

ponents on the scale employed, 3% rearrangement could be measured easily in these reductions by GLC. Rearrangement between 1 and 3% could be detected but not accurately measured.

Acknowledgment. The authors are most grateful to Professors John F. Reed and Stephen F. Pavkovic of this Department for the derivation of eq 9 and the iterative computer program data. In addition, the interest and constructive comments of Professor Cheves Walling (University of Utah) and Dr. Keith U. Ingold of the National Research Council of Canada are deeply appreciated.

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Kinetics of the Formation and Decomposition of Carbon-Cobalt(III) Bonds in Aqueous Solutions by the Reaction of Aliphatic Free Radicals with a Coenzyme B-12r Model Cobalt(II) Complex

Hanoch Elroi and Dan Meyerstein*

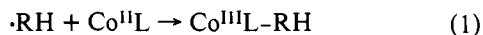
Contribution from the Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva, Israel, and Nuclear Research Centre Negev, Beer Sheva, Israel.

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Abstract: The reactions of $\cdot\text{CH}_2\text{OH}$, $\text{CH}_3\dot{\text{C}}\text{HOH}$, $\text{HO}\dot{\text{C}}\text{HCH}_2\text{OH}$, and $\cdot\text{CH}_2\text{CHO}$ with a $\text{Co}^{\text{II}}\text{L}$ complex were studied (L = macrocyclic $\text{Me}_6[14]\text{dieneN}_4$). In all systems the product of these reactions is a $\text{Co}^{\text{III}}\text{L-RH}$ complex. The mechanism of decomposition of these products depends on the nature of the aliphatic residue-RH. $\text{Co}^{\text{III}}\text{L-CH}_2\text{OH}$ decomposes by a heterolytic cleavage of the carbon metal bond forming $\text{Co}^{\text{I}}\text{L} + \text{CH}_2\text{O}$. $\text{Co}^{\text{III}}\text{L-CH(OH)CH}_3$ seems to decompose by a hydride transfer from the β -carbon yielding $\text{Co}^{\text{III}}\text{L-H} + \text{CH}_3\text{CHO}$. $\text{Co}^{\text{III}}\text{L-CH(OH)CH}_2\text{OH}$ rearranges by loss of water to $\text{Co}^{\text{III}}\text{L-CH}_2\text{CHO}$, which then hydrolyzes to $\text{Co}^{\text{III}}\text{L} + \text{CH}_3\text{CHO}$. The latter reaction is a model reaction to that of the diol dehydratase enzyme which contains the coenzyme B-12. The mechanism of these reactions and their implication on the chemistry of other systems containing σ carbon-cobalt bonds are discussed.

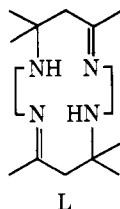
The discovery that coenzyme B-12 is a cobalt(III) complex containing a cobalt-carbon bond initiated many studies concerning the mechanisms of formation and decomposition

of these bonds.¹ One of the mechanisms leading to the formation of carbon-cobalt bonds is the reaction of free radicals with cobalt(II) complexes:¹⁻⁵

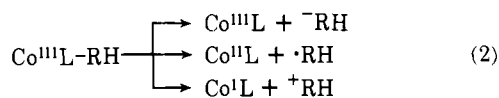


The kinetics of reactions of this type can be conveniently studied by the pulse-radiolytic technique.³⁻⁷ This technique has the further advantage that it enables the study of the chemical properties of the $\text{Co}^{\text{III}}\text{L}-\text{RH}$ compounds formed even if they are unstable, e.g., $\text{Co}^{\text{III}}\text{L}-\text{CH}_2\text{OH}$.

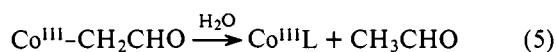
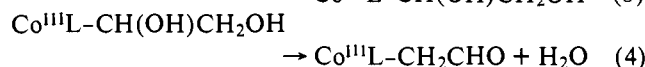
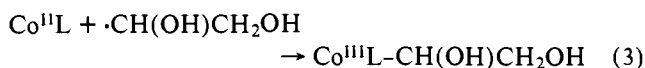
We have decided to study the kinetics of reaction of $\cdot\text{CH}_2\text{OH}$, CH_3CHOH , $(\text{CH}_3)_2\text{COH}$, CF_3CHOH , $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$, $\dot{\text{C}}\text{H}(\text{OH})\text{CH}_2\text{OH}$, $\cdot\text{CH}_2\text{CO}_2^-$, and $\cdot\text{CH}_2\text{CHO}$ with a cobalt(II) complex with the macrocycle $\text{Me}_6[14]\text{dieneN}_4$ ligand L.



It was hoped that the variety of free radicals used will help in elucidating the factors affecting the rates of formation of cobalt-carbon bonds in this system. Most of the product molecules have an OH group on the carbon α or β to the cobalt and are therefore expected to be unstable, thus enabling the study of the factors affecting the mechanism and rate of decomposition of the carbon-cobalt bond which can follow one of three routes:¹



Of special interest was the system $\cdot\text{CH}(\text{OH})\text{CH}_2\text{OH}$, where the following mechanism could be expected:



This reaction scheme is one of the suggested mechanisms for the action of the diol dehydratase enzyme.^{1c,d,8} Thus, the observation of the proposed intermediates in the model system studied would prove that cobalt complexes might induce such a rearrangement via a free-radical mechanism. Other authors^{1,9} have suggested different mechanisms of reaction of the diol dehydratase enzyme including one which involves $\text{Co}^{\text{III}}\text{L}-\text{RH}$ and $\text{Co}^{\text{I}}\text{L}$ only.¹⁰

We have chosen the macrocyclic ligand L for this study as its $\text{Co}^{\text{II}}\text{L}$ complex is stable in aqueous solutions and has no strong absorption band at $\lambda > 375$ nm, thus enabling the study over a wide spectral range. During this study the results of a similar study on the coenzyme B-12 itself were reported.⁵ However, it seems that due to the simple model chosen in our study we were able to get more detailed information on the mechanism of the reactions. The ligand chosen also has the advantage that its properties can be easily changed by saturating the double bonds, by increasing the number of unsaturated bonds, or by changing the ring size. Thus, the effect of the structure of the equatorial ligand on the reaction mechanism can be studied.

Experimental Section

The ligand 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene perchlorate was synthesized by the very slow addition of 27 g of 60% HClO_4 to a cold mixture of 400 cm^3 of acetone

and 17.6 g of ethylenediamine.¹¹ The temperature was kept below 5 °C to decrease the danger of this procedure. The ligand precipitated as white crystals and was purified by recrystallization.

The complex $\text{Co}^{\text{II}}\text{L}$ was prepared by dissolving $\text{Co}(\text{CH}_3\text{CO}_2)_2$ and the ligand in a molar ratio of 1.5:1.0 in a 1:1 mixture of methanol and water under nitrogen. This mixture was heated to boiling and most of the solvent was evaporated; after cooling the yellow crystals were recrystallized in a minimal quantity of water. The purity of the $\text{Co}^{\text{II}}\text{L}$ complex was checked by its UV-visible absorption spectrum, which was identical with that reported in the literature and with a sample obtained from Professor D. H. Busch. Anal. Calcd: C, 35.69; H, 6.30; N, 10.54. Found: C, 35.60; H, 5.97; N, 10.42.

The $\text{Co}^{\text{III}}\text{L}(\text{ClO}_4)_3$ complex was prepared by the method described by Endicott et al.¹²

The ADH (alcohol dehydrogenase) and DPNH (reduced form of nicotinamide adenine dinucleotide) used for the determination of aldehydes were supplied by Sigma Ltd. N_2O and Ar were purified from O_2 traces by passing them through three washing bottles containing acidic (H_2SO_4) solutions of VSO_4 over Zn amalgam and through another washing bottle containing triple-distilled water. All other chemicals were AR grade and were used without further treatment. All solutions were prepared from triple-distilled water and the pH was adjusted by addition of HClO_4 or NaOH .

