

It is worthwhile noting that, owing to the relative magnitudes of  $k_6$ ,  $k_7$ , and  $k_8$ ,<sup>17</sup> in our experimental conditions the order of magnitude of the quantum yield for the photosubstitution reaction is principally determined by the geminate recombination process. We would like to point out that processes of this kind could be of primary importance in other photoreactions of Pt(II) complexes, although in many cases they cannot be experimentally distinguished from the photophysical deactivation processes.

Of course, the question concerning the intimate mechanism of the primary photochemical process (eq 5) is still an unsolved problem. In fact, the formation of  $\text{Pt}(\text{dien})^{2+} \cdot \text{Br}^-$  (mechanism IIa) certainly involves a dissociative photochemical process, but the formation

(17) Note that  $k_6$  and  $k_7$  are second-order rate constants, while  $k_8$  is first order.

of  $\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+} \cdot \text{Br}^-$  (mechanism IIb) could follow either dissociative or associative paths. In this last case, however, since it is known that in the thermal substitution reactions (which follow mainly associative-type mechanisms)  $\text{Br}^-$  and  $\text{NO}_2^-$  are much better entering ligands than  $\text{H}_2\text{O}$ , one should expect that a direct  $\text{NO}_2^-$  photosubstitution would also occur. Such a possibility, however, has already been ruled out in the discussion of mechanism I. Therefore, the experimental evidence seems to suggest that the primary chemical reaction proceeds by an essentially dissociative mechanism.

**Acknowledgment.** The authors are indebted to Professor V. Carassiti for his interest in this work and for his helpful criticism, and to Professor A. Indelli for his helpful discussions.

## Induced Electron Transfer. The Action of One-Electron Oxidants on Pyridinemethanolpentaamminecobalt(III) Complexes

James E. French and Henry Taube

*Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received March 27, 1969*

**Abstract:** The direct,  $\text{Ag}^+$ - and  $\text{Co}^{2+}$ -catalyzed oxidations by Ce(IV) of pentaammine(4-pyridinemethanol)cobalt(III) (A) or pentaammine(3-pyridinemethanol)cobalt(III) (B) yield both the aldehyde complexes of Co(III) and  $[\text{Co}^{2+} + \text{free aldehyde}]$ , the ratio of Co(III)-CHO/Co(II) in the products increasing with the concentration of the oxidizing agent. These observations, together with the fact that the rate of consumption of A or B is strictly first order in the concentration of the external oxidizing agent, show that an oxidized intermediate is produced in each system by the external oxidant. The kinetic isotope effects obtained for the  $\text{CD}_2\text{OH}$  derivative of A ( $k_{\text{H}}/k_{\text{D}} = 2.7 \pm 0.2$  and  $2.2 \pm 0.2$  for the Ce(IV) and  $\text{Co}^{3+}$  oxidations in 4 M  $\text{HClO}_4$ , respectively) indicate that the rate-determining step involves attack on the alcohol function. A detailed examination of the product ratio as a function of the concentration of external oxidant shows that, in fact, two intermediates are formed which differ in the rate of internal reduction yielding Co(II), relative to reaction with external oxidant yielding Co(III)-CHO (rate ratio  $k_{\text{R}}/k_{\text{T}}$ ). The ratio  $k_{\text{R}}/k_{\text{T}}$  is observed to be significantly greater for the radicals derived from A than for the radicals derived from B, showing that internal electron transfer is more facile from the 4 than from the 3 position. For A, the ratio in which the intermediates are formed varies as the oxidizing agent is changed; this observation suggests that the intermediates are generated by parallel processes. The rates of oxidation by Ce(IV) of A and B and the free but protonated ligands are similar, as are the kinetic isotope effects observed for the  $-\text{CD}_2\text{OH}$  derivative of A and the analogous protonated free ligand, supporting the view that the Co(III) center of the complex does not assist the external oxidant, and the conclusion that radical intermediates of finite lifetime are generated in the rate-determining step of the reaction.

Several investigations<sup>1,2</sup> have shown that when a ligand L in a complex of the type  $(\text{NH}_3)_5\text{Co}^{\text{III}}\text{-L}$  is oxidized by an external one-electron oxidizing agent, the Co(III) center may be reduced. These reactions are of particular interest when the ligand L has an oxidizable group located at some distance from the atom coordinated to Co(III). If radical intermediates are formed, electron transfer can be induced from various remote positions, and if internal reduction of the cobalt center competes with further reaction of the radical with external oxidant, a measure of the rate of internal reduction from different positions can be obtained.

(1) P. Saffir and H. Taube, *J. Amer. Chem. Soc.*, **82**, 13 (1960); R. T. M. Fraser and H. Taube, *ibid.*, **82**, 4152 (1960); J. P. Candlin and J. Halpern, *ibid.*, **85**, 2518 (1963).

(2) R. Robson and H. Taube, *ibid.*, **89**, 6487 (1967).

The investigation by Robson and Taube<sup>2</sup> of the reaction between 4-hydroxymethylbenzoatopentaamminecobalt(III) and one-electron oxidizing agents raised an interesting but incompletely resolved issue. Their evidence showed that the oxidation of this complex by Ce(IV) produces two radical intermediates, one which is not trapped even at high concentrations of Ce(IV) or oxygen, and one which is trapped by both Ce(IV) and oxygen. However, the identity of the two radical intermediates remained obscure.

The present investigation of the reaction of pentaammine(pyridinemethanol)cobalt(III) complexes with various oxidants was initiated in an attempt to study the mechanism of the oxidation processes, particularly the nature of the radical intermediates produced and the relative rate of internal electron transfer from different

positions in the ligand. In addition, it was hoped that some of the questions raised by Robson's work could be resolved and the behavior of the two types of ligands contrasted.

## Experimental Section

**Reagents.** Cerium(IV) perchlorate solutions were obtained from stock supplied by G. F. Smith and Co. (ca. 0.5 M Ce(IV) in 6 M HClO<sub>4</sub>). The Ce(IV) content of the stock solution was determined as described by Smith,<sup>3</sup> the total Ce content as described by Medalia and Byrne,<sup>4</sup> and the acidity as described by Baker, *et al.*<sup>5</sup> The Ce(IV) content of diluted solutions was determined spectrophotometrically in 1 M H<sub>2</sub>SO<sub>4</sub>, using the extinction coefficients measured by Robson<sup>2</sup> and Medalia and Byrne.<sup>4</sup>

**Cerium(III) perchlorate** solutions were obtained from recrystallized reagent grade G. F. Smith cerous perchlorate, and were standardized as described by Medalia and Byrne.<sup>4</sup> A second solution containing cerous ion (supplied by Dr. D. P. Rudd) was prepared by reducing reagent grade ceric ammonium sulfate with 30% hydrogen peroxide, precipitating cerous carbonate with sodium carbonate, rinsing with water, and dissolving the dried salt in perchloric acid.

**Cobalt(III) perchlorate** solutions were obtained by adding a solution of triscarbonatocobalt(III)<sup>6</sup> to a known excess of perchloric acid. The Co(III) content of these solutions was determined by adding aliquots to standardized Fe<sup>2+</sup> solution and back-titrating with dichromate.

**Cobalt(II) perchlorate** solutions were prepared from G. F. Smith cobaltous perchlorate, which was twice recrystallized from water, and were standardized as described by Kitson.<sup>7</sup>

**Silver(I) perchlorate** solutions were prepared by dissolving reagent grade Ag<sub>2</sub>CO<sub>3</sub> in known amounts of perchloric acid and filtering and diluting to volume. The solutions were analyzed gravimetrically for Ag and, after removing silver ion with excess NaCl, were analyzed for acid by titration with standardized NaOH. Solutions were stored in blackened flasks.

**Silver(II) perchlorate** solutions were prepared from standardized Ag(I) solutions by treating a solution, protected from light and cooled in ice, with ozone. When reaction appeared complete, the solution was purged of ozone with oxygen, purged of oxygen with nitrogen, and used promptly.

**Lithium Perchlorate Solutions.** A concentrated lithium perchlorate stock solution was obtained from Alfa Inorganics LiClO<sub>4</sub>, which had been twice recrystallized from water. The solution was standardized by analyzing for perchlorate.<sup>8</sup>

**Perchloric Acid Solutions.** Stock solutions of perchloric acid for use in stoichiometric and kinetic experiments were obtained from reagent grade 70% perchloric acid which had been purified of traces of chloride ion by adding a slight excess of either ceric perchlorate or cobaltic perchlorate, purging vigorously with nitrogen to remove chlorine, and allowing excess oxidant to be destroyed by the slow oxidation of water. The solutions were standardized by titration with sodium hydroxide.

**4-Pyridinemethanyl Acetate.** Aldrich 4-pyridinemethanol was recrystallized from benzene, heated with an equimolar amount of acetic anhydride on a steam bath for 4 hr, and vacuum distilled through an insulated Vigreux column.

**4-Pyridinemethanyl-*d*<sub>2</sub>-Acetate.** Recrystallized 4-pyridinemethanol was refluxed in 1 M NaOD in 99.7% D<sub>2</sub>O for 10 days. Most of the spent D<sub>2</sub>O was removed by distillation, the ligand was extracted from the remaining material with hot benzene, and the benzene was removed on a rotary evaporator. After repeating this process twice, the ligand was found by nmr to be 95% deuterated. Treatment with acetic anhydride yielded the deuterated ester.

**3-Pyridinemethanol.** The Baker product was dried over molecular sieve and used without further purification.

**Pentaammine(4-pyridinemethanol)cobalt(III) Perchlorate.** Sulfonane (Aldrich) was dried over NaOH and vacuum distilled. Azidopentaamminecobalt(III) perchlorate<sup>9</sup> (10 g) was dissolved in 50

ml of sulfolane in a 250-ml flask topped with a CaSO<sub>4</sub> drying tube and containing approximately 1 g of molecular sieve. Nitrosyl perchlorate<sup>10</sup> was added slowly, with stirring, until the purple solution turned pink and vigorous gas evolution ceased.<sup>11</sup>

The solution was stirred for approximately 30 min to allow excess nitrosyl perchlorate to react, and 30 ml of 4-pyridinemethanolacetate was added. The solution was heated gently at 30–40° for 3 hr, kept overnight at room temperature, and extracted several times with an excess of ether. The ether extracts were discarded and the remaining oil was dissolved in methanol and filtered from molecular sieve. The methanol was evaporated, the remaining material dissolved in approximately 40 ml of 6 M HClO<sub>4</sub>, and the solution heated at 90–100° for 1 hr to reduce the volume to 40 ml. After remaining overnight at room temperature, the solution was cooled in ice; the fine precipitate was filtered, rinsed with ethanol and ether, sucked dry, redissolved in methanol, and filtered to remove the small residue of aquopentaamminecobalt(III) perchlorate. Slow evaporation of the methanol solution yielded crystals which were separated by filtration, rinsed with ethanol and ether, and dried in a vacuum desiccator. The absorption spectrum of this salt shows maxima at 475 mμ (ε 67.0) and 340 mμ (ε 55.5). *Anal.* Calcd for [(NH<sub>3</sub>)<sub>5</sub>CoNC<sub>4</sub>H<sub>4</sub>CH<sub>2</sub>OH](ClO<sub>4</sub>)<sub>3</sub>: C, 13.1; H, 4.02; Cl, 19.3; Co, 10.7; N, 15.2. Found: C, 13.1; H, 3.9; Cl, 19.1; Co, 10.7; N, 15.3.

**Pentaammine(4-pyridine-*d*<sub>2</sub>-methanol)cobalt(III) perchlorate** was prepared as above. Analysis by nmr showed deuteration to be 95% complete. *Anal.* Calcd for [(NH<sub>3</sub>)<sub>5</sub>CoNC<sub>4</sub>H<sub>4</sub>CD<sub>2</sub>OH](ClO<sub>4</sub>)<sub>3</sub>: C, 13.0; H, 4.00; Cl 19.2; N, 15.2. Found: C, 12.5; H, 3.96; Cl, 19.2; N, 15.1.

