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Reduction of Fluoropentaamminecobalt(III) by 1-Ethoxyethyl and 2-Hydroxy-2-propyl Radicals: A Kinetic Competition Study

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Kinetic competition experiments on the indicated reactions were conducted at 25 °C and μ = 1.00 M. The rate constants are as follows: $\cdot C(CH_3)_2OH$, 2.2×10^6 M^{-1} s^{-1}; $\cdot CH(CH_3)OC_2H_5$, 1.1×10^6 M^{-1} s^{-1}. The independently known rate constants for the competing reagents ($Co(en)_3^{3+}$ and $Co(NH_3)_5Cl^{2+}$, respectively) were used in the evaluation of the results.

Introduction

We recently reported the coupling reactions of benzylaquocobaloxime[1] with the radicals $\cdot C(CH_3)_2OH$ and $\cdot CH(CH_3)OC_2H_5$[2] (eq 1). The determination of the rate constants

$$PhCH_2Co(dmgH)_2OH_2 + R\cdot \rightarrow PhCH_2R + Co(dmgH)_2OH_2 \qquad (1)$$

for these reactions depends upon the competition for the free radical between the organocobaloxime and a suitably chosen second reagent whose rate constant with the radical is known. It is also necessary that this reagent react rapidly with $Cr(aq)^{2+}$. The latter requirement exists because $(H_2O)_5CrR^{2+}$ complexes—species whose homolytic cleavage is promoted by selected oxidizing agents[3]—serve as the source of free radicals in many of the experiments concerning eq 1.

Likely competing reagents are the halopentaamminecobalt(III) complexes, $Co(NH_3)_5X^{2+}$, where X = Cl, Br, and F. The chloro and bromo complexes, whose rate constants for reduction by $\cdot CH(CH_3)OC_2H_5$ radical have previously been determined by the pulse radiolysis technique,[4] proved too reactive to be useful in competition with benzyl(aquo)cobaloxime.

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 the reaction of any aliphatic radical studied by pulse radiolysis (considering the detection limits and the rate constants for radical self-reaction). 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. Moreover, the mechanism of reduction of metal complexes by aliphatic radicals is of considerable interest in its own right and provided a second motivation for this work.

Experimental Section

Materials. The organochromium complexes $(H_2O)_5CrC(CH_3)_2OH^{2+}$ and $(H_2O)_5CrCH(CH_3)OC_2H_5^{2+}$ were prepared by literature procedures.[3,5] The complex derived from 2-propanol was prepared in situ in the presence of a small but known excess of Cr^{2+} (to retard decomposition prior to the initiation of homolysis by addition of the cobalt complex) and used immediately. Because of its longer lifetime in solution,[5] solutions of $(H_2O)_5CrCH(CH_3)OC_2H_5^{2+}$ were chromatographically purified by elution from an air-free column of Sephadex C-25 ion-exchange resin in the Na^+ form.

The perchlorate salts $[Co(NH_3)_5F](ClO_4)_2$, $[Co(NH_3)_5Cl](ClO_4)_2$, and $[Co(en)_3](ClO_4)_3$ were prepared by literature methods. 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 washes with copious quantitites of 9:1 $MeOH-H_2O$ containing 0.01 M $HClO_4$ 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 F^-, which was applied as a correction to the F^- concentrations determined at the end of the reaction.

Fluoride Determination. Concentrations of free fluoride ions at the end of the reaction were determined with use of a method[6] based on the Zr(IV)–SPADNS complex.[7] The reactions were carried out under rigorously oxygen-free conditions at 25.0 °C with use of lithium perchlorate to adjust the ionic strength to 1.0 M. 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). Spectrophotometric measurements associated with the procedure[6] were made with a Cary Model 219 spectrophotometer. The method was calibrated with use of standard solutions of fluoride ions originally contained in the same medium and carried through the same procedure. The method responds sensitively to fluoride ion concentration in the range 10^{-5}–(3×10^{-4}) M, although the nonlinear response at the higher concentrations required use of a calibration curve. The noninterference of $(H_2O)_5CrF^{2+}$, provided it was first removed by ion-exchange separation, was confirmed in blank experiments. Chloride ions, even at much higher concentrations, do not interfere.

