

tion of the amide grouping, $-\text{NHCOCH}_3$, should decrease the donor ability of the N atom resulting in loss of 1 mole of en to give structure iv. The presence of an extra HCl indicated by the analytical data could then be accounted for by association through H bonding to one of the donor N atoms or by formation of an adduct as in the well-known complex $\text{trans}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}\cdot\text{HCl}$.

There appears, therefore, to be some support for

structures i and iv in the formation of which reactions are assumed to occur at two anionic sites in *cis* positions which could be initially present in $[\text{Co}(\text{en}-\text{H})_2(\text{en})]\text{I}$ or might be formed by anionic site migration during the reactions.

Acknowledgments. This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

The Oxidation of *p*-Hydroxymethylbenzoatopentaamminecobalt(III) by One-Electron Oxidizing Agents

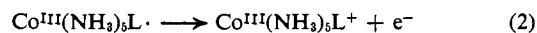
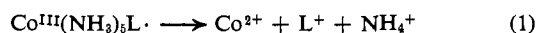
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Abstract: In the oxidation of *p*-hydroxymethylbenzoatopentaamminecobalt(III) by Ce(IV) in perchloric acid medium and by Co^{3+} in perchloric and sulfuric acid media both $[\text{Co}(\text{NH}_3)_5\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CHO}]^{2+}$ and Co^{2+}

are formed (with free *p*-formylbenzoic acid accompanying the latter product). The ratio of the Co(III) product to Co^{2+} ("product ratio") increases with the concentration of Ce(IV) when this is low but reaches a limiting value of about 1.2 at 25° when the Ce(IV) concentration is increased. The product ratio is not affected by the presence of O_2 when "saturation" with respect to Ce(IV) is reached, but it is increased by O_2 at low Ce(IV) concentration. The observations are interpreted on the basis that two radical intermediates are formed. For one of these, the external oxidant can interfere with internal electron transfer (the latter process gives rise to Co^{2+}), but for the other, internal electron transfer is so rapid that reaction with external oxidants does not compete effectively with it.

Other work¹⁻³ has shown that when the ligand L^- in a complex of the type $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{L}^-$ is oxidized by an external one-electron oxidizing agent, the Co(III) center may be reduced. When reduction of the Co(III) center does take place, it is of interest to learn whether the internal oxidizing agent Co(III) and the external oxidizing agent act in concert, or whether rate-determining attack by the external oxidizing agent takes place followed then by internal electron transfer. In the latter event an intermediate $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{L}\cdot$ would be formed, and competition between the processes 1 and 2 might be expected.

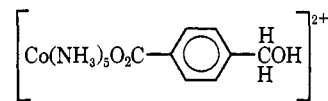


Equation 2 represents attack on the intermediate by an external oxidizing agent (which may but need not be the oxidizing agent used to generate the intermediate) preserving the oxidation state of Co(III). No evidence for successful competition of a process such as 2 against process 1 was found in the oxidation of coordinated oxalate² by Ce(IV), but the competition studies³ on the reaction of MnO_4^- with $\text{Co}(\text{NH}_3)_5\text{O}_2\text{CH}_2^{2+}$ pro-

vided clear-cut evidence for the formation of an intermediate in this case.

These reactions become particularly interesting when the ligand L^- bears an oxidizable group located at some distance from the carboxyl coordinated to Co(III). If a radical intermediate is formed, the ratio k_2/k_1 can be measured for a particular external oxidizing agent. It is of interest to compare these ratios for various locations of the oxidizing group. Measurements of this type can be considered to be complementary to those which have been done with reducing agents, attempting to reduce the Co(III) center by "remote attack." They can in principle be carried a step further so as to yield the actual value of k_1 , which is of course of interest in itself as measuring the rate of internal electron transfer. When the ratio k_2/k_1 is determined for a particular external oxidizing agent, and k_2 can be measured or estimated, k_1 can then be calculated. The strategy would be to use for the determination of k_2/k_1 not necessarily the one-electron oxidizing agent used for primary attack on the oxidizable ligand but one for which k_2 has been independently estimated.

We turned to the one-electron oxidation of

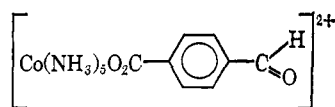


(1) P. Saffir and H. Taube, *J. Am. Chem. Soc.*, **82**, 13 (1960).

(2) R. T. M. Fraser and H. Taube, *ibid.*, **82**, 4152 (1960).

(3) J. P. Candlin and J. Halpern, *ibid.*, **85**, 2518 (1963).

as being a relatively simple system which might provide some of the opportunities discussed in the foregoing paragraph. The reaction of Ce(IV) and Co^{3+} with an alcohol function is fairly rapid, and the report² that



reacts only slowly with Ce(IV) encouraged us to believe that, with this oxidizing agent at least, the reaction stage involving oxidation of the alcohol function to the aldehyde could be isolated. Kinetic^{4,5} studies which have been published support the view that Ce^{IV} and Co^{3+} react with alcohols by one-electron changes.