Procedure. All solutions were deaerated by saturation with Ar or N_2O using the syringe technique. The pulse radiolytic experiments were carried out at the electron linear accelerator of the Hebrew University of Jerusalem. The pulses used were 0.1–1.5 μs , 200 mA, of 5 MeV electrons. The samples thus received a dose of 100–5000 rd per pulse. The details of the experimental technique and the method used for evaluating the results were described elsewhere in detail.¹³

Rates of reaction of free radicals with $\text{Co}^{\text{II}}\text{L}$ were calculated from the pseudo-first-order plots obtained in solutions containing at least three different $\text{Co}^{\text{II}}\text{L}$ concentrations which were prepared from different stock solutions. For the solutions containing low concentrations of $\text{Co}^{\text{II}}\text{L}$ the effect of doubling the dose of the pulse was checked in order to ensure that second-order reactions of the free radicals do not affect the results.

The rates of decomposition of the different $\text{Co}^{\text{III}}\text{L}-\text{RH}$ intermediates reported were derived from at least ten kinetic plots. In all cases studied the decomposition reaction obeyed a first-order rate law for at least 3 half-lives. In order to verify the first-order nature of these processes we checked the effects of: (a) changing the dose of the pulse by a factor of three and (b) changing the wavelength at which the kinetics were followed so that $\Delta\epsilon$ was changed by over a factor of two. For all first-order processes studied we found that the rates of reaction were independent of pulse intensity and the wavelength at which the reaction was followed.

The low dose rate irradiations were carried out in a Gamma Cell 200, Atomic Energy of Canada Ltd., with a dose rate of ~ 15 000 rd/min. The dose rate was determined by the Fricke dosimeter.⁶

Analysis. The yield of aldehydes was determined by an enzymatic method using ADH and DPNH.¹⁴ This method is applicable only to neutral solutions. The method was calibrated by determining the yield of acetaldehyde formed by irradiating an O_2 -saturated neutral solution containing 0.1 M ethanol. The yield of acetaldehyde in this system is known to be $G(\text{acetaldehyde}) = 2.65$.⁶ Doses of $4\text{--}10 \times 10^4$ rd were used. For each determination, a blank solution, which received an identical treatment but was not irradiated, was analyzed.

Experiments to determine the yield of aldehydes by chemical methods failed as it was found that the complex decomposed in solutions containing high concentrations of H_2SO_4 yielding compounds with aldehydic groups.

Spectroscopic determinations were performed using a Cary 17 spectrophotometer. The difference spectra between irradiated solutions and unirradiated solutions were measured (after irradiation in the low dose rate γ source). In blank experiments it was found that for solutions at $2 < \text{pH} < 10$, $\epsilon_{\text{Co}^{\text{III}}\text{L}} - \epsilon_{\text{Co}^{\text{II}}\text{L}} = (1.20 \pm 0.10) \times 10^4$ and $-(2.00 \pm 0.25) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at λ 225 and 330 nm, respectively (the maxima of absorption of these complexes). The solutions of $\text{Co}^{\text{II}}\text{L}$ in the pH range 1–10 were found to be stable for several hours by following the UV absorption spectra. In no case was any dissociation or oxidation of the complex observed within the time required for preparations of the solutions and their irradiation.

Results

The specific rates of reaction of $\text{Co}^{\text{II}}\text{L}$ with the primary

Table I. Reactions of Primary Free Radicals with Solutes Used in This Study

reaction	$k, M^{-1} s^{-1}$	ref
$OH + CH_3OH \rightarrow CH_2OH + H_2O$	7×10^8	17
$H + CH_3OH \rightarrow \cdot CH_2OH + H_2$	1.6×10^6	15
$OH + CH_3CH_2OH \xrightarrow{87\%} CH_3\dot{C}HOH + H_2O$	1.7×10^9	17
$\xrightarrow{13\%} \cdot CH_2CH_2OH + H_2O$		
$H + CH_3CH_2OH \xrightarrow{94\%} CH_3\dot{C}HOH + H_2$	2.5×10^7	15
$\xrightarrow{6\%} \cdot CH_2CH_2OH + H_2$		
$OH + (CH_2OH)_2 \rightarrow HO\dot{C}HCH_2OH + H_2O$	1.5×10^9	17
$H + (CH_2OH)_2 \rightarrow HO\dot{C}HCH_2OH + H_2O$	2.1×10^7	15
$e_{aq}^- + \text{alcohols} \rightarrow \text{products}$	$k < 5 \times 10^5$	16
$e_{aq}^- + BrCH_2CH_2OH \rightarrow Br^- + \cdot CH_2CH_2OH$	1.6×10^9	16
$H + BrCH_2CH_2OH \rightarrow HBr + \cdot CH_2CH_2OH$	2.7×10^8	15
$H + BrCH_2CH_2OH \rightarrow BrCH_2\dot{C}HOH + H_2$	2.7×10^7	15
$OH + BrCH_2CH_2OH \rightarrow BrCH_2\dot{C}HOH + H_2O$	7.7×10^8	17
$2CH_2OH \xrightarrow{96\%} (CH_2OH)_2$	2.4×10^9	22
$\xrightarrow{4\%} CH_2O + CH_3OH$		
$2CH_3\dot{C}HOH \rightarrow CH_3CHO + CH_3CH_2OH$	2.3×10^9	22
$2OH\dot{C}HCH_2OH \rightarrow HOCH_2CHO + HOCH_2CH_2OH$	6.7×10^8	21b
$e_{aq}^- + N_2O \xrightarrow{H^+} N_2 + OH$	8.7×10^9	16
$e_{aq}^- + H_3O_{aq}^+ \rightarrow H$	2.2×10^{10}	16
$e_{aq}^- + Co^{II}L \rightarrow Co^{II}L$	4.4×10^{10}	this study
	4.4×10^{10}	3
$OH + Co^{II}L \rightarrow Co^{III}L'$ (probably OH adduct to double bond)	2.7×10^9	this study ^a
	3.2×10^9	4
$H + Co^{II}L \rightarrow Co^{III}L-H$	1.8×10^9	this study ^a
	$\sim 1 \times 10^{10}$	4
$Co^I L + N_2O \rightarrow Co^{III}L + N_2$	2.5×10^7	this study ^a
	3.9×10^7	3

^a Product not identified in this study.

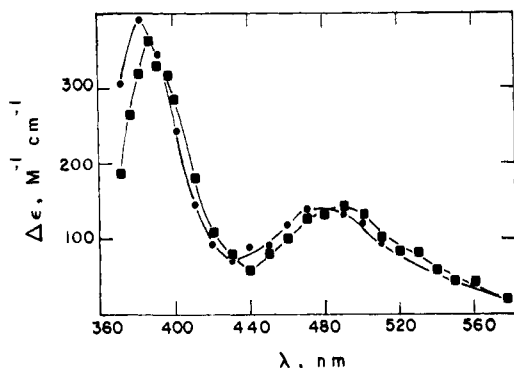


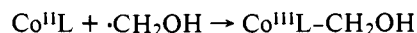
Figure 1. Spectra of $Co^{III}L-CH_2OH$. Solution composition: 1 M CH_3OH , N_2O saturated, pulse intensity 800 rd, measured 500 μs after the pulse: (■) pH 6.0, 2×10^{-4} M $Co^{II}L$; (●) pH 1.1, 5×10^{-4} M $Co^{II}L$.

radicals, e_{aq}^- , H, and OH, were measured. $k_{e_{aq}^- + Co^{II}L} = 4.4 \times 10^{10} M^{-1} s^{-1}$ was found by measuring the effect of $Co^{II}L$ on the rate of disappearance of e_{aq}^- at 600 nm. $k_{OH + Co^{II}L} = (2.7 \pm 0.2) \times 10^9 M^{-1} s^{-1}$ was measured by direct observation of the rate of formation of a transient in an N_2O -saturated neutral solution containing $1-3 \times 10^{-5}$ M $Co^{II}L$. These rates are in full agreement with those reported by Tait et al.⁴ $k_{H + Co^{II}L} = (1.8 \pm 0.2) \times 10^9 M^{-1} s^{-1}$ was determined by measuring the effect of $Co^{II}L$ on the yield of the hydrogen atom adduct to benzoic acid ($k_{H + \text{benzoic acid}} = 4.5 \times 10^9 M^{-1} s^{-1}$)¹⁵ in Ar-saturated solution at pH 1.0 containing 0.1 M *tert*-butyl alcohol and 1×10^{-4} M benzoic acid. This rate is considerably lower than $k_{H + Co^{II}L} \approx 1 \times 10^{10} M^{-1} s^{-1}$ re-

ported by Tait et al.⁴ We have no explanation for this discrepancy.