Results

2-Hydroxy-2-propyl Radical. The rate constant was determined via competition with $Co(en)_3^{3+}$, whose rate constant for reduction by $\cdot C(CH_3)_2OH$ is known.[8,9]. The competition experiments are then defined by eq 2–5.

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

$$Cr^{2+} + Co(NH_3)_5F^{2+} \xrightarrow{(+5H^+)} CrF^{2+} + Co^{2+} + 5NH_4^+ \qquad (3)$$

$$\cdot C(CH_3)_2OH \xrightarrow{Co(en)_3^{3+}(+2H^+)} (CH_3)_2CO + Co^{2+} + 3enH^+ \qquad (4)$$

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

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(1) Cobaloxime is the trivial name given to bis(dimethylglyoximato)cobalt complexes (Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97), designated $Co(dmgH)_2$, where $dmgH^-$ is the monoanion of dimethylglyoxime (2,3-butanedione dioxime).

(2) McHatton, R. C.; Espenson, J. H.; Bakač, A. *J. Am. Chem. Soc.* **1982**, *104*, 3531.

(3) Kirker, G. W.; Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 1249.

(4) Cohen, H.; Meyerstein, D. *J. Chem Soc., Dalton Trans.* **1977**, 1056.

(5) Schmidt, W.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117.

(6) Belcher, R.; Leonard, M. A.; West, T. S. *J. Chem. Soc.* **1959**, 3577.

(7) SPADNS = sodium 2-(*p*-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonate.

(8) Espenson, J. H.; Shimura, M.; Bakač, A. *Inorg. Chem.* **1982**, *21*, 2537.

(9) It should be noted that while the reactions of interest are characterized by very large rate constants, the overall time scale of the experiment is quite long. The rates at which the radicals are generated, and hence the time scales over which the experiments were conducted, are those of the homolysis of the organochromium complexes. Homolysis of $CrC(CH_3)_2OH^{2+}$ and $CrCH(CH_3)OC_2H_5^{2+}$ complexes are characterized by $k_2 = 0.127 \pm 0.003$ s^{-1} and $k_8 = 2.03 \times 10^{-3}$ s^{-1};[3] thus the competition experiments occur over approximately 60 s and 1 h, respectively, and mixing effects are negligible. This situation contrasts with that in which competition occurs upon and during mixing: Ogino, H.; Kikkawa, E.; Shimura, M.; Tanaka, N. *J. Chem. Soc., Dalton Trans.* **1981**, 894. Carlyle, D. W; Espenson, J. H. *Inorg. Chem.* **1969**, *8*, 575.

0020-1669/83/1322-0784$01.50/0

Table I. Kinetic Competiton Experiments (25 °C, μ = 1.00 M)

init concn/M						
$[H^+]$	$10^3[CrR^{2+}]$	$10^3[Co(NH_3)_5F^{2+}]$	$10^3[X]^a$	$10^4[F^-]_\infty{}^b$/M	$([CrR^{2+}]_0 - [F^-]_\infty)/[F^-]_\infty$	$k_X/k_F{}^c$
			1. $\cdot C(CH_3)_2OH$			
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
						av 0.077
			2. $\cdot CH(CH_3)OC_2H_5$			
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
						av 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 sample of $[Co(NH_3)_5F](ClO_4)_2$. [c] By eq 7 or 14.

