]_0 - [F^-]_\infty}{[F^-]_\infty} \right\} \frac{[Co(NH_3)_5F^{2+}]_0}{[Co(en)_3^{3+}]_0} \qquad (106)$$

The data obtained, Table II-2, afford the ratio $k_{102}/k_{103} = 7.7 \times 10^{-2}$ at 25.0°C and 1.0M ionic strength. The value of k_{102}, $k_{102} = (1.7 \pm 0.3) \times 10^5\ M^{-1}\ s^{-1}$, in strongly acidic solution has been independently determined by kinetic competition methods (10). The uncertainty reported for k_{102} reflects the uncertainties in its determination by kinetic competition as well as the original pulse radiolytic reference, which goes back to the rate constant $5.1 \times 10^7\ M^{-1}\ s^{-1}$ (22 ± 2°C) for the reaction of $Cr^{2+}(aq)$ with $\cdot C(CH_3)_2OH$ radical (64). Reflecting these uncertainties the value of k_{103} is thus $(2.2 \pm 0.2) \times 10^6\ M^{-1}\ s^{-1}$.

α-Ethoxyethyl radical

The rate constant for reduction of $Co(NH_3)_5F^{2+}$ by $\cdot CH(CH_3)OC_2H_5$ radical was determined via competition experiments involving $Co(NH_3)_5Cl^{2+}$, whose rate constant for reduction by $\cdot CH(CH_3)OC_2H_5$ radical has been independently determined by pulse radiolysis (4). Homolysis of the

Table II-2. Kinetic competition experiments (25°C, μ = 1.00M)

Initial concentration/M							
$[H^+]$	$10^3[CrR^{2+}]$	$10^3[Co(NH_3)_5F^{2+}]$	$10^3[X]$[a]	$10^4[F^-]$[b]	$\frac{[CrR^{2+}]_0-[F^-]_\infty}{[F^-]_\infty}$		$\frac{k_X}{k_F}$[c]
PART I. $\cdot C(CH_3)_2OH$							
0.10	0.350	2.00	0	0.350	0		-
0.10	0.350	2.00	20.0	2.01	0.74		0.074
0.50	0.430	2.00	20.0	2.40	0.79		0.079
						Ave:	0.077
PART II. $\cdot CH(CH_3)OC_2H_5$							
0.10	2.50	6.00	0	2.50	0		-
0.10	3.00	20.0	3.15	1.04	1.88		12.0
0.10	3.00	30.0	3.15	1.31	1.29		12.3
0.10	3.00	30.0	3.94	1.13	1.66		12.6
						Ave:	12.3

[a] X = Competing reagent, $Co(en)_3^{3+}$ for $\cdot C(CH_3)_2OH$ and $Co(NH_3)_5Cl^{2+}$ for $\cdot C(CH_3)OC_2H_5$.

[b] Corrected for 0.5% free F^- present in the sample of $[Co(NH_3)_5F](ClO_4)_2$.

[c] By Equation 103 or Equation 110.

$CrCH(CH_3)OC_2H_5^{2+}$ complex (15) in the presence of mixtures of $Co(NH_3)_5F^{2+}$ and $Co(NH_3)_5Cl^{2+}$, as well as the subsequent reactions of the organic radical and $Cr^{2+}(aq)$ produced from homolysis are represented in Equations 107-111.

$$CrCH(CH_3)OC_2H_5^{2+} \rightarrow Cr^{2+} + \cdot CH(CH_3)OC_2H_5 \qquad (107)$$

$$Cr^{2+} \xrightarrow{Co(NH_3)_5F^{2+}\ (+5H^+)} CrF^{2+} + Co^{2+} + 5NH_4^+ \qquad (108)$$

$$Cr^{2+} \xrightarrow{Co(NH_3)_5Cl^{2+}\ (+5H^+)} CrCl^{2+} + Co^{2+} + 5NH_4^+ \qquad (109)$$

$$\cdot CH(CH_3)OC_2H_5 \xrightarrow{Co(NH_3)_5F^{2+}\ (+H_2O + 4H^+)} CH_3CHO + CH_3CH_2OH + Co^{2+} + F^- + 5NH_4^+ \qquad (110)$$

$$\cdot CH(CH_3)OC_2H_5 \xrightarrow{Co(NH_3)_5Cl^{2+}\ (+H_2O + 4H^+)} CH_3CHO + CH_3CH_2OH + Co^{2+} + Cl^- + 5NH_4^+ \qquad (111)$$