The rate of reaction of $Co^I L$, formed by $e_{aq}^- + Co^{II}L \rightarrow Co^I L$, with N_2O was measured by following the effect of N_2O on the rate of disappearance of $Co^I L$. This reaction was followed at 630 nm where $Co^I L$ has a strong absorption band.⁴ Argon-saturated solutions containing 2×10^{-3} M $Co^{II}L$, 1 M *tert*-butyl alcohol, and $2-8 \times 10^{-3}$ M N_2O at pH 7.0 were used. $k[Co^I L + N_2O \rightarrow Co^{III}L + N_2] = (2.5 \pm 0.4) \times 10^7 M^{-1} s^{-1}$ was determined in fair agreement with $k = 3.9 \times 10^7 M^{-1} s^{-1}$ reported by Tait et al.⁴ In the absence of N_2O the decomposition of $Co^I L$ is much slower than in its presence. The latter reaction was studied in detail by Tait et al.⁴

Reactions with CH_2OH Radicals. N_2O -saturated solutions containing $1-10 \times 10^{-4}$ M $Co^{II}L$ and 1 M CH_3OH at $1 < pH < 6$ were irradiated. Under these conditions all the primary radicals formed are transformed into $\cdot CH_2OH$ radicals as can be deduced from Table I. In acidic solutions $[Co^{II}L] < 2 \times 10^{-4}$ M was kept in most experiments in order to decrease the contribution of the reaction $H + Co^{II}L \rightarrow Co^{III}L-H$ vs. the reaction $H + CH_3OH \rightarrow CH_2OH$ (Table I). In these solutions the formation of an unstable intermediate was observed. The spectrum of the intermediate is slightly dependent on pH as can be seen from Figure 1. (Note that the results are given as $\Delta\epsilon = \epsilon(\text{intermediate}) - \epsilon(Co^I L)$). The rate of the reaction:



$$k_6 = (7 \pm 1) \times 10^7 M^{-1} s^{-1} \quad (6)$$

was measured and found to be pH independent. (For the identification of the product see the Discussion.) The inter-

Table II. Difference Spectra between the "Final" Products and the Unirradiated Solutions^a

solute	pH	dose, rd	λ_1^b	$\Delta\epsilon_1^c$	λ_2^b	$\Delta\epsilon_2^c$
<i>d</i>	1.0		330	-2000	235	12 000
<i>d</i>	6.5		325	-2200	240	12 000
<i>d</i>	9.7		330	-1750	230	12 000
1 M CH ₃ OH	1.0	2 200	337	-1850	255	3 100
	1.0	20 000	337	-1850	255	3 100
	2.0	2 200	340	-1300	255	3 200
	5.0	2 200	330	-1500	235	9 600
	5.0	20 000	330	-850	235	5 000
1 M CH ₃ CH ₂ OH	5.0	20 000	330	-750	235	4 700
	1.0	20 000	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>
0.5 M (CH ₂ OH) ₂	1.2	20 000	335	-2250	240	12 500
	2.5	20 000	335	-1650	240	10 500
	4.2	20 000	340	-380	240	2 000
	6.0	20 000	330	-250	240	1 650
1 M C(CH ₃) ₃ OH	9.6	20 000	335	-1000	260	1 500
	1.0	2 200	330	-670	240	2 750
	5.0	2 200	330	-550	230-250	1 100-1300

^a All solutions contained $2-5 \times 10^{-4}$ M Co^{II}L and were saturated with N₂O. Irradiations were carried out in a γ source with a dose rate of $\sim 27\,000$ rd/min; measured 20-30 min after end of irradiation. ^b Wavelength at which maxima appeared in the difference spectra. ^c The apparent molar absorption coefficient difference between products and Co^{II}L at these wavelengths. The apparent molar absorption coefficients were calculated assuming that all the primary radicals, $G = 6.1$, react with Co^{II}L and give a product molecule. ^d Difference spectra between Co^{III}L and Co^{II}L. The aldehydes CH₂O and CH₃CHO have only weak absorption bands at $\lambda > 210$ nm in aqueous solutions (K. Broden, E. A. Braude, and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946); N. Landquist, *Acta Chim. Scand.*, 9, 867 (1955)). ^e Practically no change in the spectrum was observed. As $G(\text{CH}_3\text{CHO}) = 6.0$ in these solutions, this observation is further proof that the formation of aldehydes does not affect the difference spectra.

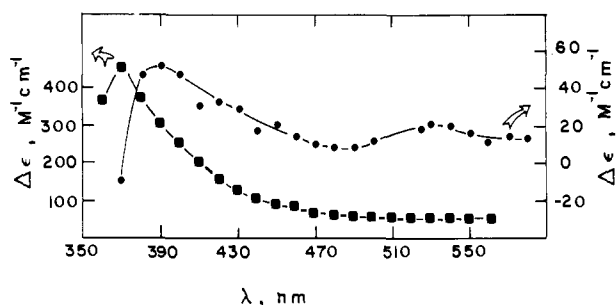


Figure 2. Spectra observed after a pulse of 2000 rd to an N₂O-saturated solution containing 1 M CH₃CH₂OH, 5×10^{-4} M Co^{II}L at pH 6.2: (■) 250 μ s after pulse; (●) 100 ms after pulse.

mediate decomposes in a first-order process, independent of [Co^{II}L], [H₃O⁺], or dose with a rate of $k = 0.10 \pm 0.02$ s⁻¹. The difference spectra between the "final" products formed and the unirradiated solutions were measured; the results are summarized in Table II. The yield of formaldehyde was measured in N₂O-saturated neutral solutions containing 0.1 M methanol and 5×10^{-4} M Co^{II}L; $G(\text{CH}_2\text{O}) = 6 \pm 0.5$ was found, i.e., the yield of formaldehyde equals that of $\cdot\text{CH}_2\text{OH}$ radicals.⁶ In the absence of Co^{II}L, $G(\text{CH}_2\text{O}) < 0.3$.

Reactions with CH₃CHOH Radicals. N₂O-saturated solutions containing 1.0 M CH₃CH₂OH and $1-10 \times 10^{-4}$ M Co^{II}L at $1 < \text{pH} < 6$ were irradiated. The data in Table I clearly indicate that under these conditions all primary radicals formed are transformed into CH₃CHOH radicals. The rate of reaction of these radicals with Co^{II}L was found to be pH independent, $k(\text{CH}_3\text{CHOH} + \text{Co}^{\text{II}}\text{L}) = (3.0 \pm 0.4) \times 10^7$ M⁻¹ s⁻¹. The spectra of the intermediates observed in this system at pH 6.2 and 2.1 are plotted in Figures 2 and 3. At pH > 4 the intermediate formed decomposes in one first-order process with a rate $k = (1.0 \pm 0.3) \times 10^2$ s⁻¹ at pH 7.0, independent of [Co^{II}L] or dose. The spectrum of the "final" product observed in the pulse radiolytic experiments (Figure 2) is different from that observed in the methanol system (Figure 1) and that of the stable products obtained in the low dose rate experiments, or of Co^{III}L (Table I).