**Pentaammine(3-pyridinemethanol)cobalt(III) Perchlorate.** The method used in complexing the 3-CH<sub>2</sub>OH ligand was similar to that described for the 4-CH<sub>2</sub>OH ligand. Esterification of the alcohol was not necessary for this isomer. The complex proved to be extremely soluble and was purified by cation exchange on silica gel.<sup>12</sup> Davison Grade 950 (60–200 mesh) silica gel was treated with several volumes of water, filtered, and rinsed copiously with water until eluent was at pH 9. The resin was stirred into a column plugged with glass wool and allowed to settle. The complex was dissolved in 0.1 M NaHCO<sub>3</sub>, and the solution was passed through the column, which was thereupon rinsed with 1 M NaHCO<sub>3</sub> until all of the pink hydroxopentaamminecobalt(III) was eluted and then rinsed with several portions of water. The complex was eluted with a minimum volume of 4 M HClO<sub>4</sub>; the eluent was filtered, evaporated in a rotary evaporator until crystals began to form, and then cooled in ice; and the product was filtered, rinsed with ethanol and ether, sucked dry, and further dried under vacuum over CaSO<sub>4</sub>. The solid contained a small amount of SiO<sub>2</sub> and was dissolved in 10<sup>-4</sup> M HClO<sub>4</sub>, filtered through an extremely fine porosity filter, and stored as a solution. It should be pointed out that solutions of the pyridine complexes are indefinitely stable to aqutation at room temperature in acidic solutions.

The absorption spectra of the complex shows maxima at 475 mμ (ε 60.0) and 338 mμ (ε 52.3). *Anal.* Calcd for [(NH<sub>3</sub>)<sub>5</sub>CoNC<sub>3</sub>H<sub>4</sub>CH<sub>2</sub>OH](ClO<sub>4</sub>)<sub>3</sub>: C:H:N:Co:Cl, 1.00:3.66:1.00:0.167:0.50. Found: 1.00:3.54:0.96:0.162:0.48.

**Determination of Ce(IV).** Ce(IV) was determined by diluting aliquots of test solutions 50- to 100-fold in 1 M H<sub>2</sub>SO<sub>4</sub>. No appreciable reaction occurs after dilution. Adherence to Beer's law in this medium has been demonstrated by Robson.<sup>2</sup> In kinetic runs, the Ce(IV) content was redetermined before reaction by its absorption at 400 mμ, using the extinction coefficients of Hardwick and Robertson<sup>13</sup> in 1 M HClO<sub>4</sub>, and using for Ce(IV), over the range from 1 × 10<sup>-2</sup> to 1 × 10<sup>-3</sup> M in 4 M HClO<sub>4</sub>, ε<sub>400</sub> 123 ± 1, as determined in the present investigation.

**Determination of Co<sup>3+</sup>(aq) and Ag(II).** The stoichiometry of the rapid reactions involving these oxidants was determined after reaction was complete and all oxidant destroyed. Initial concentrations of oxidant were determined by adding aliquots to Fe(II) and back-titrating with Cr(VI), or spectrophotometrically by using

(9) R. B. Jordan, A. M. Sargeson, and H. Taube, *ibid.*, 5, 1091 (1966).

(10) G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. I, Academic Press, New York, N. Y., 1963, p 320.

(11) Although no difficulty was encountered in our investigations, violent reactions have been reported upon adding NOClO<sub>4</sub> to organic solvents and the preparation should be done with caution.

(12) R. L. Burwell, R. G. Pearson, G. L. Haller, P. B. Tjok, and S. P. Chock, *Inorg. Chem.*, 4, 1123 (1965).

(13) T. J. Hardwick and R. Robertson, *Can. J. Chem.*, 29, 818 (1951).

(3) G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, 10, 304 (1938).

(4) A. I. Medalia and B. J. Byrne, *Anal. Chem.*, 23, 453 (1951).

(5) F. B. Baker, T. W. Newton, and M. Khan, *J. Phys. Chem.*, 64, 109 (1960).

(6) N. Hofman-Bang, *Acta Chem. Scand.*, 9, 1230 (1955).

(7) R. E. Kitson, *Anal. Chem.*, 22, 664 (1950).

(8) E. A. Deutsch and H. Taube, *Inorg. Chem.*, 7, 1532 (1968).

the following extinction coefficients: for  $\text{Co}^{3+}(\text{aq})$ ,  $\epsilon_{605}$  37.0, and for  $\text{Ag}(\text{II})$ ,  $\epsilon_{475}$  140 (4  $M$   $\text{HClO}_4$ ).<sup>14</sup>

**Determination of Co(II).** If no excess oxidant was present, an appropriate amount of test solution was added and the acidity adjusted with acid or base so that the final solution would be approximately 0.4  $M$  in  $\text{HClO}_4$ . Acetone (25.0 ml) and 50% aqueous  $\text{NH}_4\text{SCN}$  (2.5 ml) were added, the solution was brought to 25° and diluted to 50 ml, and the absorbance at 625  $m\mu$  was measured.

The Co(II) present was calculated using the molar extinction coefficient of 1693, as determined in blank experiments, making slight corrections for Cr(III) if present and for the Co(III) complexes if present in large excess.

In the presence of excess oxidant 0.5  $M$  ferrous ion was added, 1–5 ml of the quenched solution diluted to 25.0 ml with concentrated  $\text{HCl}$ , and the optical density measured at 695  $m\mu$ . Internal standards were run to determine the extinction coefficient of Co(II). Absorption by Fe(III), even in large excess, does not interfere at 695  $m\mu$ , and Fe(II) does not detectably reduce the bound aldehyde complex if solutions are diluted with  $\text{HCl}$  soon after quenching.

When Ag(I) was present in the test solutions, it was removed by adding slight excess of a saturated solution of  $\text{NaCl}$ , digesting the  $\text{AgCl}$  at room temperature, and filtering. If Co(II) was introduced by the oxidant aquocobalt(III), the total cobalt introduced was determined by an analysis of the oxidant solution.

**Determination of Pentaamminecobalt(III)-Pyridinecarboxaldehydes.** Gould's experiments<sup>15</sup> showed that 3- and 4-ketopyridine complexes of pentaamminecobalt(III) are rapidly reduced by  $\text{Cr}^{2+}$  with second-order rate constants of  $10^2$ – $10^3 M^{-1} \text{sec}^{-1}$ . Since the alcohol complexes are reduced only slowly by chromous ion ( $\sim 10^{-2} M^{-1} \text{sec}^{-1}$ ), the difference in reducibility was made the basis of an analytical determination for the 3- and 4-pyridinecarboxaldehyde complexes. Experiments on the carboxaldehyde complexes verified that  $\text{Cr}^{2+}$  reduced them rapidly ( $k > 100 M^{-1} \text{sec}^{-1}$ ), producing Co(II).

Test solutions containing Co(II), oxidant, free aldehyde, bound aldehyde, and unreacted alcohol complex were analyzed for "bound aldehyde" in the following way. Excess oxidant was destroyed by  $\text{Fe}^{2+}$  and then one aliquot was analyzed for Co(II); after degassing a second aliquot with  $\text{N}_2$ , a slight excess of chromous ion was added to it. After 5–10 sec, excess Cr(II) was destroyed by bubbling in air, or by adding Fe(III) when time was critical. Co(II) was analyzed by Kitson's method with appropriate corrections for Cr(III) absorption at 625  $m\mu$ , or by addition of concentrated  $\text{HCl}$  if the solutions contained iron. The absorption due to Cr(III) in concentrated  $\text{HCl}$  was determined by adding an aliquot of the test solution to concentrated  $\text{HClO}_4$  instead of  $\text{HCl}$ , and measuring the optical density.

**Spectrophotometric Measurement of the Stoichiometry and Kinetics of Reactions. Techniques.** Spectrophotometric measurements in the visible and ultraviolet regions were made on a Cary Model 14 recording instrument. Temperatures in the thermostated cell compartment were maintained to within 0.2° of those stated. To remove oxygen from reaction mixtures, oxygen syringe techniques were adopted. Serum caps were boiled in concentrated  $\text{NaOH}$  for several hours, rinsed, and stored under water until use. Stainless steel syringe needles were used for all transfers, but purging of strongly acidic solutions was done with platinum syringe needles. Experiments with added Fe(III) showed that trace amounts arising from needle corrosion do not influence the reactions.

A solution of one reactant was measured into a cell, purged with deoxygenated  $\text{N}_2$  for periods of not less than 30 min, and equilibrated at reaction temperature. A solution of the second reactant was similarly treated and thermostated at reaction temperature. A syringe was flushed with  $\text{N}_2$  and used to transfer reagent to the serum-capped cell to initiate reaction.

**Stoichiometric Measurements from Optical Data.** In addition to direct product analysis, the stoichiometry of the uncatalyzed and catalyzed oxidation of the pentaamminecobalt(III)-pyridinemethanol complexes by Ce(IV) was studied by monitoring the changes in optical density at two wavelengths as the reaction proceeded. This was accomplished by rapidly changing wavelengths at intervals and interpolating to obtain two measurements simultaneously.

Reactions were followed at 400 (predominantly Ce(IV) absorption) and at 475  $m\mu$  (predominantly absorption due to the Co(III)

complexes). By assuming that Beer's law holds for all components, that the total absorption is the sum of the absorptivities of the individual species, and that the Co(III) alcohol and aldehyde species have the same extinction coefficients at these wavelengths, eq 1 can be derived, where  $\Delta\text{OD}_{400} = (\text{OD}_0 - \text{OD}_t)_{400}$  and  $\epsilon_{\text{Co(III)}} = \epsilon_{\text{Co(III)-CH}_2\text{OH}} = \epsilon_{\text{Co(III)-CHO}}$ .

$$\frac{[\text{Ce(IV)}]_0 - [\text{Ce(IV)}]_t}{[\text{Co(II)}]_t} = \frac{\{[\epsilon_{\text{Co(III)475}} - \epsilon_{\text{Co(II)475}}](\Delta\text{OD}_{400}/\Delta\text{OD}_{475}) - (\epsilon_{\text{Co(III)400}} - \epsilon_{\text{Co(II)400}})\} / \{[\epsilon_{\text{Ce(IV)400}} - \epsilon_{\text{Ce(III)400}}] - (\epsilon_{\text{Ce(IV)475}} - \epsilon_{\text{Ce(III)475}})(\Delta\text{OD}_{400}/\Delta\text{OD}_{475})\}} \quad (1)$$

The alcohol and aldehyde complexes were shown to have similar extinction coefficients at each of the two wavelengths. Over the concentration range studied, deviations from Beer's law for Ce(IV) were usually minor, but the enhancement of Ce(IV) absorption by interaction with the alcohol function, often as high as 10–20%, necessitated slight corrections of the Ce(IV) extinction coefficients.

Thus, apparent extinction coefficients of Ce(IV) were obtained after addition of the alcohol complex by extrapolating to zero time, subtracting the contribution of the Co(III) species, and dividing the remaining absorbance by the Ce(IV) concentration. The stoichiometry of the reaction in the initial phase was determined by plotting  $\Delta\text{OD}_{400}$  vs.  $\Delta\text{OD}_{475}$ , and using the slope of the line at zero time in eq 1, along with the apparent extinction coefficients of Ce(IV) at zero time (the slope is a function of the various extinction coefficients as well as of the stoichiometric ratio).

**Kinetic Measurements from Optical Data.** Limitations of the spectrophotometric method made the use of large excesses of Ce(IV) or of alcohol complex in kinetic and stoichiometric runs unsuitable. All runs were thus done under second-order conditions. Rate constants were determined by one or more of the following three methods: (1) initial rate measurements. (2) If  $m[\text{Co(III)-CH}_2\text{OH}]_0 = [\text{Ce(IV)}]_0$ , where  $m$  = moles of Ce(IV) consumed/moles of complex oxidized, rate constants were plotted by using the stoichiometry determined optically, calculating the  $\text{OD}_\infty$  using this stoichiometry and known extinction coefficients, and following the disappearance of Ce(IV) at 400  $m\mu$ . From these data a plot of  $1/([\text{Ce(IV)}]_t + \Delta/2)$  vs. time, where  $\Delta = m[\text{Co(III)}]_0 - [\text{Ce(IV)}]_0$ , yields a second-order rate constant.<sup>16</sup> (3) If  $m[\text{Co(III)-CH}_2\text{OH}]_0 - [\text{Ce(IV)}]_0$  was large enough so that  $\ln([\text{Co(III)-CH}_2\text{OH}]/[\text{Ce(IV)}])$  changed sufficiently as a function of time, plots of this quantity were made to determine a second-order rate constant using the optical stoichiometry and concentration data.