Since CrF^{2+} is kinetically stable for the duration of these experiments, the only source of free F^- is reaction 5. Experiments were carried out with $[Co(en)_3{}^{3+}]_0$ and $[Co(NH_3)_5F^{2+}]_0 >> [CrC(CH_3)_2OH^{2+}]_0$. Integration of the rate ratio (eq 6) with these as boundary conditions affords an

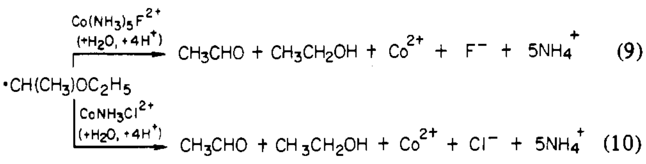
$$\frac{-d[Co(en)_3{}^{3+}]/dt}{d[F^-]/dt} = \frac{k_4[\cdot C(CH_3)_2OH][Co(en)_3{}^{3+}]}{k_5[\cdot C(CH_3)_2OH][Co(NH_3)_5F^{2+}]} \quad (6)$$

$$\frac{k_4}{k_5} = \frac{[CrC(CH_3)_2OH^{2+}]_0 - [F^-]_\infty}{[F^-]_\infty} \frac{[Co(NH_3)_5F^{2+}]_0}{[Co(en)_3{}^{3+}]_0} \quad (7)$$

expression (eq 7) that permits calculation of the desired rate constant ratio. The change in concentration of $Co(en)_3{}^{3+}$ is given by the difference between the experimentally determined quantities, $[CrC(CH_3)_2OH^{2+}]_0 - F^-]_\infty$. The data obtained (Table I) give the ratio $k_4/k_5 = 7.7 \times 10^{-2}$ at 25.0 °C and 1.0 M ionic strength. The value of k_4 is $(1.7 \pm 0.3) \times 10^5$ M^{-1} s^{-1}, where the uncertainty includes the uncertainties in its determination by kinetic competition[8] and in the original pulse radiolytic reference, which goes back to the rate constant 5.1×10^7 M^{-1} s^{-1} (22 ± 2 °C) for the reaction of Cr^{2+} with this free radical.[10] The value of k_5 is thus $(2.2 \pm 0.3) \times 10^6$ M^{-1} s^{-1}.

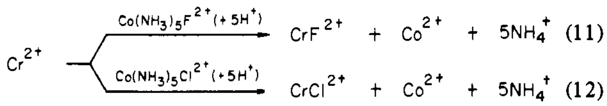
1-Ethoxyethyl Radical. This rate constant was determined via competiton experiments involving $Co(NH_3)_5F^{2+}$ and $Co(NH_3)_5Cl^{2+}$ (eq 8–12). With $[Co(NH_3)_5X^{2+}]_0 >> [CrCH(CH_3)OC_2H_5{}^{2+}]_0$, the rate ratio (eq 13) yields, upon integration, eq 14. The quantity $[Cl^-]_\infty$ was taken as the difference between $[CrCH(CH_3)OC_2H_5{}^{2+}]_0$ and $[F^-]_\infty$.

$$CrCH(CH_3)OC_2H_5{}^{2+} \longrightarrow Cr^{2+} + \cdot CH(CH_3)OC_2H_5 \quad (8)$$



$$\cdot CH(CH_3)OC_2H_5 \xrightarrow[(+H_2O,\ +4H^+)]{Co(NH_3)_5F^{2+}} CH_3CHO + CH_3CH_2OH + Co^{2+} + F^- + 5NH_4{}^+ \quad (9)$$

$$\cdot CH(CH_3)OC_2H_5 \xrightarrow[(+H_2O,\ +4H^+)]{CoNH_3Cl^{2+}} CH_3CHO + CH_3CH_2OH + Co^{2+} + Cl^- + 5NH_4{}^+ \quad (10)$$



$$Cr^{2+} \xrightarrow{Co(NH_3)_5F^{2+}(+5H^+)} CrF^{2+} + Co^{2+} + 5NH_4{}^+ \quad (11)$$

$$Cr^{2+} \xrightarrow{Co(NH_3)_5Cl^{2+}(+5H^+)} CrCl^{2+} + Co^{2+} + 5NH_4{}^+ \quad (12)$$

$$\frac{d[Cl^-]dt}{d[F^-]/dt} = \frac{k_{10}[\cdot CH(CH_3)OC_2H_5][Co(NH_3)_5Cl^{2+}]}{k_9[\cdot CH(CH_3)OC_2H_5][Co(NH_3)_5F^{2+}]} \quad (13)$$

$$\frac{k_{10}}{k_9} = \frac{[Cl^-]_\infty}{[F^-]_\infty} \frac{[Co(NH_3)_5F^{2+}]_0}{[Co(NH_3)_5Cl^{2+}]_0} \quad (14)$$