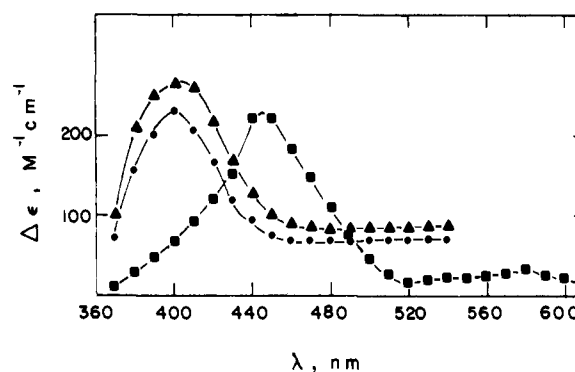


Figure 3. Spectra observed after a pulse of 1500 rd to an N₂O-saturated solution containing 1 M CH₃CH₂OH, 5×10^{-4} M Co^{II}L at pH 2.1: (▲) 100 μ s after pulse; (●) 5 ms after pulse; (■) 100 ms after pulse.

In acidic solutions, pH < 4 , three consecutive reactions were observed. The rates of the two reactions following the formation of Co^{III}L-CH(OH)CH₃ were found to be pH dependent (Figure 4). Also in this pH range the spectrum of the "final" product observed in the pulse radiolytic experiments differs from that found at longer times after low dose irradiation (Table II). (It should be noted that the stability of the signal in the pulse radiolytic experiments does not allow measurements at times longer than 1 min.) The yield of acetaldehyde in neutral solutions was found to be $G(\text{acetaldehyde}) = 6.0 \pm 0.5$; the yield in the absence of Co^{II}L was $G(\text{acetaldehyde}) = 2.65$.

Reactions with $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$, $\cdot\text{CH}_2\text{CO}_2^-$, $\cdot\text{C}(\text{OH})(\text{CH}_3)_2$, and $\cdot\text{CH}(\text{OH})\text{CF}_3$ Radicals. The rates of reaction of $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$, $\cdot\text{CH}_2\text{CO}_2^-$, and $\cdot\text{C}(\text{OH})(\text{CH}_3)_2$ with Co^{II}L are lower than 1×10^7 M⁻¹ s⁻¹. Therefore, very small pulses have to be used in order to eliminate the dimerization or disproportionation reactions of the free radicals (Table I). (The concentration of Co^{II}L cannot be increased due to the competition between the reactions $e_{\text{aq}}^- + \text{Co}^{\text{II}}\text{L}$ and $e_{\text{aq}}^- + \text{N}_2\text{O}$.) Under these conditions the absorptions due to the transients formed were too low to be followed accurately.

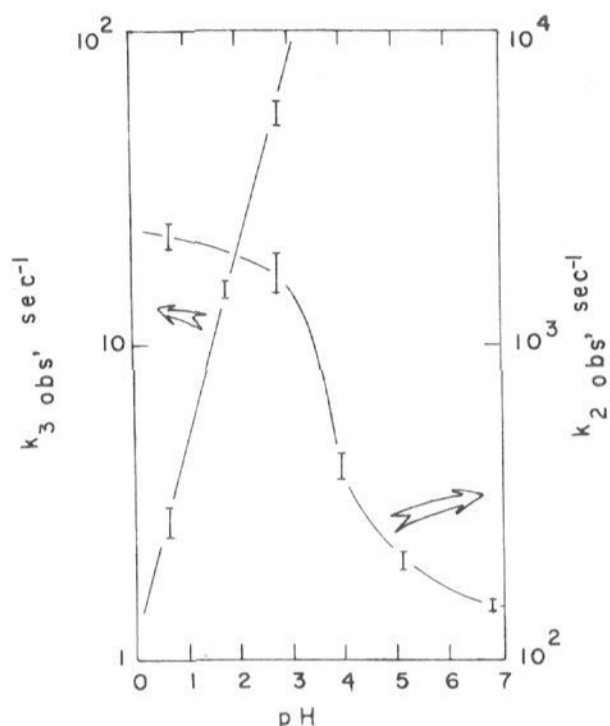


Figure 4. pH dependence of the second, k_2 , and third, k_3 , reactions observed in N_2O -saturated solutions containing 1 M CH_3CH_2OH , 5×10^{-4} M $Co^{II}L$, pulse intensity 800 rd.

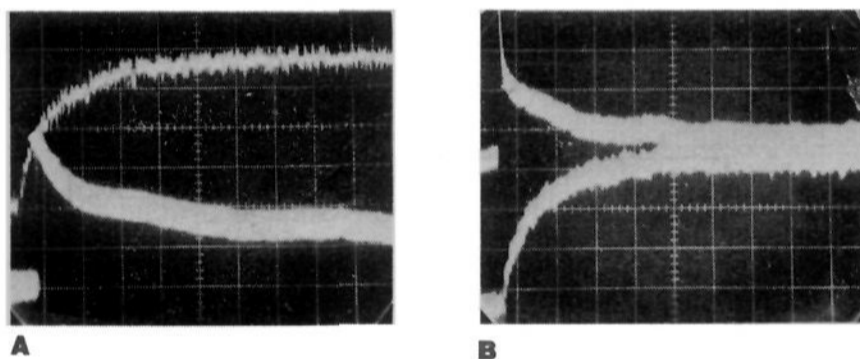


Figure 5. Oscillograms obtained after a pulse of ~ 800 rd was delivered to an N_2O -saturated solution containing 1 M $(CH_2OH)_2$, 5×10^{-4} M $Co^{II}L$ at pH 3.9. Measured at 390 nm total light signal, ordinate, 800 mV, ordinate 10 mV/division: (A) upper trace 100 μs /division, lower trace 20 ms/division; (B) upper trace 200 ms/division, lower trace 100 μs /division.

The rate of the reaction $Co^{II}L + \cdot CH(OH)CF_3 \rightarrow Co^{III}L-CH(OH)CF_3$ was found to be $(1 \pm 0.5) \times 10^7 M^{-1} s^{-1}$ at pH 6. The decomposition of this intermediate obeyed a first-order rate law with $k = (6 \pm 1) \times 10^{-2} s^{-1}$. In acid solutions the radical $\cdot CH(OH)CF_3$ was found to decompose by fast reactions which were not studied in detail, and therefore its reactions with $Co^{II}L$ could not be studied.

Reactions with $\cdot CH_2CHO$ and $\cdot CH(OH)CH_2OH$ Radicals. N_2O -saturated solutions containing 1 M ethylene glycol and $1-10 \times 10^{-4}$ M $Co^{II}L$ in the pH range 1-10 were irradiated. The data in Table I clearly indicate that under these conditions all the primary radicals are transformed into $HO\dot{C}HCH_2OH$ radicals. The formation of unstable intermediates was observed in the whole pH range. In acid, pH < 3, and alkaline, pH > 7, two reactions were observed, whereas in "neutral solutions" three consecutive reactions were observed (Figure 5). The spectra of these intermediates at different pHs are plotted in Figure 6.