Because of the limited sensitivity of the stoichiometry to oxidant concentration,  $m$  can be assumed constant, under most conditions, for one half-life. Second-order plots were linear for 30–75% reaction, deviations being due primarily to a secondary reaction, the oxidation of free aldehyde.

## Results

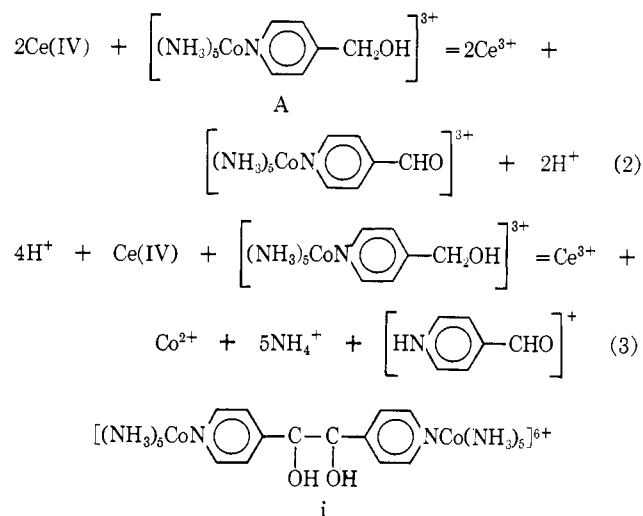
**General Features of the Reactions.** Analysis of the products yielded by the uncatalyzed Ce(IV) oxidation of the complexes showed that considerable amounts of Co(II), free aldehyde, and pentaamminepyridinecarboxaldehydes were produced under most conditions. Quantitative determination of Ce(IV) consumption, Co(II), and pentaamminepyridinecarboxaldehyde production as previously described and analysis for aldehydes by the method of Critchfield<sup>17</sup> are consistent with stoichiometry based on two net changes (eq 2 and 3), the ratio in which the two changes occur being dependent on conditions. Cation exchange of product mixtures yielded no evidence of highly charged species (i) such as might result from dimerization of radicals.

(14) D. H. Huchital, N. Sutin, and B. Warnquist, *Inorg. Chem.*, **6**, 838 (1967).

(15) E. S. Gould, *J. Amer. Chem. Soc.*, **89**, 5792 (1967).

(16) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 18–21.

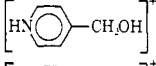
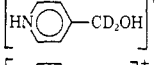
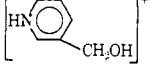
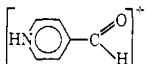
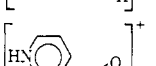
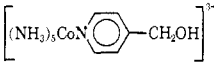
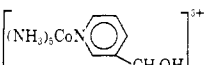
(17) F. Critchfield, "Organic Functional Group Analysis," The Macmillan Co., New York, N. Y., 1963, pp 78–79.



Carboxylic acids are produced in the latter stages of reaction through secondary oxidation of the aldehydes. However, these secondary reactions are slow enough, relative to the primary reaction, so that the primary reaction is essentially isolated during the initial stages of reaction.

In Table I, the rates of complex and ligand oxidation by Ce(IV) are reported. Kinetic measurements on the aldehyde complexes were not made because of our failure to obtain pure preparations, but product analyses show that they are oxidized at least as slowly as the free aldehyde ligands.

**Table I.** Rate of Oxidation by Ce(IV) of the Protonated and Complexed Pyridine Alcohols and Aldehydes (25.0°)<sup>a</sup>

| Ligand  | k <sup>b</sup>         | k <sup>c</sup>          |
|---|------------------------|-------------------------|
|  (C) | 8.3 × 10 <sup>-3</sup> | 1.7 × 10 <sup>-2</sup>  |
|  (D) |                        | 0.65 × 10 <sup>-2</sup> |
|      | 5.1 × 10 <sup>-3</sup> |                         |
|  (E) | 7.8 × 10 <sup>-4</sup> |                         |
|      | 2.0 × 10 <sup>-3</sup> |                         |
|  (A) | 9.2 × 10 <sup>-3</sup> | 3.2 × 10 <sup>-2</sup>  |
|  (B) | 5.5 × 10 <sup>-3</sup> | 2.2 × 10 <sup>-2</sup>  |

<sup>a</sup>  $k = k_{\text{Ce(IV)}/2}$  (for ligands);  $k = k_{\text{Ce(IV)}/m}$  (for complexes);  $m$  = moles of Ce(IV) consumed/moles of alcohol oxidized.  $k$  is expressed in  $M^{-1} \text{sec}^{-1}$ . <sup>b</sup>  $\text{HClO}_4 = 1.0 \text{ M}$ ,  $\mu = 2.0$ . <sup>c</sup>  $\text{HClO}_4 = 4.0 \text{ M}$ ,  $\mu = 4.1$ .

**The Oxidation of Pentaammine(4-pyridinemethanol)cobalt(III) by Ce(IV).** A number of investigations of the reaction of Ce(IV) and the pentaammine(4-pyridinemethanol)cobalt(III) complex were conducted, determining kinetics and stoichiometry spectrophotometrically, with supplemental product analyses to

**Table II.** Stoichiometry and Kinetics of the Reaction between Ce(IV) and Pentaammine(4-pyridinemethanol)cobalt(III)<sup>a</sup>

| [Co(III)] <sub>0</sub><br>× 10 <sup>3</sup> | [Ce(IV)] <sub>0</sub><br>× 10 <sup>3</sup> | [H <sup>+</sup> ] | μ <sup>b</sup>   | % Red.            | k × 10 <sup>3</sup> c<br>(M <sup>-1</sup> sec <sup>-1</sup> ) |
|---|--|-------------------|------------------|-------------------|---|
| 3.02  | 4.90                                       | 1.0               | 1.1              | 89.5              | 4.96  |
| 5.03  | 5.27                                       | 1.0               | 1.1              | 89.4              | 5.01  |
| 6.79  | 7.00                                       | 1.0               | 1.1              | 78.4              |   |
| 7.86  | 8.62                                       | 1.0               | 1.1              | 91.0              | 5.00  |
| 18.4  | 85.4                                       | 1.0               | 1.7              | 68.9              | 1.83  |
| 4.60  | 5.26                                       | 1.0               | 2.1              | 87.5              | 9.17  |
| 1.19  | 2.51                                       | 1.0               | 2.8 <sup>d</sup> | 93.5              | 13.5  |
| 5.13  | 12.1                                       | 1.0               | 4.2              | 74.2              | 30.6  |
| 1.55  | 1.36                                       | 1.8               | 1.8              | 88.0              | 12.9  |
| 3.50  | 44.0                                       | 2.0               | 2.3              | 59.8              | 6.94  |
| 5.13  | 14.4                                       | 4.0               | 4.1              | 65.0              | 30.4  |
| 5.13  | 6.80                                       | 4.0               | 4.5              | 72.1              | 31.4  |
| 11.8  | 60.0                                       | 4.0               | 4.4              | 58.0              | 21.2  |
| 2.41  | 1.93                                       | 4.0               | 4.0              | 86.2              | 31.8  |
| 4.00  | 3.28                                       | 4.0               | 4.5 <sup>e</sup> | 79.3              | 31.5  |
| 3.16  | 7.46                                       | 8.0               | 8.1              | 43.6              |   |
| 11.7  | 60.0 (55.0)                                | 4.0               | 4.5              | 60.5 <sup>f</sup> |   |
| 34.8  | 51.5 (40.2)                                | 4.0               | 5.8 <sup>g</sup> | 55.3 <sup>f</sup> |   |
| 16.2  | 92.0 (90.0)                                | 1.0               | 4.7              | 59.1 <sup>f</sup> |   |
| 4.03  | 5.11 <sup>h</sup>                          | 4.0               | 4.1              | 63.6              | 33.2  |
| 5.39  | 8.27 <sup>h</sup>                          | 4.0               | 4.1              | 60.6              | 27.0  |

<sup>a</sup> At 25.0°; all runs in the absence of O<sub>2</sub>; μ maintained with LiClO<sub>4</sub> unless stated otherwise; molar concentrations. <sup>b</sup> Ionic strength calculated assuming CeOH<sup>3+</sup> is the dominant form of Ce(IV) in all solutions. <sup>c</sup>  $k = k_{\text{Co(III)-CH}_2\text{OH}} = k_{\text{Ce(IV)}/m}$ .  $k$  is expressed in  $M^{-1} \text{sec}^{-1}$ . <sup>d</sup> 0.10 M Ce(ClO<sub>4</sub>)<sub>3</sub> added; μ maintained with NaClO<sub>4</sub>; ClO<sub>4</sub><sup>-</sup> = 2.5 M. <sup>e</sup> 0.10 M Ce(ClO<sub>4</sub>)<sub>3</sub> added. <sup>f</sup> Stoichiometry determined by product analysis only. The Ce(IV) concentration in parentheses is the average concentration from initial time to the time of quenching of the reaction. <sup>g</sup> 0.20 M Ce(ClO<sub>4</sub>)<sub>3</sub> added. <sup>h</sup> 1 atm of O<sub>2</sub>; [O<sub>2</sub>] = 1.3 × 10<sup>-3</sup> M.

confirm the optical data and to determine stoichiometry at high Ce(IV) concentrations (>1 × 10<sup>-2</sup> M), where the optical method is more difficult to apply. Table II lists the stoichiometric and kinetic data obtained under a number of conditions. % Red. in this and other tables refers to Co<sup>2+</sup> produced from the reaction of the cobalt-ammine complex, *i.e.*, % Red. = [Co(II)]/[Co(II) + Co(III)-CHO].

The rate constants represent the rate of consumption of the alcohol complex which is equal to the rate of consumption of Ce(IV) divided by  $m$ . Individual rate constants are estimated to be accurate to ± 5%.

The linearity of second-order plots and the invariance of the apparent rate constant over a range of reactant concentrations verifies the rate law

$$-\frac{d[\text{Co(III)-CH}_2\text{OH}^{3+}]}{dt} = k[\text{Ce(IV)}][\text{Co(III)-CH}_2\text{OH}^{3+}]$$

However, at high concentrations of Ce(IV), the specific rate decreases noticeably. This can be attributed to the formation of relatively unreactive polymeric species of Ce(IV). The existence of such species has been demonstrated by several investigators.<sup>13,18</sup>

Comparing the experiments done at high Ce(IV) concentrations to others done at low Ce(IV), and assuming the rate difference is due to the formation of nonreactive dimers, one can calculate the constants  $K_D = [\text{Ce(IV)}_2]/[\text{Ce(IV)}_1]^2$ , where [Ce(IV)<sub>2</sub>] is the concentration of Ce(IV) in dimeric form *in gram-atoms per liter*. The

(18) E. L. King and M. L. Pandow, *J. Amer. Chem. Soc.*, **74**, 1966 (1952).

dimerization constants obtained,  $K_D = 46$  and 13 in 2 and 4  $M$   $HClO_4$ , respectively, are consistent with those obtained by King<sup>18</sup> in direct spectrophotometric measurements on  $Ce(IV)$  solutions.