The ratio of the rate constants for the reaction of the radical with $Co(NH_3)_5F^{2+}$ and $Co(NH_3)_5Cl^{2+}$ can be obtained from analysis of the rate ratio, Equation 112a. As was the case for the study of the $\cdot C(CH_3)_2OH$

$$\frac{d[Cl^-]/dt}{d[F^-]/dt} = \frac{k_{111}[\cdot CH(CH_3)OC_2H_5][Co(NH_3)_5Cl^{2+}]}{k_{110}[\cdot CH(CH_3)OC_2H_5][Co(NH_3)_5F^{2+}]} \qquad (112a)$$

radical, experiments were carried out with $[Co(NH_3)_5Cl^{2+}]_0$ and $[Co(NH_3)_5F^{2+}]_0 >> [CrCH(CH_3)OC_2H_5^{2+}]_0$ such that neither substrate concentration change appreciably throughout the run. Integration of Equation 112a with these as boundary conditions yields,

$$\frac{[Cl^-]_\infty}{[F^-]_\infty} = \frac{k_{111}[Co(NH_3)_5Cl^{2+}]_0}{k_{110}[Co(NH_3)_5F^{2+}]_0} \qquad (112b)$$

where $[Cl^-]_\infty = [CrCH(CH_3)OC_2H_5^{2+}]_0 - [F^-]_\infty$.

Figure II-2 depicts a plot of the data obtained, Table II-2, showing the linear variation of $[Cl^-]_\infty/[F^-]_\infty$ with the ratio of competing reagent concentrations, as predicted by Equation 112b. Analysis of the data presented in Table II-2 according to Equation 112b affords the ratio $k_{111}/k_{110} = 12.3 \pm 0.3$ at 25.0°C and 1.0M ionic strength. The value reported for k_{111} from pulse radiolysis (4) is 1.4×10^7 M^{-1} s^{-1}, affording the average value $k_{110} = (1.1 \pm 0.2) \times 10^6$ M^{-1} s^{-1}. As was the case for the rate constant for reduction of $Co(NH_3)_5F^{2+}$ by $\cdot C(CH_3)_2OH$, the uncertainty indicated for k_{110} reflects the error in the ratio determination and that attributed separately to k_{111} (4).