The rate of formation of the first intermediate is pH dependent (Figure 7). The absolute rates calculated range between $\sim 1 \times 10^7$ and $8 \times 10^7 M^{-1} s^{-1}$. The second reaction observed in neutral solutions is well separated in time from the last reaction only in the pH range 3.5-5.0. In this pH range the rate of this reaction, which obeys a first-order rate law, changes from 15 to 4 s^{-1} , respectively. The rate of the last reaction, the second in the acid and alkaline region and the third at $3 < pH$

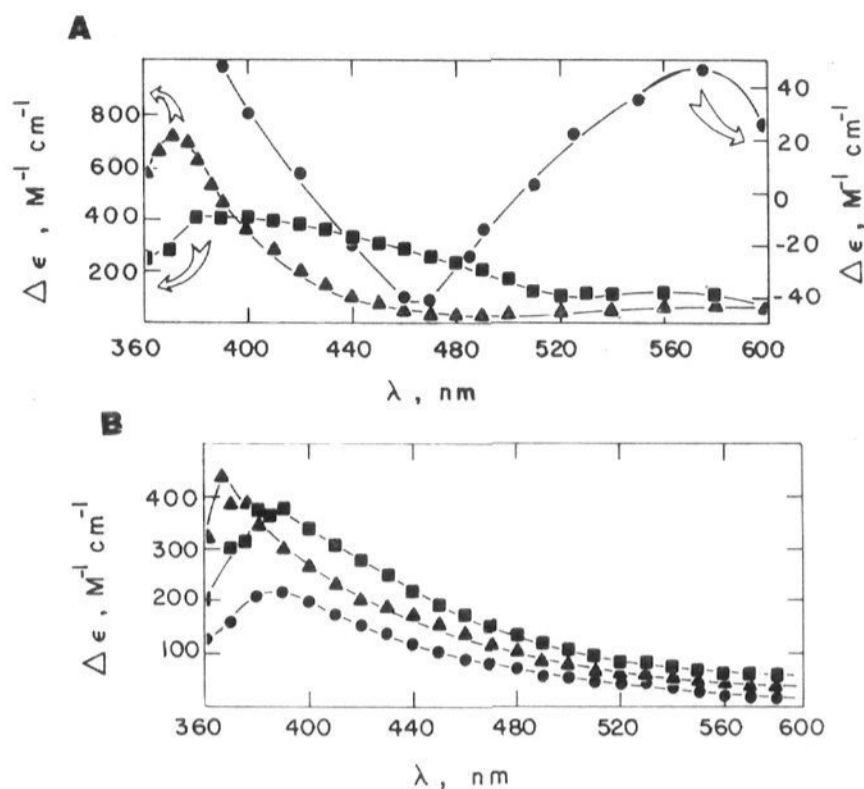


Figure 6. Absorption spectra observed in N_2O -saturated solutions containing 1 M $(CH_2OH)_2$ and 5×10^{-4} M $Co^{II}L$. (A) Pulse intensity 2000 rd: (\blacktriangle) pH 8.8, 50 μs after pulse; (\blacksquare) pH 1.4, 50 μs after pulse; (\bullet) pH 1.4, 1 ms after pulse. (B) Pulse intensity 1200 rd: (\blacksquare) pH 4.6, 2 ms after pulse; (\bullet) pH 4.6, 20 ms after pulse; (\blacktriangle) pH 6.4, 1 ms after pulse.

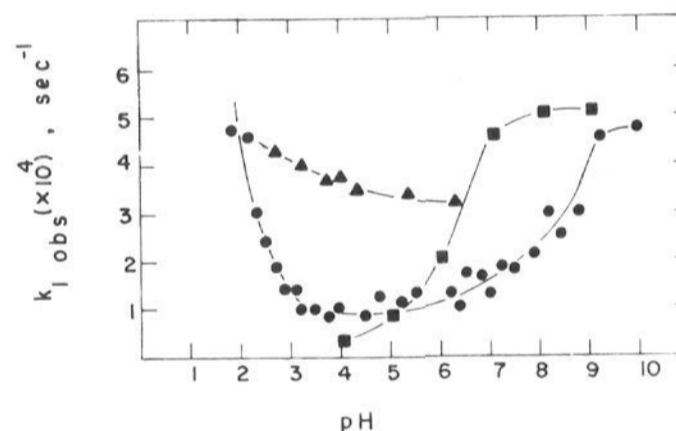


Figure 7. pH dependence of the observed rates of formation of the $Co^{III}L-RH$ intermediate in N_2O -saturated solutions containing 5×10^{-4} M $Co^{II}L$, dose per pulse 500 rd: (\bullet) 1 M $(CH_2OH)_2$; (\blacktriangle) 0.01 M 2-bromoethanol; (\blacksquare) 0.1 M 2-aminoethanol.

< 7, was found to be pH dependent (Figure 8). (The reason for plotting these reactions together will be discussed below.) The difference spectra between the "final" products after low dose irradiation and the unirradiated solutions were measured and are summarized in Table II.

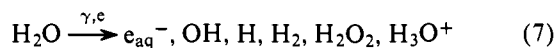
The yields of acetaldehyde in N_2O -saturated neutral solutions containing 0.1 M ethylene glycol and 5×10^{-4} M $Co^{II}L$ were measured: $G(\text{acetaldehyde}) = 6.0 \pm 0.5$; in the absence of $Co^{II}L$ $G(\text{acetaldehyde}) = 2.6 \pm 0.2$. N_2O -saturated solutions containing 1×10^{-2} M 2-bromoethanol and $2-5 \times 10^{-4}$ M $Co^{II}L$ in the pH range $1 < pH < 6$ were irradiated. The data in Table I indicate that under these conditions $\sim 85\%$ of the primary radicals are transformed into $BrCH_2\dot{C}HOH$ radicals and $\sim 15\%$ into $\cdot CH_2CH_2OH$ radicals. The formation of an unstable intermediate, which decomposed in one step, was observed in these solutions. The pH dependence of the rates of formation and decomposition of this intermediate are plotted in Figures 7 and 8.

Reactions with Radicals Derived from 2-Aminoethanol. N_2O -saturated solutions containing 0.1 M $NH_2CH_2CH_2OH$ and $1-10 \times 10^{-4}$ M $Co^{II}L$ were irradiated. The pH dependence of the rate of formation of the intermediates in this system is plotted in Figure 7. At pH 7.0 this rate is $4.0 \times 10^7 M^{-1} s^{-1}$. The decomposition of this intermediate seemed to

consist of two, not well separated, first-order reactions at pH < 7.0. At pH 7.0 the rates of these reactions are $\sim 2.5 \pm 1$ and $7.0 \pm 1.5 \text{ s}^{-1}$. At higher pHs only one reaction was observed with $k \sim 5.5 \pm 1.5 \text{ s}^{-1}$. The pK_a of $^+\text{NH}_3\text{CH}_2\text{CH}_2\text{OH}$ is 9.25.¹⁸ OH radicals are expected to react with the acid form to give the radical $^+\text{NH}_3\text{CH}_2\dot{\text{C}}\text{HOH}$ and with the basic form to give a mixture of $\text{NH}_2\text{CH}_2\dot{\text{C}}\text{HOH}$ and $\text{NH}_2\dot{\text{C}}\text{HCH}_2\text{OH}$;¹⁵ thus, above pH 7.25 a mixture of free radicals is expected in this system. Furthermore, the pK of the radical $^+\text{NH}_3\text{CH}_2\dot{\text{C}}\text{HOH}$ is expected to be lower than 9.25 and we have therefore not studied this system in detail.