The rate increases by a factor of approximately 1.5 when acidity is doubled (1–2  $M$ ) at an ionic strength of 2.0, changing to  $D_2O$  (90%) as the solvent increases the rate by a factor of 1.7. The rate was studied as a function of temperature in a reaction medium ( $[HClO_4] = 1.0 M$ ,  $[Ce(III)] = 0.10 M$ ,  $[ClO_4^-] = 2.5 M$ ,  $\mu \approx 2.8$ ) chosen to duplicate that used by Rudd<sup>19</sup> in studying the oxidation of pentaammine(4-pyridinemethanol) ruthenium(III) by  $Ce(IV)$ .<sup>19</sup> The activation parameters obtained from an Eyring plot are  $\Delta H^\ddagger = 24.7 \pm 0.7$  kcal/mol and  $\Delta S^\ddagger = 15.3 \pm 2.0$  eu

Figure 1 illustrates an interesting feature of the stoichiometry. When the ratio of  $Co(III)-CHO/Co(II)$  is plotted against the  $Ce(IV)$  concentration, it approaches zero at low  $Ce(IV)$ , but it reaches a limiting value at high  $Ce(IV)$  concentrations. As is shown in Figure 1, the stoichiometry appears to "saturate" at the same value in 1  $M$   $HClO_4$ ,  $\mu = 4.0$ , as in 4  $M$   $HClO_4$  at high  $Ce(IV)$ . However, for a given level of  $Ce(IV)$ , considerably more reduction takes place at the lower acidity if  $Ce(IV)$  is at low ( $10^{-3} M$ ) concentration.

In solutions saturated with 1 atm of oxygen, the ratio  $Co(III)-CHO/Co(II)$  appears to approach the same limiting value at high  $Ce(IV)$  as in its absence, but much less reduction occurs at low concentrations of  $Ce(IV)$ . Under these conditions, oxygen present at  $1.3 \times 10^{-3} M$  yielded a stoichiometry that would be obtained if 10 to 15 times this concentration of  $Ce(IV)$  were added to the reaction. No peroxides were detected as reaction products.

Experiments with added  $Hg(ClO_4)_2$ ,  $Cu(ClO_4)_2$ , and  $HgCl_2$  at concentrations in the range of 0.1 to 0.3  $M$  revealed no specific effects of these species on the stoichiometry or kinetics of this reaction.

**The  $Ag(I)$ - and  $Co(II)$ -Catalyzed Oxidations of Pentaammine(4-pyridinemethanol)cobalt(III) by  $Ce(IV)$ .**  $Ag(I)$  catalyzes the reaction, and with  $Ag(I)$  present the reaction rate follows the law

$$-\frac{d[Co(III)-CH_2OH]}{dt} = k_{obsd}[Ce(IV)][Ag(I)]$$

First-order plots were linear for at least two half-lives and showed no inhibition by  $Ce(III)$  generated from the reaction and no dependence of rate on the concentration of the complex. Investigation of the direct oxidation of the complex by  $Ag(II)$  showed the reaction to be complete on mixing.

Table III lists the kinetic and stoichiometric results for oxidations of the *para* alcohol complex by  $Ce(IV)$  as catalyzed by  $Ag(I)$ . The dependence of the ratio  $Co(III)-CHO/Co(II)$  on  $[Ce(IV)]$  resembles that for the uncatalyzed reaction. The ratio approaches zero at low  $[Ce(IV)]$ , but reaches a limiting value at approximately 1.4, almost twice that for the uncatalyzed reaction. The effects of acid and oxygen on the stoichiometry are similar to those observed for the uncatalyzed reaction.

When enough  $Co(II)$  is present, an acceleration of the initial rate of the reaction between  $Ce(IV)$  and the complexes occurs. The catalyzed reaction appears to be inhibited by  $Ce(III)$  produced in the reaction. In a series

(19) D. P. Rudd, unpublished observations, 1967.

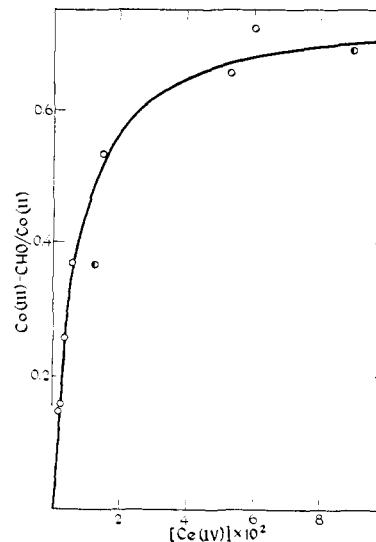


Figure 1. Plot of  $Co(III)-CHO/Co(II)$  vs.  $[Ce(IV)]$  for the oxidation of pentaammine(4-pyridinemethanol)cobalt(III) by  $Ce(IV)$ :  $T = 25^\circ$ ;  $\circ$ ,  $[HClO_4] = 4.0 M$ ;  $\bullet$ ,  $[HClO_4] = 1.0 M$ ,  $[LiClO_4] = 3.0 M$ .

of experiments devoted to the catalyzed reaction, the concentration of  $Co(II)$  was kept low enough so as not to change the ionic medium significantly. Under these conditions, the catalyzed and uncatalyzed reactions occur at comparable rates. The rate constants and

**Table III.** Kinetics and Stoichiometry of the  $Ag(I)$ -Catalyzed Oxidation of Pentaammine(4-pyridinemethanol)cobalt(III) by  $Ce(IV)$ <sup>a</sup>

| $[Co(III)] \times 10^3$ | $[Ce(IV)] \times 10^3$   | $[Ag(I)]$ | $[H-ClO_4]$ | $\mu$            | % Red. | $k \times 10^2 (M^{-1} sec^{-1})$ |
|-------------------------|--------------------------|-----------|-------------|------------------|--------|-----------------------------------|
| 6.71                    | 8.62                     | 0.065     | 1.06        | 1.2              | 71.6   | 0.720                             |
| 5.05                    | 8.62                     | 0.108     | 2.02        | 2.2              | 62.0   | 1.93                              |
| 4.13                    | 8.62                     | 0.074     | 1.14        | 4.2              | 66.3   | 1.85                              |
| 4.44                    | 8.62                     | 0.098     | 4.00        | 4.0              | 50.8   | 3.36                              |
| 5.13                    | 2.72                     | 0.093     | 4.00        | 4.1              | 64.1   | 3.43                              |
| 5.13                    | 2.58                     | 0.093     | 2.00        | 4.1              | 69.5   | 2.52                              |
| 5.13                    | 3.22                     | 0.101     | 0.98        | 4.1              | 75.5   | 1.61                              |
| 5.13                    | 2.92                     | 0.431     | 4.00        | 4.4              | 61.4   | 3.47                              |
| 5.13                    | 7.59                     | 0.093     | 4.0         | 4.2              | 53.7   | 3.20                              |
| 5.13                    | 13.9                     | 0.047     | 4.0         | 4.2              | 46.7   | 3.08                              |
| 5.13                    | 5.53                     | 0.093     | 4.0         | 4.2              | 54.0   | 3.42                              |
| 1.19                    | 1.24                     | 0.085     | 4.0         | 4.1              | 74.0   | 3.51                              |
| 4.02                    | 2.34                     | 0.046     | 4.0         | 4.1              | 68.0   | 3.98                              |
| 4.02                    | 4.91                     | 0.025     | 4.0         | 4.1              | 54.1   | 3.39                              |
| 8.89                    | 52.4 (51.0) <sup>b</sup> | 0.054     | 4.0         | 4.5 <sup>c</sup> | 42.0   |                                   |
| 4.86                    | <i>d</i>                 | 0.135     | 4.0         | 4.2              | 61.0   |                                   |
| 2.48                    | <i>d</i>                 | 0.333     | 4.35        | 4.7              | 50.0   |                                   |
| 1.19                    | 1.24 <sup>e</sup>        | 0.085     | 4.0         | 4.1              | 50.0   | 3.35                              |
| 4.03                    | 5.11 <sup>e</sup>        | 0.043     | 4.0         | 4.1              | 45.4   | 3.22                              |

<sup>a</sup>  $\mu$  maintained with  $LiClO_4$ ;  $25^\circ$ . <sup>b</sup> Stoichiometry determined by product analysis only. The  $Ce(IV)$  concentration in parentheses is the average concentration from initial time to the time of quenching of the reaction. <sup>c</sup>  $\mu$  calculated assuming  $CeOH^{3+}$  is the dominant  $Ce(IV)$  species. <sup>d</sup> Direct reaction of  $Ag(II)$  with complex.  $Ag(II) = 2.37 \times 10^{-3} M, 1.24 \times 10^{-3} M$ , respectively. <sup>e</sup> 1 atm of  $O_2$ ,  $[O_2] = 1.3 \times 10^{-3} M$ .

stoichiometry were determined from spectrophotometric measurements in the initial stages of reaction, and the stoichiometry of the catalyzed reaction was determined after correcting for the contribution to the stoichiometry of the reaction occurring by the uncatalyzed

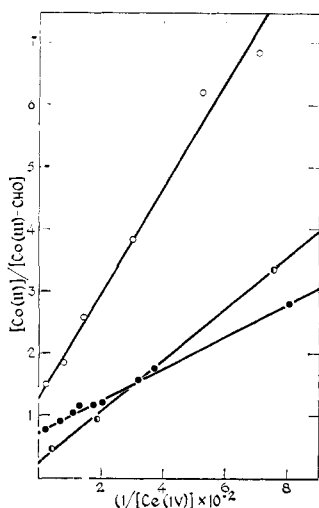


Figure 2. Plot of Co(II)/Co(III)-CHO vs.  $1/[\text{Ce(IV)}]$  for the uncatalyzed, Ag(I)-catalyzed, and Co(II)-catalyzed oxidation of pentaammine(4-pyridinemethanol)cobalt(III) by Ce(IV):  $[\text{HClO}_4] = 4.0 \text{ M}$ ;  $T = 25^\circ$ ;  $\circ$ , Ce(IV);  $\bullet$ , Ce(IV) + Ag(I);  $\bullet$ , Ce(IV) + Co(II).

path. The results of these experiments are shown in Table IV.

Table IV. Co(II)-Catalyzed Oxidation of Pentaammine(4-pyridinemethanol)cobalt(III) by Ce(IV)<sup>a</sup>

| $[\text{Co(III)-CH}_2\text{OH}]_0 \times 10^3$ | $[\text{Ce(IV)}]_0 \times 10^3$ | $[\text{Co(II)}]_0$ | $\text{HClO}_4$ | % Red. <sup>b</sup> | $k_{\text{cat}}^c \times 10^3$ |
|--|---------------------------------|---------------------|-----------------|---------------------|--------------------------------|
| 4.68   | 5.20                            | 0.0486              | 4.0             | 47.5                | 3.1                            |
| 2.41   | 1.34                            | 0.0470              | 4.0             | 77.2                | 3.7                            |
| 4.85   | 22.0                            | 0.159               | 4.0             | 32.0                | 2.3                            |
|  |                                 |                     |                 |                     | (2.8) <sup>d</sup>             |
| 5.41   | 5.31                            | 0.0075              | 1.0             | 69.5                | 2.0                            |

<sup>a</sup> At  $25^\circ$ ;  $\mu \approx [\text{HClO}_4]$ . <sup>b</sup> % reduction of catalyzed path, after correcting for uncatalyzed reaction using previously determined rate and stoichiometry data. <sup>c</sup>  $k = k_{\text{Ce(IV)}/m}$ , where  $k_{\text{Ce(IV)}}$  is obtained assuming the rate law  $-d[\text{Ce(IV)}]/dt = k_{\text{Ce(IV)}}[\text{Ce(IV)}][\text{Co(II)}]$ , for the initial rate of the catalyzed reaction. <sup>d</sup>  $k = 2.83 \times 10^{-3}$  assuming Ce(IV) dimers are unreactive and using  $K_D = 13$ , as previously determined.