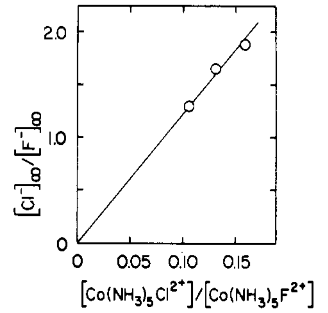


Figure 1. Results of the competition experiments for $\cdot CH(CH_3)OC_2H_5$ with $Co(NH_3)_5F^{2+}$ and $Co(NH_3)_5Cl^{2+}$, according to eq 14.

Table II. Rate Constants for Reduction of $Co(NH_3)_5X^{2+}$ Complex Complexes by $\cdot C(CH_3)_2OH$ and $\cdot CH(CH_3)OC_2H_5$ Radicals

	$10^{-6}k/M^{-1}$ s^{-1}	
complex	$\cdot C(CH_3)_2OH$	$\cdot CH(CH_3)OC_2H_5$
$Co(NH_3)_5F^{2+}$	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 10.

Figure 1 depicts a plot showing the linear variation of $[Cl^-]_\infty/[F^-]_\infty$ with the ratio of competing concentrations. Analysis of the data (Table I) according to eq 14 gives the ratio $k_{10}/k_9 = 12.3 \pm 0.3$ (25.0 °C, μ = 1.0 M). The value reported for k_{10} from pulse radiolysis[10] is 1.4×10^7 M^{-1} s^{-1}, affording the average value $k_9 = (1.1 \pm 0.2) \times 10^6$ M^{-1} s^{-1}. The uncertainty shown for k_9 includes the error in the ratio determination and that attributed[10] separately to k_{10}.

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 radical from diethyl ether to be useful there, however. Also, the pH independence of k_4 in the strongly acidic region was known from earlier work,[8] whereas it is an assumption (albeit almost certainly correct) that k_9 is independent of pH in the same region.

Table II 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]

It seems premature, however, to conclude from the strong halogen dependence that the reactions proceed by halogen

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(10) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

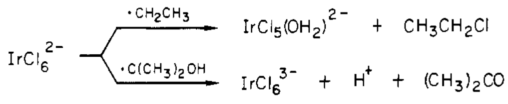
atom abstraction (eq 15a,b) rather than by direct electron

$$\cdot C(CH_3)_2OH + Co(NH_3)_5X^{2+} \xrightarrow{(+5H^+)} Co^{2+} + 5NH_4^+ + XC(CH_3)_2OH \quad (15a)$$

$$XC(CH_3)_2OH \rightarrow (CH_3)_2CO + H^+ + X^- \quad (15b)$$

$$\cdot C(CH_3)_2OH + Co(NH_3)_5X^{2+} \xrightarrow{(+4H^+)} Co^{2+} + 5NH_4^+ + (CH_3)_2CO + X^- \quad (15c)$$

transfer (eq 15c). Caution is particularly warranted considering that reduction of $IrCl_6^{2-}$ by aliphatic radicals proceeds by two pathways,[11] the former predominating for alkyl radicals (e.g., $\cdot CH_2CH_3$, eq 16a) and the latter for α-OH and α-OR radicals (eq 16b).



$$IrCl_6^{2-} \xrightarrow{\cdot CH_2CH_3} IrCl_5(OH_2)^{2-} + CH_3CH_2Cl \quad (16a)$$

$$IrCl_6^{2-} \xrightarrow{\cdot C(CH_3)_2OH} IrCl_6^{3-} + H^+ + (CH_3)_2CO \quad (16b)$$

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Registry No. $Co(NH_3)_5F^{2+}$, 15392-06-0; $\cdot C(CH_3)_2OH$, 5131-95-3; $\cdot CH(CH_3)OC_2H_5$, 2229-06-3.