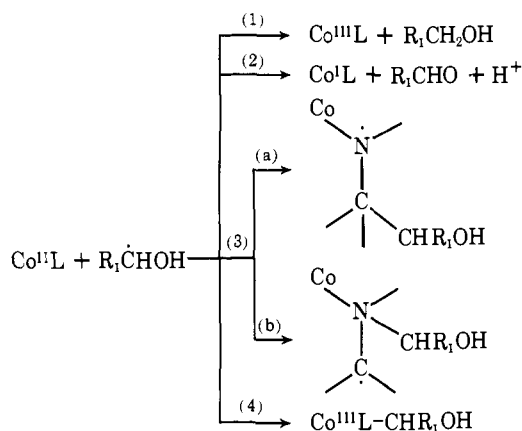
Discussion

The radiolysis of water may be summed up by the equation:⁶



The yields of these products are $G_{e_{\text{aq}}^-} = 2.65$, $G_{\text{OH}} = 2.65$, $G_{\text{H}} = 0.60$, $G_{\text{H}_2} = 0.45$, and $G_{\text{H}_2\text{O}_2} = 0.75$ (where G is defined as the number of product molecules formed per 100 eV absorbed by the solution; $1 \text{ rd} = 6.24 \times 10^{13} \text{ eV}$).⁶ Thus, if by adding appropriate solutes (Table I) all the primary radicals, e_{aq}^- , H, and OH, are transformed into one aliphatic radical, $\cdot\text{RH}$, its yield is $G(\cdot\text{RH}) = 5.9$. (In solutions containing high concentrations of solutes the radical yield is often somewhat larger whereas the yields of H_2 and H_2O_2 are somewhat smaller.)⁶

Mechanism of Reaction of Free Radicals with $\text{Co}^{\text{II}}\text{L}$. In principle, free radicals of the type $\text{R}_1\dot{\text{C}}\text{HOH}$ may react with $\text{Co}^{\text{II}}\text{L}$ according to one of the following reactions:



According to alternative 1, the radical oxidizes, via an outer sphere mechanism, the $\text{Co}^{\text{II}}\text{L}$ complex. (Free radicals of this type are known to be strong oxidizing as well as strong reducing agents.¹⁹) This mechanism is ruled out as it does not explain the formation of aldehydes or unstable intermediates. It should be pointed out that although the redox potential of the couples $\cdot\text{CH}_3/\text{CH}_4$ ^{19c} or $\cdot\text{CH}_2\text{OH}/\text{CH}_3\text{OH}$ is high enough to oxidize $\text{Co}^{\text{II}}\text{L}$ to $\text{Co}^{\text{III}}\text{L}$ we do not think that these reactions can follow the outer sphere mechanism. According to the latter mechanism the primary products would be CH_3^- or $^-\text{CH}_2\text{OH}$ and the redox potential of the couples $\cdot\text{CH}_3/\text{CH}_3^-$ and $\cdot\text{CH}_2\text{OH}/^-\text{CH}_2\text{OH}$ is too low to oxidize $\text{Co}^{\text{II}}\text{L}$.^{19c,d} This conclusion is in disparity with the suggestion that $\cdot\text{CH}_3$ oxidizes $\text{Co}^{\text{II}}\text{L}$ also via the outer sphere mechanism.^{2a} To our knowledge no evidence for the existence of CH_4^+ or $^+\text{CH}_3\text{OH}$, which might oxidize $\text{Co}^{\text{II}}\text{L}$ via the outer sphere mechanism in aqueous media, exists. According to alternative 2, the radical reduces, via the outer sphere mechanism, the $\text{Co}^{\text{II}}\text{L}$ complex. This mechanism would explain the formation of aldehydes but not the formation of long-lived unstable intermediates in neutral solutions as the reaction:

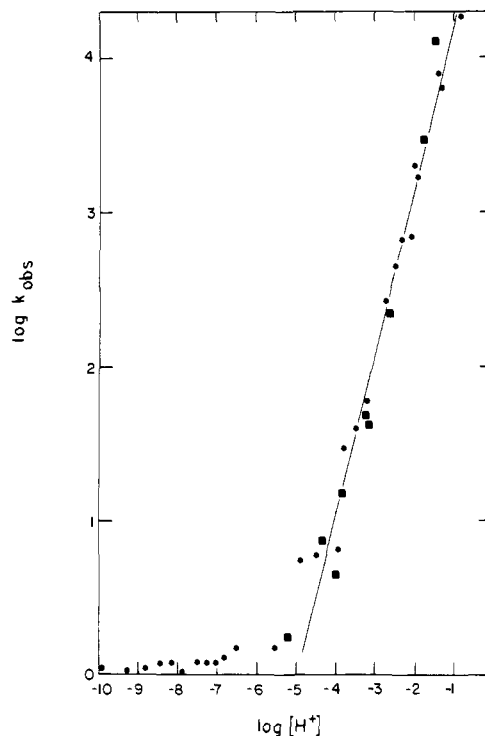
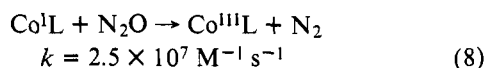


Figure 8. pH dependence of the rate of the last decomposition reaction, see text; observed in N_2O -saturated solutions containing $5 \times 10^{-4} \text{ M}$ $\text{Co}^{\text{II}}\text{L}$; dose per pulse 500 rd: (●) 1 M $(\text{CH}_2\text{OH})_2$; (▲) 0.01 M 2-bromoethanol.

yields stable products. According to alternative 3 the radical adds to the double bond and in principle two possibilities exist: (a) addition to the carbon end of the double bond and it is difficult to conceive a mechanism which would yield aldehydes from this intermediate; (b) addition to the nitrogen end of the double bond, a mechanism which would end in the formation of aldehydes. However, it is difficult to envisage reasons why the properties of the radical formed via this mechanism depend so strongly on R_1 as observed. Finally, according to alternative 4, a σ cobalt-carbon bond is formed. The detailed mechanisms of formation of the aldehydes and the mechanisms of reactions observed are discussed later in detail. The suggestion that the product of reaction of the free radicals studied, $\cdot\text{RH}$, with $\text{Co}^{\text{II}}\text{L}$ is $\text{Co}^{\text{III}}\text{L}-\text{RH}$ is in agreement with expectation.¹ Furthermore, the spectral features of $\text{Co}^{\text{III}}\text{L}-\text{CH}_2\text{OH}$ resemble those of $\text{Co}^{\text{III}}\text{L}-\text{CH}_3$.^{2a} The spectra of all the other intermediates studied consist also of a band at 370–400 nm. However, the second band at longer wavelength is less pronounced for the other intermediates.

It is of interest to compare the rates of reaction of the different free radicals with $\text{Co}^{\text{II}}\text{L}$, Table III. The order of reactivity is $\cdot\text{CH}_3 > \cdot\text{CH}_2\text{CHO} > \cdot\text{CH}_2\text{OH} > \text{CH}_3\dot{\text{C}}\text{HOH} > \cdot\text{CHOHCH}_2\text{OH} > \text{CF}_3\dot{\text{C}}\text{HOH} > (\text{CH}_3)_2\dot{\text{C}}\text{OH}$, $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$, $\cdot\text{CH}_2\text{CO}_2^-$. It thus seems that both electron-withdrawing groups, compare $\cdot\text{CH}_3$ with $\cdot\text{CH}_2\text{CHO}$, and electron-donating groups, compare $\cdot\text{CH}_2\text{OH}$ with $\text{CH}_3\dot{\text{C}}\text{HOH}$, slow down this reaction. These observations can be explained if the governing factor is steric hindrance to the formation of the carbon-cobalt bond, which is expected to be large mainly if its formation involves a seven-coordinated intermediate.¹³ The observation that the rate of the reaction $\text{Co}^{\text{II}}\text{L} + \cdot\text{CH}_2\text{CO}_2^-$ is low may be due to the fact that the acetate ions in these solutions, $[\text{CH}_3\text{CO}_2^-] = 0.5 \text{ M}$, are expected to complex the $\text{Co}^{\text{II}}\text{L}$.