The direct oxidation of the 4-pyridinemethanol complex and related ligands by hexaaquocobalt(III) was briefly studied. Results are shown in Table V. Prod-

Table V. Direct Oxidation by Aquocobalt(III)<sup>a</sup>

| $[\text{Reductant}] \times 10^3$ | $[\text{Co(H}_2\text{O)}_6^{3+}] \times 10^4$ | $[\text{HClO}_4]$ | % Red. <sup>b</sup> | $k \text{ (M}^{-1} \text{sec}^{-1})^c$ |
|----------------------------------|---|-------------------|---------------------|--|
| 2.49 <sup>d</sup>                | 16.8  | 2.0               | 100                 | 2.10                                   |
| 0.095 <sup>d</sup>               | 3.90  | 1.0               | 100                 | 2.26                                   |
| 0.870 <sup>d</sup>               | 9.63  | 4.0               | 100                 | 2.15                                   |
| 33.0 <sup>e</sup>                | 3.50  | 4.0               |                     | 0.23                                   |
| 19.7 <sup>e</sup>                | 2.94  | 1.0               |                     | 0.73                                   |
| 2.02 <sup>f</sup>                | 15.4  | 4.0               |                     | 1.89                                   |

<sup>a</sup> At  $25.0^\circ$ ; no added electrolyte. <sup>b</sup> As arising from the ammine complex only. <sup>c</sup>  $k = k_{\text{Co(III)-CH}_2\text{OH}} = k_{\text{Co}^{3+}/m}$  for complex;  $k = k_L = k_{\text{Co}^{3+}/2}$  for ligands. <sup>d</sup> Structure A. <sup>e</sup> Structure E, Table I. <sup>f</sup> Structure C, Table I.

uct analysis showed that the reaction yielded no extraneous species, but a considerable amount of secondary oxidation of the free aldehyde occurred.

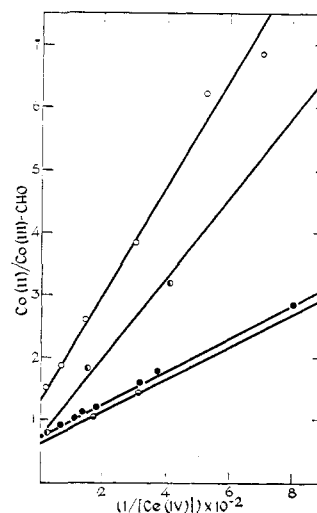


Figure 3. Plot of Co(II)/Co(III)-CHO vs.  $1/[\text{Ce(IV)}]$  for the uncatalyzed and Ag(I)-catalyzed oxidation of (4-pyridine- $d_2$ -methanol) and (4-pyridinemethanol)pentaamminecobalt(III) by Ce(IV):  $[\text{HClO}_4] = 4.0 \text{ M}$ ;  $T = 25^\circ$ ;  $\circ$ , Ce(IV)- $\text{CH}_2\text{OH}$ ;  $\bullet$ , Ce(IV) + Ag(I)- $\text{CH}_2\text{OH}$ ;  $\bullet$ , Ce(IV)- $\text{CD}_2\text{OH}$ ; and  $\bullet$ , Ce(IV) + Ag(I)- $\text{CD}_2\text{OH}$ .

Figure 2 shows the ratio of Co(II)/Co(III)-CHO plotted against  $1/[\text{Ce(IV)}]$  for the uncatalyzed, Ag(I)-catalyzed, and Co(II)-catalyzed oxidations. The plots are linear and differences between the three oxidants are evident.

**Oxidation of Pentaamminecobalt-(4-Pyridine- $d_2$ -methanol)cobalt(III).** The kinetic and stoichiometric results obtained in the study of the oxidation of deuterated complex are summarized in Table VI. The uncatalyzed Ce(IV) oxidation shows a kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}}$ ) of  $2.7 \pm 0.2$  in  $4 \text{ M HClO}_4$ . The uncatalyzed Co(III) oxidation shows a kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}}$ ) of  $2.0 \pm 0.2$  in  $4 \text{ M HClO}_4$ . There is no kinetic isotope effect on the observed rate of the Ag(I)-catalyzed reaction.

Figure 3 shows the ratio  $[\text{Co(II)}]/[\text{Co(III)-CHO}]$  produced plotted against  $1/[\text{Ce(IV)}]$ , for the uncatalyzed oxidation of the normal complex and of the deuterated complex, as well as for the Ag(I)-catalyzed oxidation of the normal complex and of the deuterated complex. The rate of oxidation by Ce(IV) of the deuterated and nondeuterated free ligands in  $4 \text{ M HClO}_4$  is also shown in Table VI. The isotope effect  $k_{\text{H}}/k_{\text{D}} = 2.6 \pm 0.1$  is essentially the same as that obtained for the complex under these conditions.

**The Oxidation of Pentaammine(3-pyridinemethanol)cobalt(III).** A number of experiments were performed on the Ce(IV) oxidation of the pentaammine(3-pyridinemethanol)cobalt(III) complex. Table VII shows the kinetic and stoichiometric results obtained.

The reaction is first order in each reactant at low Ce(IV) concentrations but, as observed also for the 4- $\text{CH}_2\text{OH}$  complex, the apparent rate constant decreases at high Ce(IV) concentrations. The rate increases 1.6 times with a fourfold increase in acidity at an ionic strength of four. The solvent isotope effect ( $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$  in 90%  $\text{D}_2\text{O}$ ) is 2.1 at  $[\text{DCIO}_4] = 1.0 \text{ M}$ ,  $\mu = 1.0$ .

Table VIII illustrates the results obtained for the Ag(I)- and Co(II)-catalyzed reactions. The rate law and rate constants for the Ag(I)-catalyzed reaction are consistent with those obtained for the catalyzed reac-

Table VI. The Effect of Deuteration on Alcohol Oxidations<sup>a</sup>

| [Complex]<br>× 10 <sup>3</sup> | [Oxidant]<br>× 10 <sup>3</sup> | [Ag(I)] | [HClO <sub>4</sub> ] | μ   | % Red. | k × 10 <sup>2</sup> | k <sub>H</sub> /k <sub>D</sub> |
|--------------------------------|--------------------------------|---------|----------------------|-----|--------|---------------------|--------------------------------|
| 10.6                           | 6.73 <sup>b</sup>              |         | 1.0                  | 1.1 | 73.0   | 0.21                | 2.3 ± 0.2                      |
| 6.13                           | 6.73 <sup>b</sup>              |         | 4.0                  | 4.1 | 64.6   | 1.2                 | 2.7 ± 0.2                      |
| 2.52                           | 2.44 <sup>b</sup>              |         | 4.0                  | 4.0 | 76.0   | 1.3                 |                                |
| 39.6                           | 50.5 <sup>b</sup>              |         | 4.0                  | 4.6 | 44.8   |                     |                                |
| 4.73                           | 5.84 <sup>b</sup>              | 0.092   | 4.0                  | 4.1 | 51.8   | 3.2                 | 1.0 ± 0.1                      |
| 2.09                           | 3.15 <sup>b</sup>              | 0.047   | 4.0                  | 4.1 | 59.8   | 3.4                 |                                |
| 0.713                          | 0.555 <sup>c</sup>             |         | 4.0                  | 4.0 | 100    | 107                 | 2.0 ± 0.2                      |
| (4.21) <sup>d</sup>            | 8.13 <sup>b</sup>              |         | 4.0                  | 4.1 |        | 0.65                | 2.6 ± 0.1                      |
| (4.25) <sup>e</sup>            | 7.92 <sup>b</sup>              |         | 4.0                  | 4.1 |        | 1.70                |                                |

<sup>a</sup> At 25.0°. <sup>b</sup> Ce(IV). <sup>c</sup> Co<sup>3+</sup>(aq). <sup>d</sup> Structure D, Table I. <sup>e</sup> Structure C, Table I.

Table VII. Reaction between Pentaammine(3-pyridinemethanol)cobalt(III) and Ce(IV)<sup>a</sup>

| [Co(III)]<br>× 10 <sup>3</sup> | [Ce(IV)]<br>× 10 <sup>3</sup> | [HClO <sub>4</sub> ] | % Red. | k <sup>b</sup> × 10 <sup>2</sup> |
|--------------------------------|-------------------------------|----------------------|--------|----------------------------------|
| 5.34                           | 13.2                          | 1.0                  | 64.3   | 0.303                            |
| 5.34                           | 4.53                          | 1.0                  | 70.6   | 0.32                             |
| 3.14                           | 2.17                          | 1.0                  | 74.0   |                                  |
| 8.00                           | 11.4                          | 1.0 <sup>c</sup>     | 71.9   | 0.306                            |
| 5.34                           | 9.08                          | 1.0 <sup>d</sup>     | 56.8   | 1.35                             |
| 1.71                           | 4.50                          | 1.0 <sup>e</sup>     | 66.2   | 0.66                             |
| 4.01                           | 1.4 <sup>f</sup>              | 4.0                  | 54.5   |                                  |
| 5.34                           | 6.43                          | 4.0                  | 48.3   | 2.15                             |
| 5.34                           | 2.54                          | 4.0                  | 48.3   | 2.28                             |
| 14.9                           | 51.0                          | 4.0                  | 30.2   | 1.65                             |
| 4.41                           | 3.90                          | 4.0 <sup>g</sup>     | 72.6   | 2.07                             |
| 12.0                           | 9.00                          | 1.0 <sup>h</sup>     | 53.0   | 0.278                            |
| 12.0                           | 8.40                          | 1.0 <sup>i</sup>     | 53.0   | 0.290                            |

<sup>a</sup> At 25.0°; μ ≈ [HClO<sub>4</sub>] unless stated otherwise. <sup>b</sup> k = k<sub>CH<sub>2</sub>OH</sub> = k<sub>Ce(IV)</sub>/m (M<sup>-1</sup> sec<sup>-1</sup>). <sup>c</sup> Ce(ClO<sub>4</sub>)<sub>3</sub> = 0.687 M added. <sup>d</sup> LiClO<sub>4</sub> added; μ = 4.0. <sup>e</sup> 90% D<sub>2</sub>O. <sup>f</sup> Reaction studied by product analysis only. [Ce(IV)] is the average concentration during the reaction. <sup>g</sup> Ce(ClO<sub>4</sub>)<sub>3</sub> = 0.019 M added. <sup>h</sup> 1 atm of O<sub>2</sub>; [O<sub>2</sub>] = 1.3 × 10<sup>-3</sup> M. <sup>i</sup> 1 atm of O<sub>2</sub> = 1.3 × 10<sup>-3</sup> M; Ce(ClO<sub>4</sub>)<sub>3</sub> = 0.080 M added.

Table VIII. Catalyzed Oxidation of Pentaammine(3-pyridinemethanol)cobalt(III)<sup>a</sup>

| [Co(III)]<br>× 10 <sup>3</sup> | [Ce(IV)]<br>× 10 <sup>3</sup> | [HClO <sub>4</sub> ] | [Catalyst]         | % Red.              | k <sup>b</sup> × 10 <sup>2</sup> |
|--------------------------------|-------------------------------|----------------------|--------------------|---------------------|----------------------------------|
| 2.66                           | 4.55                          | 1.0                  | 0.052 <sup>c</sup> | 69.0                | 0.68                             |
| 1.27                           | 1.64                          | 1.0                  | 0.046 <sup>c</sup> | 74.0                | 0.68                             |
| 1.27                           | 3.05                          | 1.0                  | 0.055 <sup>c</sup> | 74.0                | 0.71                             |
| 5.30                           | 4.20                          | 1.0 <sup>c</sup>     | 0.046 <sup>c</sup> | 66.2                | 1.44                             |
| 1.34                           | 4.81                          | 4.0                  | 0.094 <sup>c</sup> | 51.4                | 3.50                             |
| 5.34                           | 12.7                          | 4.0                  | 0.047 <sup>c</sup> | 42.5                | 3.37                             |
| 2.66                           | 4.30                          | 4.0                  | 0.048 <sup>c</sup> | 50.8                | 3.76                             |
| 0.910                          | 1.49                          | 4.0                  | 0.051 <sup>c</sup> | 52.3                | 3.75                             |
| 12.1                           | 5.25                          | 1.0                  | 0.048 <sup>d</sup> | 86.5 <sup>f</sup>   | 0.17 <sup>f</sup>                |
|                                |                               |                      |                    | (81.5) <sup>g</sup> | (0.17) <sup>g</sup>              |
| 8.06                           | 7.65                          | 1.0                  | 0.048 <sup>d</sup> | 80.0 <sup>f</sup>   | 0.12 <sup>f</sup>                |
|                                |                               |                      |                    | (75.0) <sup>g</sup> | (0.12) <sup>g</sup>              |

<sup>a</sup> At 25.0°; no added electrolyte other than catalyst. <sup>b</sup> k = k<sub>Co(III)-CH<sub>2</sub>OH</sub> = k<sub>Ce(IV)</sub>/m, (M<sup>-1</sup> sec<sup>-1</sup>). <sup>c</sup> AgClO<sub>4</sub>. <sup>d</sup> Co(ClO<sub>4</sub>)<sub>2</sub>. <sup>e</sup> 90% D<sub>2</sub>O. <sup>f</sup> Rate and stoichiometry measurements corrected for the uncatalyzed reaction, assuming this reaction is unaffected by Co(II). <sup>g</sup> Rate and stoichiometry measurements corrected for the uncatalyzed reaction, assuming Co(II) affects both reactions equally, causing the stoichiometry of the catalyzed and uncatalyzed reactions to be identical.

tions of Ce(IV) with the 4-CH<sub>2</sub>OH complex. A solvent isotope effect (k<sub>D<sub>2</sub>O</sub>/k<sub>H<sub>2</sub>O</sub> = 2.1) is also observed for the Ag-catalyzed reaction. The rate constant obtained for the Co(II)-catalyzed reaction with the 3-CH<sub>2</sub>OH complex is 40% lower than that observed for the 4-CH<sub>2</sub>OH complex.