Experimental Section

Materials. Ceric perchlorate solutions in aqueous perchloric acid were obtained by dilution of the solutions available from the G. F. Smith Chemical Co. which contained appreciable quantities of cerous ion. The ceric ion concentration was found to decrease slowly upon storage. It was determined immediately prior to use by titration with ferrous ion which was standardized at the same time against dichromate. The perchloric acid concentration was calculated from the concentrations of ceric ion (above), cerous ion, and total perchlorate. The total cerium content was determined by the method of Medalia and Byrne,⁶ and the total perchlorate content was determined gravimetrically as tetraphenylarsonium perchlorate.⁷

Cobalt(III) sulfate (solid), prepared electrolytically and handled as described by Moore and Waters,⁸ was dissolved in the appropriate quantity of standardized aqueous sulfuric acid at 0°. The cobalt(III) content was determined immediately prior to use by addition of an aliquot to an excess of standardized ferrous solution and back-titration with dichromate (in duplicate). Significant amounts of cobalt(II) were found in these solutions, and the total cobalt introduced thereby into reaction mixtures was determined by running the appropriate blanks alongside the reaction as described in the section dealing with results.

Cobalt(III) perchlorate solutions in aqueous perchloric acid were prepared *via* cobalt(II) carbonate as follows. A slight excess of a saturated aqueous solution of sodium bicarbonate was added with stirring to cobaltous sulfate in water. The precipitated solid was collected, washed well with water, and dissolved in the appropriate quantity of standardized aqueous perchloric acid. The resulting solution was electrolyzed at 0° using a platinum gauze anode and a copper sheet cathode, the two compartments being separated by a sintered-glass disk. After 5 hr electrolysis at a current of 0.3 amp, ca. 60% of the cobalt was in the +3 state. The cobalt(III) and cobalt(II) introduced into reaction mixtures were determined as described for cobalt(III) sulfate solutions.

Vanadium(V) Perchlorate Solutions. Reagent grade ammonium metavanadate was dissolved in ca. 50 times its weight of hot water. Perchloric acid was added to the cooled solution and the mixture made up to volume with distilled water. The vanadium(V) content was determined by the titrimetric method of Morette and Gaudefroy.⁹

Lithium Perchlorate. A 4 M solution of LiClO_4 for ionic strength adjustments was prepared from a weighed amount of lithium carbonate (reagent grade, Merck Co.) and a slight excess of perchloric acid. After the initial effervescence had ceased, the mixture was heated at 90° for some time to drive off all the CO_2 , cooled, and made up to the volume with water. The concentration of excess perchloric acid was determined by titration against standard

base. The unexpected but reproducible behavior observed when reactions between ceric ion and the *p*-hydroxymethylcobalt(III) complex were conducted in 1.5 M LiClO_4 from the above source was traced to the presence of sulfate ion. Therefore sulfate-free 4 M LiClO_4 was prepared from the above solution by adding $\text{Ba}(\text{ClO}_3)_2$ in twofold excess of the contained SO_4^{2-} , the barium sulfate precipitated thereby being removed by centrifuging.

Purification of Cation-Exchange Resins. Dowex AG 50W-X2 (200–400 mesh) and AG 50W-X4 (50–100 mesh) as supplied in the "purified" analytical reagent grade by Bio-Rad Laboratories were further purified as follows. The resin, after being stirred for 15 min with boiling reagent grade acetone which removed some pink material, was collected in a large sintered-glass Büchner funnel and washed with stirring in the funnel with the following: cold acetone repeatedly, distilled water repeatedly, 2 M HCl, 2 M NaOH, 2 M HCl, 2 M NaOH, distilled water repeatedly. The resin was then stirred with distilled water at 60° for 1 hr, filtered, and twice more extracted with water (60°) for 1 hr. Finally the almost colorless resin was washed several times with cold distilled water and stored under water in the dark.

***p*-Hydroxymethylbenzoic Acid.** *p*-Bromomethylbenzoic acid prepared by the method of Daub and Castle¹⁰ was heated for 3 hr under reflux with approximately four times its weight of aqueous methanolic sodium hydroxide ($\text{NaOH}:\text{CH}_3\text{OH}:\text{H}_2\text{O}$ (1:3:6)). The solution was cooled to 0° and acidified with concentrated HCl, and the precipitated solid was collected. Recrystallization from hot water and then from ethyl acetate afforded *p*-hydroxymethylbenzoic acid as colorless needles, mp 179–181° uncor; lit.¹¹ 181°.