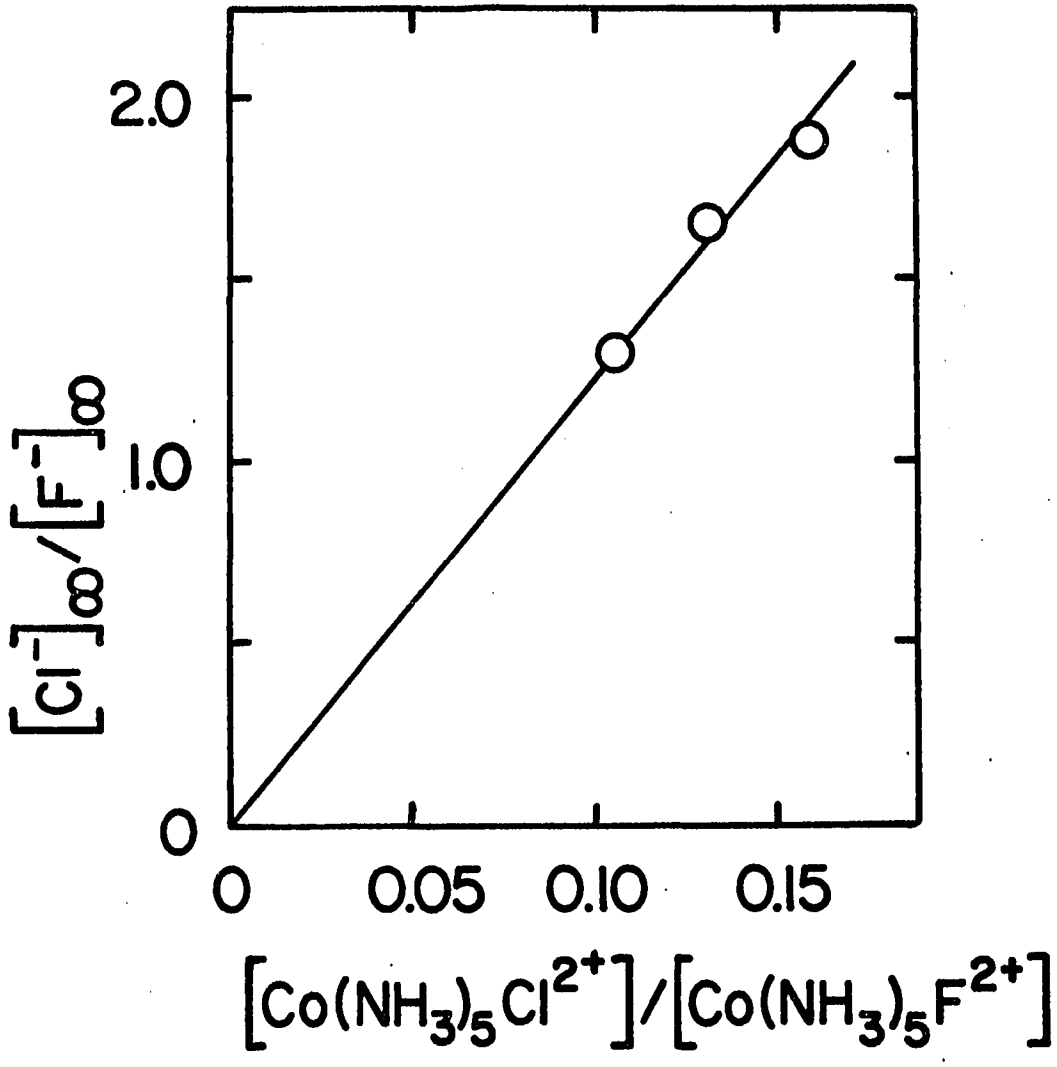


Figure II-2. Illustrating the results of the competition experiments for $\cdot CH(CH_3)OC_2H_5$ with $Co(NH_3)_5F^{2+}$ and $Co(NH_3)_5Cl^{2+}$, according to Equation 110

DISCUSSION

The choice of $Co(en)_3^{3+}$ as the competing reagent in the one case and $Co(NH_3)_5Cl^{2+}$ in the other was, in part, arbitrary. The former complex does react too slowly with the $\cdot CH(CH_3)OC_2H_5$ radical to have been of any use in competition with $Co(NH_3)_5F^{2+}$ for the $\cdot CH(CH_3)OC_2H_5$ radical. In addition, the pH independence of k_{102} in the strongly acidic region was known from earlier work (10), whereas it is an assumption that k_{111} is independent of pH in the same region. Of the two radicals investigated, $\cdot C(CH_3)_2OH$ would be the one most likely to exhibit a pH dependence, although not very likely in the region pH 0-1, owing to the presence of the acidic OH function. From the constancy of the rate constant for reduction of $Co(NH_3)_5F^{2+}$ by $\cdot C(CH_3)_2OH$ radical, k_{103}, obtained at 0.10M and 0.50M H^+, it may be concluded that k_{103} is independent of pH in the region pH 0-1. This makes the assumption that the rate constant for reduction of $Co(NH_3)_5F^{2+}$ by $\cdot CH(CH_3)OC_2H_5$ radical, used in PART I, is independent of pH in strongly acidic solution almost certainly correct.

Table II-3 gives the values of the rate constants for the reduction of $Co(NH_3)_5X^{2+}$ complexes by these two radicals. The values determined for the fluoro complex are fully in accord with what would be expected from the trends established from the previous pulse radiolytic determinations. The pronounced trend in k with the variation of X can be seen from these comparisons and, indeed, has been noted before (4).

The tendency to ascribe this strong dependence on the identity of the ligand X to a halogen abstraction mechanism, Equations 97 and 98,

Table II-3. Rate constants for reduction of $Co(NH_3)_5X^{2+}$ complexes by $\cdot C(CH_3)_2OH$ and $\cdot CH(CH_3)OC_2H_5$ radicals

Complex	10^{-6} k/M^{-1} s^{-1}	
	$\cdot C(CH_3)_2OH$	$\cdot CH(CH_3)OC_2H_5$
$Co(NH_3)_5F^{2+}$	2.2[a]	1.2[a]
$Co(NH_3)_5Cl^{2+}$	40[b]	14[b]
$Co(NH_3)_5Br^{2+}$	300[b]	160[b]

[a]This work.