Figure 4 is a plot of the ratio Co(II)/Co(III)-CHO against 1/[Ce(IV)] for the Ag(I)-catalyzed and uncatalyzed reactions. It can be seen that, for the Ce(IV) and the Ag(I)-Ce(IV) systems, the ratio is not simply linearly proportional to Ce(IV), but approaches zero at high [Ce(IV)] and appears to reach a saturation value at low [Ce(IV)].

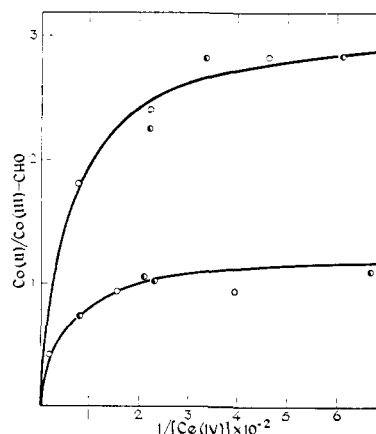


Figure 4. Plot of Co(II)/Co(III)-CHO vs. 1/[Ce(IV)] for the uncatalyzed and Ag(I)-catalyzed oxidation of (3-pyridinemethanol)pentaamminecobalt(III) by Ce(IV): T = 25°; μ = [HClO<sub>4</sub>]; [HClO<sub>4</sub>] = 1.0 M (upper curve); [HClO<sub>4</sub>] = 4.0 M (lower curve); ○, Ce(IV); and ◐, Ce(IV) + Ag(I).

The ratio of Co(III)-CHO/Co(II) is plotted against [Ce(IV)] in Figure 5. The plots are linear except for an experiment not shown which was done at high Ce(IV), [HClO<sub>4</sub>] = 4.0 M. However, when the concentration of Ce(IV) monomer is plotted, calculated using K<sub>D</sub> = 13, as previously determined, the stoichiometry agrees well with the other measurements.

Two experiments showed the stoichiometry of the uncatalyzed and Ag(I)-catalyzed reactions in 90% D<sub>2</sub>O to be the same within experimental error at the same Ce(IV) concentration, and to agree closely with that observed in H<sub>2</sub>O at a Ce(IV) concentration 2.0 times greater.

A series of experiments was conducted to determine if excess Ce(III) has an effect on the Ce(IV) oxidation. Indeed, in the presence of excess Ce(III), the uncatalyzed reaction yielded more Co(II). The rate of reaction was unaffected by Ce(III), however. Two sources of Ce(III) gave identical results. It should be noted that no such effect on the rate or stoichiometry of the Ce(IV) oxidation of the 4-CH<sub>2</sub>OH complex was observed.

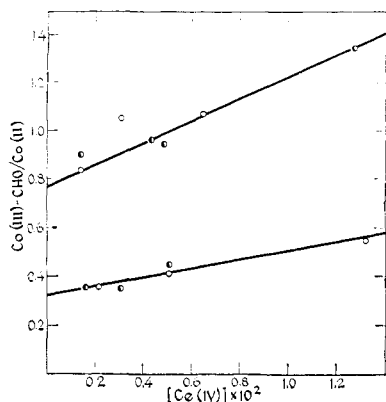


Figure 5. Plot of Co(III)-CHO/Co(II) vs. [Ce(IV)] for the uncatalyzed and Ag(I)-catalyzed oxidation of (3-pyridinemethanol)pentammine cobalt(III) by Ce(IV):  $T = 25^\circ$ ;  $\mu = [\text{HClO}_4]$ ;  $[\text{HClO}_4] = 1.0 \text{ M}$  (lower line);  $[\text{HClO}_4] = 4.0 \text{ M}$  (upper line);  $\circ$ , Ce(IV); and  $\bullet$ , Ce(IV) + Ag(I).

In the presence of oxygen at 1 atm, a higher Co(III)-CHO/Co(II) ratio is measured than in its absence. (No stable peroxides were detected as products.) The ratio is equivalent to that which would be obtained by replacing the oxygen in solution ( $[\text{O}_2] = 1.3 \times 10^{-3} \text{ M}$ ) by  $2 \times 10^{-2} \text{ M}$  Ce(IV). In the presence of 1 atm of oxygen, excess Ce(III) has no effect on the stoichiometry of the uncatalyzed oxidation.

When  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  is added to the reaction mixture of Ce(IV) and the 3- $\text{CH}_2\text{OH}$  complex, the oxidation of the complex is accelerated, and the Co(III)-CHO/Co(II) ratios for a given Ce(IV) concentration are less than those obtained for the uncatalyzed and Ag(I)-catalyzed oxidations. If it is assumed that  $\text{Co}^{2+}$  in solution does not affect the stoichiometry of the concurrent direct oxidation by Ce(IV), stoichiometric data for the Co(II)-catalyzed reaction can be calculated. But, in view of the observation that Ce(III) can affect the stoichiometry observed for direct Ce(IV) oxidation of this complex, this assumption is of doubtful validity. Alternately, it can be assumed that similar intermediates are generated in both systems, and thus that excess  $\text{Co}^{2+}$  affects the stoichiometry of both uncatalyzed and Co(II)-catalyzed oxidations equally. Table VIII shows the results of calculations based on both of these assumptions. The available data do not distinguish between these or other alternatives, and further studies of the  $\text{Co}^{2+}$ -catalyzed reaction and of the effect of other cations on stoichiometries will be necessary to resolve this ambiguity.

## Discussion

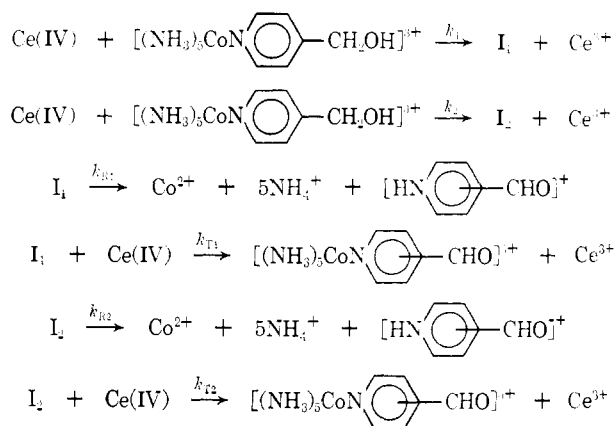
**General Features of the Reaction Mechanism.** The product ratios obtained for the catalyzed and uncatalyzed Ce(IV) oxidations of both complexes are observed to depend on Ce(IV) concentration, although the rates of these oxidations, as measured by the consumption of the Co(III) complexes, are strictly first order in Ce(IV). This suggests that for each system an intermediate is formed and that the stoichiometry is determined by the competition between two reactions for the intermediate: (1) production of  $[\text{Co}^{2+} + \text{"free aldehyde"}]$  by a first-order process, or (2) reaction with Ce(IV) to produce Co(III)-aldehyde complexes. The sensitivity of the rates to deuterium substitution in the

alcohol function shows that the rate-determining step involves attack on the alcohol group.

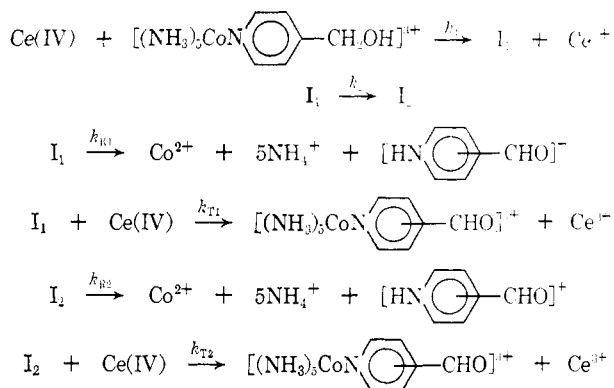
The variation of the product ratio with [Ce(IV)] found for the oxidation by Ce(IV) of the 4- $\text{CH}_2\text{OH}$  complex is similar to that reported<sup>2</sup> for the oxidation of 4-hydroxymethylbenzoatopentaamminecobalt(III). The ratio Co(III)-CHO/Co(II) for the 4- $\text{CH}_2\text{OH}$  complex approaches zero as [Ce(IV)] approaches zero, ruling out primary attack by a two-electron change. The ratio approaches a limit at high [Ce(IV)] showing that two intermediates are formed, only one of which can be prevented by competitive reaction with Ce(IV) from yielding  $\text{Co}^{2+}$ .

The stoichiometric behavior observed for the oxidation of the 3- $\text{CH}_2\text{OH}$  complex likewise suggests that Ce(IV) generates two intermediates, one which can either produce Co(II) or react further with Ce(IV) to produce Co(III)-CHO, and the other of which always yields Co(III)-CHO over the Ce(IV) concentration range studied. Two general schemes for the production of the intermediates must be considered, and these are outlined; see Schemes I and II.

### Scheme I



### Scheme II



In Scheme I, the intermediates are generated by parallel paths, while in Scheme II one intermediate is a precursor of the other. The data require that  $\text{I}_1$  be the intermediate which is more reactive to internal reduction in Scheme II, and that under the conditions studied,  $k_{R1} \gg k_{T1}[\text{Ce(IV)}]$  for the 4-pyridinemethanol complex and  $k_{T2}[\text{Ce(IV)}] \gg k_{R2}$  for the 3-pyridinemethanol complex. The labeling of the intermediates by Scheme I is arbitrary, but to keep the notation consistent with that required by Scheme II,  $\text{I}_1$  is assumed to have greater rate of internal electron transfer compared to oxidation.