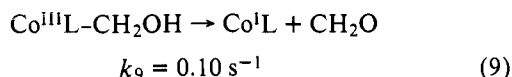
Mechanism of Decomposition of $\text{Co}^{\text{III}}\text{L}-\text{CH}_2\text{OH}$. The decomposition reaction of $\text{Co}^{\text{III}}\text{L}-\text{CH}_2\text{OH}$ in neutral solution obeys a first-order rate law. The products of reaction are

Table III. Reactions of Co^{III}L with Aliphatic Free Radicals

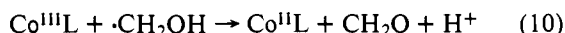
reaction	<i>k</i>
CH ₃ + Co ^{III} L → Co ^{III} L-CH ₃	7 × 10 ⁸ M ⁻¹ s ⁻¹ ^a 1-2 × 10 ⁸ M ⁻¹ s ⁻¹ ^b
·CH ₂ OH + Co ^{III} L → Co ^{III} L-CH ₂ OH	7 × 10 ⁷ M ⁻¹ s ⁻¹
CH ₃ ·CHOH + Co ^{III} L → Co ^{III} L-CH(CH ₃)OH	3 × 10 ⁷ M ⁻¹ s ⁻¹
CF ₃ ·CHOH + Co ^{III} L → Co ^{III} L-CH(CF ₃)OH	~1 × 10 ⁷ M ⁻¹ s ⁻¹
·CH ₂ CHO + Co ^{III} L → Co ^{III} L-CH ₂ CHO	8 × 10 ⁷ M ⁻¹ s ⁻¹
HOCHCH ₂ OH + Co ^{III} L → Co ^{III} L-CH(OH)CH ₂ OH	~1 × 10 ⁷ M ⁻¹ s ⁻¹
(CH ₃) ₂ COH + Co ^{III} L → products ^c	<1 × 10 ⁷ M ⁻¹ s ⁻¹
·CH ₂ CO ₂ ⁻ + Co ^{III} L → products ^c	<1 × 10 ⁷ M ⁻¹ s ⁻¹
·CH ₂ C(CH ₃) ₂ OH + Co ^{III} L → products ^c	<1 × 10 ⁷ M ⁻¹ s ⁻¹
Co ^{III} L-CH ₂ OH → Co ^I L + CH ₂ O + H ₃ O ⁺	0.1 s ⁻¹
Co ^{III} L-CH(CH ₃)OH → products ^d	1 × 10 ² s ⁻¹ (at pH 7) ~2 × 10 ³ s ⁻¹ (at pH 1)
Co ^{III} L-CH(OH)CH ₂ OH → Co ^{III} L-CH ₂ CHO + H ₂ O	4 s ⁻¹ (at pH 5.0) 15 s ⁻¹ (at pH 3.5)
Co ^{III} L-CH ₂ CHO $\xrightarrow{H^+}$ Co ^I L + CH ₃ CHO	1.3 + 1.5 × 10 ⁵ [H ₃ O ⁺] s ⁻¹
Co ^{III} L-CH(CF ₃)OH → products (probably Co ^I L + CF ₃ CHO)	6 × 10 ⁻² s ⁻¹

^a From ref 2. ^b From ref 4. ^c No reaction observed. ^d First decomposition reaction observed; as to plausible mechanism see Discussion.

CH₂O, *G*(CH₂O) = 6.0, and Co^{III}L as can be deduced from the spectrum of the final products (Table II). These results can be explained by the sequence:

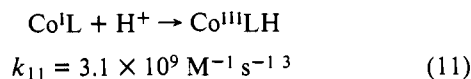


followed by reaction 8. The observation that the yield of Co^{III}L is not linear with dose seems to be due to the competition between reactions 6 and 10:



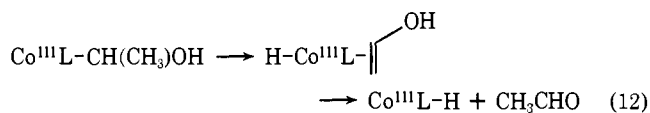
The parallel reaction Co^{III}L + (CH₃)₂COH has a rate of 1.1 × 10⁸ M⁻¹ s⁻¹ at pH 6.0.⁴

The rate of decomposition of Co^{III}L-CH₂OH in acid solutions, pH 1.0 and 2.0, is identical with that observed in neutral solutions. However, the spectral data indicate that though Co^{II}L is destroyed the product differs from Co^{III}L (Table I). It is suggested that in this case reaction 9 is followed by:



The maximum observed at 255 nm could be due to Co^{III}LH or its reaction products with other constituents of the solution in the steady-state radiolysis experiment.

Mechanism of Decomposition of Co^{III}L-CH(CH₃)OH. In neutral solutions the decomposition of Co^{III}L-CH(CH₃)OH obeys a first-order rate law with *k* = (1 ± 0.3) × 10² s⁻¹ at pH 7.0. This rate is three orders of magnitude higher than that observed for Co^{III}L-CH₂OH. The difference in the rates could be explained by the electron-donating properties of the CH₃ group which makes the CH₃·CHOH radical a stronger reducing agent than ·CH₂OH. However, the spectrum of the product formed in this reaction, Figure 2, differs considerably from that of Co^{III}L or the final products observed in this system after longer times (Table II). We suggest therefore that the reaction occurring in this case is most probably:

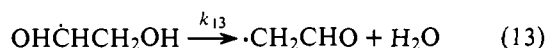


Reaction 12 represents a hydride transfer from a β-carbon to a metal, a reaction which is well known in aprotic solvents, and was recently also demonstrated in water.²⁰ Reaction 12 cannot occur naturally in Co^{III}L-CH₂OH or Co^{III}L-CH(CF₃)OH and indeed the decomposition rates of the latter two complexes are similar. The Co^{III}L-H complex or any other product of reaction 12, if the suggested mechanism is wrong, seems to be unstable as the spectrum after several minutes, Table II, indicates that Co^{III}L is formed.

The rate of the reaction CH₃·CHOH + Co^{III}L is nearly pH independent in the range 1.0 < pH < 7.0. Thus, we conclude that the same primary product is formed in this reaction over this pH range. The different spectra of the products at pH 6.2 and 2.1, Figures 2 and 3, are attributed to a *pK* of the trans-axial water molecule ligand, which is expected in this pH range for a Co^{III}L complex. The pH dependence of the rate of decomposition of Co^{III}L-CH(CH₃)OH, *k*₂ in Figure 4, indicates an apparent *pK* around pH 3.5. In acidic solutions a third reaction, *k*₃ in Figure 4, was observed in this system with a rate proportional to [H⁺]⁻¹. The latter reaction seems to be due to a reaction of Co^{III}L-H in this system. However, the spectrum of the final products after a higher dose irradiation in the γ source indicated (Table I) no major change in the Co^{II}L complex. This result can be rationalized by assuming that the CH₃·CHOH radicals reduce the Co^{III}L or the other products back to Co^{II}L. The latter reaction is expected to be more efficient in the ethanol system than in the methanol system as CH₃·CHOH radicals react slower with Co^{II}L than ·CH₂OH radicals and are stronger reducing agents.^{19b} We could not study therefore the nature of the decomposition reactions of Co^{III}L-CH(CH₃)OH in acid media in detail.

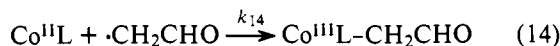
Reactions Observed in the Co^{II}L-Ethylene Glycol System.