[b]Reference 4.

$$\cdot C(CH_3)_2OH + Co(NH_3)_5X^{2+} \xrightarrow{(+5H^+)} Co^{2+} + 5NH_4^+ + XC(CH_3)_2OH \quad (97)$$

$$XC(CH_3)_2OH \rightarrow (CH_3)_2CO + H^+ + X^- \quad (98)$$

rather than a direct electron transfer mechanism, Equation 96, must be tempered by recent findings in the reduction of $IrCl_6^{2-}$ by aliphatic radicals (31, 32).

$$\cdot C(CH_3)_2OH + Co(NH_3)_5X^{2+} \xrightarrow{(+4H^+)} Co^{2+} + 5NH_4^+ + (CH_3)_2CO + X^- \quad (96)$$

Unlike Co(II) complexes which are substitutionally labile, leading to rapid formation of $Co^{2+}(aq)$ and free ligands in aqueous solution, reduction of $IrCl_6^{2-}$ leads to a substitutionally inert Ir(III) complex. Thus, reduction of $IrCl_6^{2-}$ by a halogen atom abstraction mechanism would lead to Ir(III) products which are distinctly different from those obtained from electron transfer. Halogen atom abstraction leads to

$IrCl_5(H_2O)^{2-}$ while electron transfer gives $IrCl_6^{3-}$, products easily distinguished by their uv-visible spectra.

The results of these studies indicate that reduction of $IrCl_6^{2-}$ by aliphatic radicals proceeds by two pathways (31, 32), the former predominating for alkyl radicals such as $\cdot CH_2CH_3$ radical, represented by Equation 113, the latter for α-hydroxy and α-alkoxy radicals, represented by Equation 114.

$$IrCl_6^{2-} \xrightarrow{\cdot CH_2CH_3} IrCl_5(OH_2)^{2-} + CH_3CH_2Cl \qquad (113)$$

$$IrCl_6^{2-} \xrightarrow{\cdot C(CH_3)_2OH} IrCl_6^{3-} + H^+ + (CH_3)_2CO \qquad (114)$$

These results as well as those presented in the introduction which indicate at least some cobalt and ruthenium complexes appear to react with α-OH and α-OR radicals by an inner sphere mechanism (4, and references therein) may also be accounted for by rate limiting formation of a halide-bridged intermediate or transition-state of the form $[L_5M^nXR]$, which subsequently decomposes into either $[L_5M^nX]$ and ROH or $[L_5M^{n-1}]$ and XR, depending on the nature of M, X, and R.

$$L_5M^nX + \cdot R \rightarrow [L_5M^nXR] \begin{cases} \xrightarrow{H_2O} [L_5M^{n-1}X] + ROH + H^+ \\ \xrightarrow{H_2O} [L_5M^{n-1}(OH_2)] + XR \end{cases}$$

GENERAL SUMMARY

Alkyl(aquo)cobaloximes, $RCo(dmgH)_2OH_2$ where R = $PhCH_2$, CH_3, CH_2CH_3, and $CH(CH_3)_2$, react with aliphatic free radicals in acidic aqueous solution to cleanly afford $Co^{2+}(aq)$ and an organic product corresponding to coupling of the α-carbon atom of the organocobaloxime with the aliphatic radical. Thus $PhCH_2Co(dmgH)_2OH_2$ reacts with $\cdot C(CH_3)_2OH$ radical to produce 2-methyl-1-phenyl-2-propanol, $PhCH_2C(CH_3)_2OH$. The reaction appears quite general in nature, with almost any radical being reactive toward benzylcobaloxime. The reaction exhibits a first-order dependence on both the organocobaloxime and the radical concentrations. The lack of sensitivity to increasing steric bulk of substituents on the α-carbon atom of the organocobaloxime makes a bimolecular homolytic substitution mechanism highly unlikely. The reaction is proposed to proceed via an addition-elimination mechanism involving addition of the radical to one of the four carbon-nitrogen double bonds of the organocobaloxime followed by reductive elimination to afford the observed products.

The kinetics of the reduction of $Co(NH_3)_5F^{2+}$ by $\cdot C(CH_3)_2OH$ and $\cdot CH(CH_3)OC_2H_5$ radicals have been studied using kinetic competition methods involving nonradiolytically generated radicals.