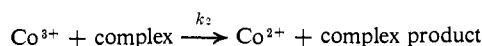
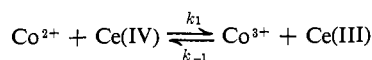


Table IX. Reactivity Ratios for Radical Intermediates<sup>a</sup>

| Ligand                                      | Oxidant              | [H <sup>+</sup> ] | $k_1/k_2$ | $k_{R1}/k_{T1}$                   | $k_{R2}/k_{T2}$                  |
|---|----------------------|-------------------|-----------|-----------------------------------|----------------------------------|
| 4-Pyridinemethanol                          | Ce(IV)               | 4.0               | 1.30      | >1                                | $3.8 \times 10^{-3}$             |
| 4-Pyridine- <i>d</i> <sub>2</sub> -methanol | Ce(IV)               | 4.0               | 0.70      | >1                                | $3.8 \times 10^{-3}$             |
| 4-Pyridinemethanol                          | Ag(II) <sup>b</sup>  | 4.0               | 0.70      | >1                                | $1.6 \times 10^{-3}$             |
| 4-Pyridine- <i>d</i> <sub>2</sub> -methanol | Ag(II) <sup>b</sup>  | 4.0               | 0.65      | >1                                | $1.5 \times 10^{-3}$             |
| 4-Pyridinemethanol                          | Co(III) <sup>c</sup> | 4.0               | 0.20      | >1                                | $3.5 \times 10^{-3}$             |
| 4-Pyridinemethanol                          | Ce(IV)               | 1.0               | $3 \pm 1$ | >1                                | $(7 \pm 3) \times 10^{-3}$       |
| 3-Pyridinemethanol                          | Ce(IV)               | 4.0               | 1.30      | $3.9 \times 10^{-2}$              | $<5 \times 10^{-5}$              |
| 3-Pyridinemethanol                          | Ag(II) <sup>b</sup>  | 4.0               | 1.30      | $3.9 \times 10^{-2}$              | $<5 \times 10^{-5}$              |
| 3-Pyridinemethanol                          | Ce(IV)               | 1.0               | 3.10      | $7.1 \times 10^{-2}$              | $<1 \times 10^{-4}$              |
| 3-Pyridinemethanol                          | Ag(II) <sup>b</sup>  | 1.0               | 3.10      | $7.1 \times 10^{-2}$              | $<1 \times 10^{-4}$              |
| 3-Pyridinemethanol                          | Co(III) <sup>c</sup> | 1.0               |           | $7.5 \times 10^{-2}$ <sup>d</sup> | $<1 \times 10^{-4}$ <sup>d</sup> |

<sup>a</sup> At 25.0°;  $\mu = [\text{HClO}_4]$ . <sup>b</sup> Ag<sup>+</sup> as catalyst for oxidation by Ce(IV). <sup>c</sup> Co<sup>2+</sup> as catalyst for oxidation by Ce(IV). <sup>d</sup> Ratios calculated assuming excess Co(II) affects both the uncatalyzed and Co(II)-catalyzed reactions equally resulting in the same stoichiometry for both reactions.  $k_1/k_2$  cannot be determined due to the effect of Co(II) on the proportions of  $T_1$  and  $T_2$  that proceed to products.

The Ag<sup>+</sup>- and Co<sup>2+</sup>-catalyzed Ce(IV) oxidations can be understood as occurring through cycles involving Co<sup>3+</sup>(aq) or Ag(II) as intermediates, as illustrated for Co<sup>2+</sup>.



Catalysis of this kind has been previously reported for Ag<sup>+</sup>.<sup>14,20,21</sup> The available thermodynamic<sup>22</sup> and kinetic data<sup>23</sup> and the rates observed in the direct oxidation by Co<sup>3+</sup>(aq) and Ag(II) of the 4-CH<sub>2</sub>OH complex are consistent with this mechanism. The Co(III)-CHO/Co(II) ratio approaches zero at low [Ce(IV)] for both catalytic systems, showing that also in the catalyzed oxidations two-electron changes are not important.

The stoichiometries of the catalyzed reactions would be expected to differ from the uncatalyzed only because of differences in nature or the relative amounts of the intermediates produced (since Co<sup>3+</sup>(aq) and Ag(II) are only present at low concentrations at the steady state, they would not be expected to compete with Ce(IV) in radical-trapping steps analogous to  $k_{T1}$  and  $k_{T2}$ ).

Applying the steady-state approximation for conditions of fixed [Ce(IV)] to the concentration of intermediates I<sub>1</sub> and I<sub>2</sub> yields

$$\frac{[\text{Co(II)}]}{[\text{Co(III)-CHO}]} = \frac{k_1/k_2 + (k_{R2}/k_{T2}[\text{Ce(IV)}])(1 + (k_1/k_2))}{k_{R1}/k_2 + (k_{R2}/k_{T2}[\text{Ce(IV)}])(1 + (k_{R1}/k_2))}$$

$$\frac{[\text{Co(II)}]}{[\text{Co(III)-CHO}]} = \frac{k_{R1}/k_2 + (k_{R2}/k_{T2}[\text{Ce(IV)}])(1 + (k_{R1}/k_2))}{k_{R1}/k_2 + (k_{R2}/k_{T2}[\text{Ce(IV)}])(1 + (k_{R1}/k_2))}$$

for the oxidations of the 4-CH<sub>2</sub>OH complex by Schemes

(20) W. C. E. Higginson, D. R. Rosseinsky, B. Stead, and A. G. Sykes, *Discussions Faraday Soc.*, **29**, 49 (1960); see also M. G. Anderson, F. S. Dainton, and P. Glentworth, *Trans. Faraday Soc.*, **61**, 701 (1965).

(21) J. B. Kirwin, P. J. Proll, and L. H. Sutcliffe, *ibid.*, **60**, 119 (1964).

(22) A. A. Noyes, D. DeValut, C. D. Coryell, and T. J. Deahl, *J. Amer. Chem. Soc.*, **59**, 1326 (1937); G. F. Smith and C. A. Goetz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191 (1938); see also ref 14.

(23) Higginson, *et al.*,<sup>20</sup> obtained the value  $(2.8 \pm 0.3) \times 10^{-2} M^{-1} \text{sec}^{-1}$  for the reaction Ce(IV) + Ag(I) → Ce(III) + Ag(II) in 4 M HClO<sub>4</sub>,  $\mu = 4.5$ , 25°. This is in fair agreement with the rate constants obtained in the present investigation,  $(3.4 \pm 0.2) \times 10^{-2} M^{-1} \text{sec}^{-1}$ , under similar conditions. From formal oxidation potentials<sup>22</sup> and the present data, one can calculate a value of  $(2.5 \pm 1.5) M^{-1} \text{sec}^{-1}$  for the reaction Co(III) + Ce(IV) → Co(II) + Ce(IV) in 4 M HClO<sub>4</sub>,  $\mu = 4.0$ , 25°. This rate constant has been found to  $1.0 M^{-1} \text{sec}^{-1}$  in 1 M HClO<sub>4</sub>,  $\mu = 1.0$ , 25°: L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, **52**, 1225 (1956).

I and II, respectively (here the condition  $k_{R1} \gg k_{T1}$  [Ce(IV)] is applied), and yields

$$\frac{[\text{Co(III)-CHO}]}{[\text{Co(II)}]} = k_2/k_1 + \frac{k_{T1}(k_1 + k_2)[\text{Ce(IV)}]}{k_1 k_{R1}}$$

and

$$\frac{[\text{Co(III)-CHO}]}{[\text{Co(II)}]} = k_2/k_{R1} + \frac{k_{T1}[\text{Ce(IV)}]}{(k_{R1})}$$

for the oxidations of the 3-CH<sub>2</sub>OH complex by Schemes I and II, respectively (here the condition  $k_{T2}[\text{Ce(IV)}] \gg k_{R2}$  is applied). Table IX lists the values of (or limits on) the rate constant ratios obtained from the appropriate stoichiometric plots by applying Scheme I to all systems.<sup>24</sup>

In Scheme I, the  $k_1/k_2$  ratios are expected to depend on the nature of the oxidant, while in Scheme II the  $k_{R1}/k_2$  ratios should remain constant as the oxidant is changed. It was on the basis of these criteria that Scheme II was proposed for oxidation of the 4-hydroxymethylbenzoato complex, and a similar mechanism is suggested by the present data for the 3-CH<sub>2</sub>OH complex. However, for the 4-CH<sub>2</sub>OH complex, the  $k_1/k_2$  ratios depend on the nature of the external oxidant, suggesting strongly that this species is oxidized by Scheme I. This scheme will be adopted in discussing the data for both complexes. Its application to the 3-CH<sub>2</sub>OH system, though arbitrary, is revealing in comparing reactivity patterns of the two reactants.

The ratio  $k_1/k_2$  is smaller for the Ce(IV) oxidation of the 4-CD<sub>2</sub>OH compared to that of normal isotopic composition. From the influence of deuteration on the over-all rate of this reaction and on the above ratio, the isotope effect ( $k_H/k_D$ ) on the rate of production of I<sub>1</sub> is calculated to be  $3.4 \pm 0.2$ , and for I<sub>2</sub> to be  $1.8 \pm 0.2$ , when the reactions producing them are assumed to be independent, as in Scheme I. The values of  $k_{R2}/k_{T2}$  are independent of deuteration.

The agreement of the ratios  $k_R/k_T$  indicates that I<sub>2</sub> generated by Ce(IV) acting on the 4-CH<sub>2</sub>OH complex is the same as that generated by Co<sup>3+</sup>(aq), and that I<sub>1</sub> generated from the 3-CH<sub>2</sub>OH complex is the same for Ce(IV), Ag(II), and possibly Co<sup>3+</sup>(aq) oxidation. The different  $k_{R2}/k_{T2}$  ratio for Ag(II) oxidation of the 4-CH<sub>2</sub>OH complex may mean that a different interme-

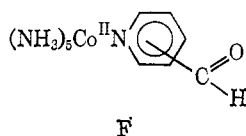
(24) If Scheme II were applied, the constants listed under  $k_1/k_2$  would become  $k_{R1}/k_2$ , and those listed under  $k_{R1}/k_{T1}$  would, for the oxidations of the 3-CH<sub>2</sub>OH complex only, become  $(k_{R1}/k_{T1})(k_1 + k_2)/k_1$ . All other constants would be unaffected.

diolate is generated by this oxidant than is generated by Ce(IV) or  $\text{Co}^{3+}(\text{aq})$ , or that  $\text{Ag}^+$  somehow effects the reactivity of  $\text{I}_2$ .

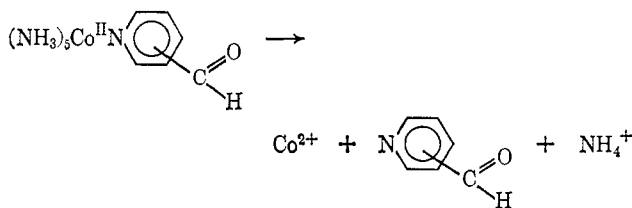
Changing acidity at constant ionic strength affects  $k_{\text{R}}/k_{\text{T}}$ , but not  $k_1/k_2$  (see Figure 1). The values of  $k_{\text{R}2}/k_{\text{T}2}$  are 2.2 and 2.4 times higher in 1 M  $\text{HClO}_4$ ,  $\mu = 4.0$ , than in 4 M  $\text{HClO}_4$  for the direct and  $\text{Ag}^+$ -catalyzed Ce(IV) oxidations of the 4- $\text{CH}_2\text{OH}$  complex, respectively. This behavior suggests that  $\text{Ce}^{4+}$  traps intermediate  $\text{I}_2$  much more efficiently than does  $\text{CeOH}^{3+}$ . The lower value of  $k_{\text{R}2}/k_{\text{T}2}$  in 4 M  $\text{HClO}_4$  can be attributed to a concentration of  $\text{Ce}^{4+}$  approximately twice as large at the higher acidity. Similarly the significant solvent isotope effects observed on the rates of Ce(IV) oxidation of the 4- $\text{CH}_2\text{OH}$  and 3- $\text{CH}_2\text{OH}$  complexes ( $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 1.7$  and 2.1, respectively) and on the  $\text{Ag}^+$ -catalyzed oxidations ( $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 2.1$ ) can be explained by the high reactivity of  $\text{Ce}^{4+}$  relative to  $\text{CeOH}^{3+}$ , if it is assumed that the first hydrolysis constant of  $\text{Ce}^{4+}$ <sup>25</sup> exhibits a "normal" solvent isotope effect<sup>26</sup> and is approximately 2.5 times smaller in  $\text{D}_2\text{O}$ .

It has been assumed in the foregoing that genuine intermediates are always generated by the attack of the external oxidant. The failure to intercept internal electron transfer for  $\text{I}_1$  derived from the 4- $\text{CH}_2\text{OH}$  complex, however, can also be explained by assuming that, for the part of the reaction ascribed to  $\text{I}_1$ , rather than a radical intermediate being generated, oxidation takes place by the external oxidant and the Co(III) center acting in concert. But arguing against this kind of mechanism is the similarity of rates of oxidation of the free and complexed ligands, the agreement of the ratio of rates for the 4- $\text{CH}_2\text{OH}$  and 3- $\text{CH}_2\text{OH}$  complexes to that observed for the protonated free ligands, and the similar kinetic isotope effects observed for Ce(IV) oxidation of the 4- $\text{CH}_2\text{OH}$  complex and free protonated ligand.