When N₂O-saturated solutions containing ethylene glycol are irradiated the radical OH·CHCH₂OH is formed. This radical is known to lose water:^{13,21}



The latter reaction is acid and base catalyzed and its mechanism was reported in detail.²¹

The pH dependence of the rate of formation of the first intermediate in the Co^{II}L + ethylene glycol system is explained as follows. In acid solutions, pH < 3, and alkaline solutions the reaction observed is:

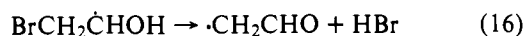


whereas in the pH range 3-7 the reaction occurring is:



From the pH dependence of the rate of reaction, *k*₁₃ can be estimated, assuming that *k*₁₄ is pH independent, and good agreement with the results of Bansal et al.^{21b} is obtained. The observation that *k*₁₄ > *k*₁₅ is in agreement with the rates of reactions of these radicals with B-12r.⁵

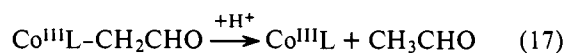
Solutions containing 2-bromoethanol instead of ethylene glycol were irradiated. In these solutions the radical BrCH₂·CHOH is formed.¹⁷ It was hoped that the reaction:



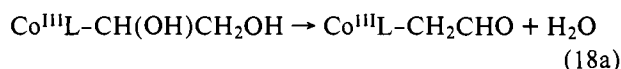
which is expected to be faster than reaction 13 will compete with *k*₁₅ at higher pHs so that the pH dependence will be

changed. However, only a slight change in reactivity with pH over the whole pH range was found in this system. We conclude that $k_{16} > k_{15}[\text{Co}^{\text{III}}\text{L}]$ in the pH range studied.

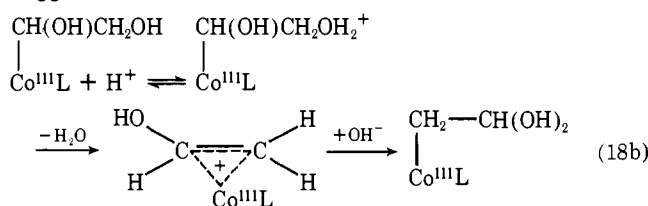
The mechanism of decomposition of $\text{Co}^{\text{III}}\text{L}-\text{CH}_2\text{CHO}$ involves one acid-catalyzed first-order process:



with $k_{17} = (1.3 \pm 0.3) + (1.5 \pm 0.1) \times 10^5 [\text{H}_3\text{O}^+] \text{ s}^{-1}$ independent of the source of $\cdot\text{CH}_2\text{CHO}$, reaction 13 or 17 (Figure 8). The observation that reaction 17 is acid catalyzed is in full agreement with the parallel reaction observed for B-12- CH_2CHO .^{8c,f} Of special interest is the observation that the rate law for the second decomposition reaction of $\text{Co}^{\text{III}}\text{L}-\text{CH}(\text{OH})\text{CH}_2\text{OH}$ obeys exactly the same rate law (Figure 8). We have thus to conclude that the first reaction observed after the formation of $\text{Co}^{\text{III}}\text{L}-\text{CH}(\text{OH})\text{CH}_2\text{OH}$, at $3 < \text{pH} < 7$, is:



Reaction 18 is acid catalyzed; k_{18} increases from 4 s^{-1} at pH 5.0 to 15 s^{-1} at pH 3.5. This observation is in accord with the suggested mechanism:^{1c,d,8}



The observation of reaction 18 is the first direct observation of the rearrangement of ethylene glycol to acetaldehyde while it is covalently bound to a $\text{Co}^{\text{III}}\text{L}$ complex. The results thus describe a model reaction for the action of the diol dehydratase enzyme and indicate that this reaction can be initiated at least in a model system by a free-radical mechanism. Our results demonstrate that in neutral solution the rearrangement in this model system does not proceed via the free-radical, carbanion, or carbonium mechanisms.^{1d}

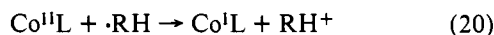
The spectral changes observed after a prolonged irradiation in the γ source, Table II, indicate that: (a) $\text{Co}^{\text{III}}\text{L}$ is formed with a high yield in the acidic solutions. This finding is reasonable as $\cdot\text{CH}_2\text{CHO}$ radicals react fast with $\text{Co}^{\text{II}}\text{L}$ and are not expected to reduce $\text{Co}^{\text{III}}\text{L}$.¹⁹ (b) The yield of $\text{Co}^{\text{III}}\text{L}$ in neutral solutions is low, a reasonable observation as $\text{HO}\cdot\text{CHCH}_2\text{OH}$ radicals react slowly with $\text{Co}^{\text{II}}\text{L}$ and are expected to reduce $\text{Co}^{\text{III}}\text{L}$.¹⁹ (c) The results in alkaline media indicate that a product different from $\text{Co}^{\text{III}}\text{L}$ is formed. We did not succeed in determining the nature of this product.

Concluding Remarks

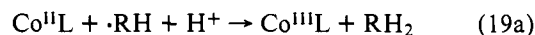
The reactions of several aliphatic free radicals with $\text{Co}^{\text{II}}\text{L}$ were studied. All these reactions involve the formation of an unstable intermediate, $\text{Co}^{\text{III}}\text{L}-\text{RH}$, containing a σ carbon-cobalt bond. This observation was not unexpected as the outer sphere redox reactions:



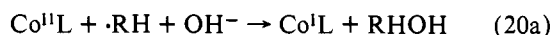
or



are expected to be endothermic,^{19d} although the reactions:

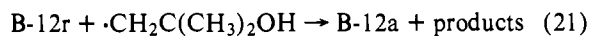


or

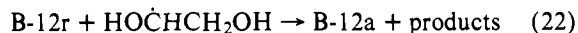


are exothermic.^{19d} It is thus expected that an intermediate in which the free radical is bound to the $\text{Co}^{\text{II}}\text{L}$ complex should be formed in all these reactions. The lifetime of this intermediate depends on its nature and might be extremely short.

It is thus suggested that the reactions



and



reported by Blackburn et al.⁵ are not simple oxidation processes as suggested by them but involve the formation of pseudoenzymes. Their arguments that the products are B-12a are based mainly on the shape of the spectral bands of the products in the near-UV and visible range. However, the spectra of the pseudoenzymes with the corresponding radicals are unknown and our data, Figures 1-4, suggest that the spectra of $\text{Co}^{\text{III}}\text{L}-\text{RH}$ depend strongly on the nature of $-\text{RH}$ and on pH.

The question whether the product of reaction 22⁵ was B-12- $\text{CH}(\text{OH})\text{CH}_2\text{OH}$ or B-12- CH_2CHO is difficult to answer. Two possibilities exist: (a) that the rearrangement reaction parallel to reaction 18 is much faster in the case of the coenzyme and thus reaction 22 is rate determining in the formation of B-12- CH_2CHO ; (b) the rearrangement reaction is slow also for B-12- $\text{CH}(\text{OH})\text{CH}_2\text{OH}$ and was thus not observed within the $500 \mu\text{s}$ during which spectroscopic observation could be carried out under the experimental conditions.⁵

It is of interest to note that the complexes $\text{Co}^{\text{III}}\text{L}-\text{CH}_2\text{OH}$, $\text{Co}^{\text{III}}\text{L}-\text{CH}(\text{OH})\text{CH}_3$, $\text{Co}^{\text{III}}\text{L}-\text{CH}(\text{OH})\text{CH}_2\text{OH}$, and $\text{Co}^{\text{III}}\text{L}-\text{CH}_2\text{CHO}$ seem to decompose via four different mechanisms. Thus, the results implicate that the mechanism of decomposition of carbon-cobalt bonds depends strongly on the nature of the aliphatic residue, $-\text{RH}$, in $\text{Co}^{\text{III}}\text{L}-\text{RH}$. Furthermore, it is reasonable that although $\text{Co}^{\text{III}}\text{L}-\text{CH}_2\text{CHO}$ is the major product formed from $\text{Co}^{\text{III}}\text{L}-\text{CH}(\text{OH})\text{CH}_2\text{OH}$, also some $\text{Co}^{\text{I}}\text{L} + \text{CH}_2\text{OHCHO}$ is formed. The formation of some B-12s via the latter mechanism might explain the partial inactivation of diol dehydratase and ethanolamine-ammonia lyase by N_2O .^{10b}

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