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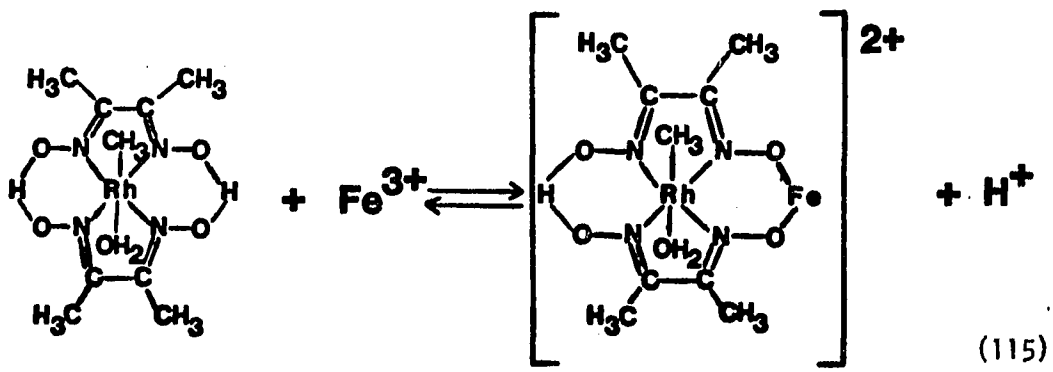
APPENDIX

Kinetics and Equilibrium of Complexation of Iron(III) Ions by Methylaquorhodoxime (I)

Methyl(aquo)rhodoxime, $CH_3Rh(dmgH)_2OH_2$, reacts reversibly with hydrated iron(III) ions to form $[CH_3Rh(dmg_2HFe)OH_2]^{2+}$ (A) in which one of the O-H···O moeities of the $(dmgH)_2$ pseudo-macrocycle is replaced by O-Fe-O according to the equilbrium of Equation 115. Incorporation



(115)

of the iron(III) ion into the O-H···O bridge is attended by dramatic spectral changes throughout the entire uv-visible region. The additional equilibria of Equations 116 and 117 must be considered in the determination of the equilibrium constant and kinetics of adduct formation. With

$$CH_3Rh(dmgH)_2OH_2 + H^+ \rightleftarrows CH_3Rh(dmg_2H_3)OH_2^+ \quad K = 5.66\ M^{-1} \tag{116}$$

$$(H_2O)_5FeOH_2^{3+} \rightleftarrows (H_2O)_5FeOH^{2+} + H^+ \tag{117}$$

due allowance for these additional equilibria, the equilibrium constant, in water at 25.0°C, for the equilibrium expressed according to Equation 115 is 68.8 ± 4.0.

The reaction approaches equilibrium according to the rate law of Equation 118

$$\frac{d[A]}{dt} = (k_{1f} + \frac{k_{2f}}{[H^+]})[Fe^{3+}][CH_3Rh(dmgH)_2OH_2] - (k_{1r}[H^+] + k_{2r})[A] \quad (118)$$

with $k_{1f} = 2.08 \pm 0.06\ M^{-1}\ s^{-1}$, $k_{2f} = 0.620 \pm 0.010\ s^{-1}$, $k_{1r} = (3.02 \pm 0.27) \times 10^{-2}\ M^{-1}\ s^{-1}$, and $k_{2r} = (0.90 \pm 0.07) \times 10^{-2}\ s^{-1}$.

The rate law for adduct formation between iron(III) ion and methyl-(aquo)rhodoxime, given by Equation 118, indicates that the reaction proceeds by two parallel pathways, differing in one proton. The mechanism is proposed to consist of two parallel pathways involving neutralization of the hydrogen-bonded O-H···O proton with the base $FeOH^{2+}$, as a result of which iron(III) is substituted in its place and an O-Fe-O unit is incorporated into the rhodoxime. Thus, $FeOH^{2+}$ reacts with $CH_3Rh(dmgH)_2OH_2$ and $CH_3Rh(dmg_2H_3)OH^{2+}$ according to the elementary reactions represented by Equations 119 and 120. Substitution of the equilibrium expressions of

$$CH_3Rh(dmg_2H_3)OH_2^+ + FeOH^{2+} \underset{k_{1r}}{\overset{k_1}{\rightleftharpoons}} A + H_2O \quad (119)$$

$$CH_3Rh(dmgH)_2OH_2 + FeOH^{2+} \underset{k_{2r}}{\overset{k_1}{\rightleftharpoons}} A + H_2O \quad (120)$$

Equations 116 and 117 gives the following values: $k_1 = k_{1f}/K_{Fe}K_{Rh} = 2.2 \times 10^2\ M^{-1}\ s^{-1}$ and $k_2 = k_{2f}/K_{Fe} = 3.8 \times 10^2\ M^{-1}\ s^{-1}$.

The full account of this work, and the basis of assigning the neutralization mechanism, are given in the article already published (1).