**The Nature of the Intermediates.** In the earlier speculation<sup>2</sup> on the nature of the two intermediates which are generated by the  $1e^-$  oxidation of the alcohol group, only carbon radicals were considered. The possibility needs to be examined that one or more of the intermediates are of type F



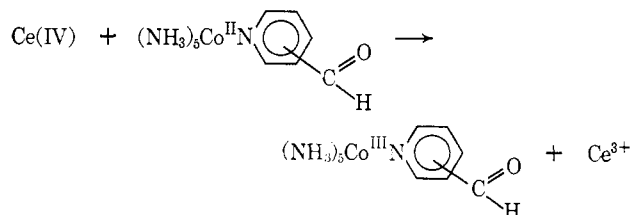
Despite the substitution lability of Co(II)



might be assumed to take place in competition with

(25) From the linear relationship between  $1/k_{\text{obsd}}$  and  $1/[\text{H}^+]$  obtained for the  $\text{Ag}^+$ -catalyzed oxidations, one can calculate this constant to be  $2.4 \pm 0.2$  at  $\mu = 4.0$ , assuming  $\text{Ce}^{4+}$  is the predominant oxidant.

(26) G. Schwarzenbach, *Z. Elektrochem.*, **44**, 46 (1938); R. C. Splinter, S. J. Harris, and R. S. Tobias, *Inorg. Chem.*, **7**, 897 (1968).



and the duality of products would be accounted for.

In principle, both intermediates could be of type F; they might differ, for example, in the spin state of Co(II), but this extreme assumption would not explain the large differences in stoichiometry between 3- $\text{CH}_2\text{OH}$  and 4- $\text{CH}_2\text{OH}$  complexes, the differing stoichiometry for differing oxidants acting on the 4- $\text{CH}_2\text{OH}$  complex, nor the effect of deuteration on the stoichiometry observed for the 4- $\text{CH}_2\text{OH}$  complex. If it be assumed that radical  $\text{I}_1$  is a carbon radical precursor to state F, in effect Scheme II is being advocated for the 4- $\text{CH}_2\text{OH}$  complex, and the differing stoichiometry with different oxidants is unaccounted for. Furthermore, it would be difficult on this basis to understand the large difference shown in Table IX for  $k_{\text{R}2}/k_{\text{T}2}$  as calculated for the 4- $\text{CH}_2\text{OH}$  vs. the 3- $\text{CH}_2\text{OH}$  complex (note that the rates of loss of pyridine from the two complexes would not be expected to differ widely, and reoxidation by Ce(IV) would, if anything, be expected to be more rapid for the 4- $\text{CH}_2\text{OH}$  complex).

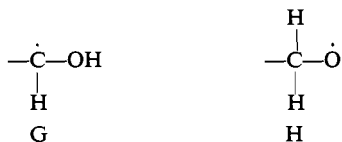
Apart from the role that a state such as F may play as intermediate  $\text{I}_1$  or  $\text{I}_2$ , it seems a reasonable possibility that the decay of a carbon-radical intermediate by internal electron transfer would produce Co(II) in a low-spin configuration, for example, as  $\text{Co}(\text{NH}_3)_5^{2+}$ . Reoxidation by an external oxidant at this stage would be expected to produce  $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ . A search was made for this or related extraneous species in all the oxidant systems, as well as when  $\text{O}_2$  at 1 atm or Cr(VI) was present, but none was detected. This finding, of course, does not prove that low-spin Co(II) is not produced during these reactions; the low-spin form may undergo electron rearrangement and/or loss of  $\text{NH}_3$  too rapidly to be trapped by the particular oxidants dealt with here.

On the basis of previous arguments, it seems probable that the differences in the two intermediates are solely a matter of ligand radicals. The similarity between the behavior of the pyridine-methanol complexes and that of the 4-hydroxymethylbenzoate complex, and the observed effects of deuteration suggest further that the two intermediates are generated on the alcohol functional group.

The Ce(IV) oxidation of the 4- $\text{CD}_2\text{OH}$  complex yielded isotope effects of  $3.4 \pm 0.2$  and  $1.8 \pm 0.2$  for production of  $\text{I}_1$  and  $\text{I}_2$ , respectively. The magnitude<sup>27</sup> of the observed isotope effects indicates that both  $\text{I}_1$  and  $\text{I}_2$  are generated by reactions that lead to  $\alpha$  carbon-hydrogen stretching in the transition state. However, the two intermediates show quite different reactivities toward internal reduction.

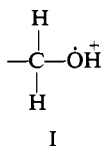
A likely candidate for the intermediate  $\text{I}_1$  is the carbon radical G. The species H is also a possible intermediate in alcohol oxidations. However, the failure to observe an effect of  $\text{D}_2\text{O}$  on the rates or stoichiometries of

(27) For a summary of kinetic isotope effect observed for the oxidation of alcohols and aldehydes, and a discussion of mechanisms, see T. J. Kemp and W. A. Waters, *Proc. Roy. Soc.*, **A 274**, 480 (1963).



the Ce(IV) oxidations, other than the effect of D<sub>2</sub>O on the first acid dissociation constant of Ce(IV), seems to argue against the latter species being produced in a rate-determining step.

A possible candidate for I<sub>2</sub> is the radical which would



be formed by the abstraction of an electron from the alcohol function. Internal electron transfer would be expected to be less rapid for such an intermediate than for a species such as G. The observed kinetic isotope effect on formation of I<sub>1</sub> ( $k_{\text{H}}/k_{\text{D}} = 1.8 \pm 0.2$ ) seems high, but not impossibly so for a secondary isotope effect. (Secondary isotope effects for formation of carbonium ions from alkyl halides by solvolysis are usually in the range  $k_{\text{H}}/k_{\text{D}} = 1.1\text{--}1.2$  per deuteron.<sup>28</sup>) The radical I may be rapidly and irreversibly converted to an alkoxy radical by a rapid deprotonation step, subsequent to its determining production, and the  $k_{\text{R}_2}/k_{\text{T}_2}$  ratios could equally well then refer to alkoxy radical intermediates.

The variation of the ratio  $k_1/k_2$  for the oxidants Ce(IV), Co(III), and Ag(II) reacting with the 4-CH<sub>2</sub>OH complex, the agreement between the ratios  $k_1/k_2$  for Ce(IV) and Ag(II) oxidizing the 3-CH<sub>2</sub>OH complex, and the agreement of the ratios  $k_1/k_2$  for Ce(IV) oxidation of both complexes could have mechanistic significance, but we have failed in our efforts to provide an explanation involving a satisfactorily small number of *ad hoc* assumptions. A particularly troublesome point is the difference between the behavior of the 4-CH<sub>2</sub>OH complex on the one hand and, on the other, the 3-CH<sub>2</sub>OH together with the 4-hydroxymethylbenzoato complex; for the 4-CH<sub>2</sub>OH but not the others,  $k_1/k_2$  is sensitive to the nature of the oxidant.

**Comparison of Rates of Internal Electron Transfer.** Independent of the nature of the intermediate, the coefficients  $k_{\text{T}_1}$  are expected to be nearly the same, regardless of whether I<sub>1</sub> is generated from the 4-CH<sub>2</sub>OH complex, the 3-CH<sub>2</sub>OH complex, or the 4-hydroxymethylbenzoato complex, and thus the ratios  $k_{\text{R}_1}/k_{\text{T}_1}$  should, to a close approximation, measure the relative rates of internal electron transfer for I<sub>1</sub>. A similar statement can, with equal force, be made with respect to I<sub>2</sub>.

The  $k_{\text{R}_1}/k_{\text{T}_1}$  ratios of Table IX show internal electron transfer for I<sub>1</sub> derived from the 4-CH<sub>2</sub>OH complex to be  $\gg 50$  times faster than that derived from the 3-

(28) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 24 (1963).

CH<sub>2</sub>OH complex. Assuming<sup>29</sup> that Ce(IV) reacts with these radicals with the rate constant of  $10^8 M^{-1} \text{sec}^{-1}$ , we conclude that I<sub>1</sub> for the 3-CH<sub>2</sub>OH complex persists for  $10^{-7}$  sec before reducing the Co(III) center. For the radical I<sub>1</sub> derived from the 1e<sup>-</sup> oxidation of 4-hydroxymethylbenzoatopentaamminecobalt(III), again only a limit on  $k_{\text{R}_1}/k_{\text{T}_1}$  can be set, and there is thus no basis for comparing carboxyl and pyridine nitrogen with respect to their efficiency as lead-in groups for electron transfer within the intermediate of type I.

The  $k_{\text{R}_2}/k_{\text{T}_2}$  ratios are also clearly greater for the 4-CH<sub>2</sub>OH complex than they are for the 3-CH<sub>2</sub>OH. The  $k_{\text{R}_2}/k_{\text{T}_2}$  ratios for the 4-CH<sub>2</sub>OH complex in 1 M HClO<sub>4</sub>,  $\mu = 1.0$ , can be compared to similar ratios obtained from the data of the 4-hydroxymethylbenzoato complex.<sup>2</sup> The difference is not large,  $(7 \pm 3) \times 10^{-3}$  for the pyridine derivative compared to  $1 \times 10^{-3}$  for the carboxylato complex. The comparison is not without complication,<sup>30</sup> however, because with carboxyl as lead-in group, the rate of internal electron transfer,  $k_{\text{R}_2}$ , may be acid dependent.

It is interesting that internal reduction of Co(III) by a remote radical is not much faster for pyridine nitrogen as a lead-in group than it is for carboxyl. The rate of Cr<sup>2+</sup> reduction of pentaamminecobalt(III) isonicotinic acid and terephthalato complexes ( $20^{31}$  and  $0.2 M^{-1} \text{sec}^{-1}$ ,<sup>32</sup> respectively) suggests that reduction by remote attack is much faster for pyridine nitrogen than it is for carboxyl as lead-in group. At present, this is the only comparison possible between the electron-deficient situation, as when an external oxidant generates a radical in a remote position, and the electron-excess situation, as when an external reductant attacks at a remote functional group. For the latter situation the rate of reduction of the Co(III) complex appears to be related to the rate of electron transfer to the ligand.<sup>33</sup> The single comparison which can be made from the present data suggests that the facility of electron transfer in the two situations is not necessarily parallel.

**Acknowledgment.** Financial support for this research by the National Institutes of Health, Grant No. GM 13638-02, and by the National Institutes of Health for predoctoral Fellowships, 1966-1968, to J. E. French, is gratefully acknowledged.

(29) O<sub>2</sub> reacts approximately 10 to 16 times more rapidly with the radicals than Ce(IV). If it is assumed that O<sub>2</sub> reacts at a diffusion-controlled rate, the rate of Ce(IV) reaction would be  $\sim 10^8 M^{-1} \text{sec}^{-1}$ .

(30) Robson<sup>2</sup> observed that their  $k_{\text{R}_2}/k_{\text{T}_2}$  ratios were relatively insensitive to acidity at constant ionic strength. To be consistent with the acid dependence of  $k_{\text{T}_2}$  observed in the present study,  $k_{\text{R}_2}$  for the carboxylato complex would have to be somewhat acid dependent. This would not be surprising considering that acid-dependent paths are often observed for reduction by remote attack of Co(III)-carboxylato complexes.

(31) F. Nordmeyer, private communication, 1968.

(32) E. Gould, *J. Amer. Chem. Soc.*, **87**, 4730 (1965). The rate of reduction of this complex includes that for attack by Cr<sup>2+</sup> on the coordinated carboxylato as well as attack on the remote carboxylic acid function. Comparison with rates of Cr<sup>2+</sup> reduction of other carboxylato complexes indicates such "adjacent" attack accounts for  $>50\%$  of the over-all observed rate.

(33) F. Nordmeyer and H. Taube, *ibid.*, **90**, 1162 (1968).