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[11] (a) Chen, J. Y.; Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 6150. (b) Steeken, S.; Neta, P. *Ibid.* **1982**, *104*, 1244.

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Kinetics and Mechanism of Reduction of a Nickel(IV) Oxime–Imine Complex by $Co(edta)^{2-}$. Stereospecific Synthesis of a Stereoselective Oxidant

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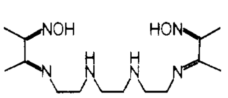
Kinetics and mechanism of the $Co(edta)^{2-}$ reduction of a nickel(IV) oxime–imine complex, $Ni^{IV}L^{2+}$, are reported at 25.0 °C and 0.10 M ionic strength. The initial reaction involves outer-sphere electron transfer to form a nickel(III) intermediate, $Ni^{III}L^+$, with a second-order rate constant of 36 M^{-1} s^{-1}. The protonated ($pK_H = 4.07$) form of the intermediate, $Ni^{III}LH^{2+}$, forms a hydrogen-bonded complex with $Co(edta)^{2-}$ ($K = 480$ M^{-1}) through which a second electron transfer ($k = 4 \times 10^{-2}$ s^{-1}) takes place to give the nickel(II) product. A minor pathway with disproportionation of $Ni^{III}L^+$ is also detected. Stereospecific synthesis of a methylated nickel(IV) derivative, $Ni^{IV}((S)\text{-}Me_2L)^{2+}$, is reported, and its properties are compared with those of the partially resolved $Ni^{IV}L^{2+}$ complex. The methylated reagent has been used to investigate stereoselectivity in the reaction with $Co(edta)^{2-}$. Both nickel(IV) and nickel(III) reactions show an excess of (+)-$Co(edta)^-$ over (−)-$Co(edta)^-$ products of around 10%.

Introduction

Oxime complexes of nickel possess extensive redox chemistry, and there are many reports[1] of species with formal metal ion oxidation states higher than nickel(II). The sexidentate di(oxime–imine) ligand 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime (H_2L (**1**)) used by Chakravorty and co-workers[2] is of particular interest since it allows formation in aqueous media of a long-lived complex that is formally nickel(IV). This complex ($Ni^{IV}L^{2+}$ (**2**)) forms with oxime deprotonation from the corresponding nickel(II) complex ($Ni^{II}LH_2^{2+}$) and is diamagnetic[2] and substitution inert,[2,3] consistent with a low-spin d^6 electronic configuration. It can be optically resolved.[3]



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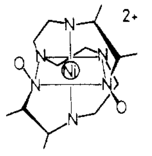

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The nickel(IV) complex undergoes[4,5] a single reversible two-electron reduction at pH < 5 (eq 1), with a potential of

$$Ni^{IV}L^{2+} + 2e^- + 2H^+ \rightleftharpoons Ni^{II}LH_2^{2+} \quad (1)$$

0.94 V (vs. NHE, the normal hydrogen electrode) while above this pH the intermediate trivalent state can be detected. Relevant potentials are 0.65 V for eq 2, 0.64 V for eq 3, and 0.42 V for eq 4, all at 25 °C and in 0.10 mol dm^{-3} $NaNO_3$ media.[5]

$$Ni^{IV}L^{2+} + e^- \rightleftharpoons Ni^{III}L^+ \quad (2)$$

$$Ni^{III}LH^{2+} + e^- \rightleftharpoons Ni^{II}LH^+ \quad (3)$$

$$Ni^{III}L^+ + e^- \rightleftharpoons Ni^{II}L \quad (4)$$

The low substitution lability and moderately high reduction potential of $Ni^{IV}L^{2+}$ are likely to result in outer-sphere electron-transfer mechanisms. Molecular structure data[6,7] on related complexes indicate that no major geometry change accompanies reduction of nickel(IV) to nickel(II), and an outer-sphere two-electron transfer was considered a possibility.[8] However, reduction of nickel(IV) by well-characterized one-[5] and two-electron[8] reagents involves consecutive electron transfer and formation of a nickel(III) intermediate.

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