***p*-Hydroxymethylbenzoatopentaamminecobalt(III) Perchlorate.** Finely ground sodium carbonate (2.86 g) and *p*-hydroxymethylbenzoic acid (9.13 g) were heated with redistilled ethylene glycol (80 ml) at 100° until all the carbonate had dissolved (ca. 10 min). After the solution had been cooled, finely powdered aquopentaamminecobalt(III) perchlorate (13.8 g), prepared as described by Butler,¹² was added and the mixture heated with stirring at 65–70° for 5 hr. The solvent was removed at 85° (high vacuum), and 1-propanol (100 ml) followed by 30% HClO_4 (10 ml) and isopropyl ether (100 ml) were added to the semisolid residue with vigorous stirring. The crystalline suspended solid (14.9 g) was collected, washed with ether, and dried. Repeated attempts at purification by recrystallization from aqueous perchloric acid failed to yield a sample with satisfactory elemental analysis. Recrystallization by very slow cooling, eventually to 5°, of a solution in the minimum volume of pure water at 40° produced *p*-hydroxymethylbenzoatopentaamminecobalt(III) perchlorate as large deep red needles, accompanied by a small quantity of a fine pink solid which was removed, after filtration, by washing with cold water. The remaining solid was washed with ethanol and ether and dried *in vacuo*.

Anal. Calcd for $\text{C}_8\text{H}_{22}\text{N}_5\text{O}_{11}\text{Cl}_2\text{Co}$: C, 19.45; H, 4.49; N, 14.17. Found: C, 19.21; H, 4.34; N, 14.33.

Reactions under Nitrogen. Air-free reactions were usually carried out on the 50-ml scale in a 100-ml three-necked reaction flask sealed by rubber serum caps and immersed in either a thermostatic bath maintained at $25 \pm 0.1^\circ$ or an ice-water bath. The deaerating stream of nitrogen was directed into solutions through stainless-steel hypodermic needles and solutions were transferred by purged hypodermic syringes fitted with stainless-steel needles.

Analytical Procedures Used for Product Distribution Studies. Absorption spectra were obtained with a Cary Model 14 recording spectrophotometer.

Determination of Cobalt(II). Kitson's spectrophotometric thiocyanate method¹³ required modification for successful application to reaction mixtures containing excess oxidant. In early experiments in which ceric ion was used, it was discovered that the excess oxidant could be destroyed merely by passing an aliquot of the mixture first into the specified¹⁴ quantity of concentrated HCl (a component of the usual spectrophotometric mixtures). Following thereafter the usual procedure¹⁴ resulted in a visible spectrum (550–650 m μ) with profile identical with that of cobalt(II) thiocyanate. However, known mixtures of ceric ion, the hydroxymethyl complex, and cobaltous ion upon treatment in this way gave cobalt(II) measurements as much as 20% high. Evidently intermediates (probably

(4) D. G. Hoare and W. A. Waters, *J. Chem. Soc.*, 965 (1962).

(5) J. S. Littler, *ibid.*, 4135 (1959).

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

(7) J. P. Hunt, Ph.D. Thesis, University of Chicago, 1950, p 65.

(8) D. G. Moore and W. A. Waters, *J. Chem. Soc.*, 971 (1962).

(9) A. Morette and G. Gaudefroy, *Bull. Soc. Chim. France*, 956 (1954).

(10) G. H. Daub and R. N. Castle, *J. Org. Chem.*, **19**, 1571 (1954).

(11) F. H. Case, *J. Am. Chem. Soc.*, **47**, 1144 (1925).

(12) R. D. Butler, Ph.D. Thesis, Stanford University, 1964, p 13.

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

(14) D. LaFollette, M.S. Thesis, Stanford University, 1964.

Table I. Comparison of Physical Properties of *p*-Formylbenzoic Acid from Various Sources

Sample	Melting behavior, °C	Equiv wt ^a	Spectral properties, λ_{\max} , $m\mu$ (ϵ_{\max})			
			Aq alkali	Aq acid	Hexane	Cyclohexane
As supplied by Aldrich	250–280°	146.6	258 (15,520)	255 (18,630)		
Twice recrystallized from water	250–260° (small quantity unmelted at 280°)	148.0	258 (16,150)	254 (19,270)		250 (20,700)
Ref 14	Ca. 250°				249 (12,750)	
Ref 15			257 (12,750)			

^a By potentiometric titration (theoretical 150.1).

chlorine atoms) liberated during the destruction of ceric ion are capable of attacking the hydroxymethyl complex with eventual production of cobalt(II). Hydrogen peroxide could not be used for destruction of excess oxidant because a small excess of peroxide produced interfering green colors upon addition of thiocyanate. A procedure which successfully circumvented these difficulties as demonstrated by accurate determinations of cobalt(II) in known mixtures of cobalt(II), ceric ion, and the hydroxymethyl complex was as follows.

An aliquot of the unknown was added to 2 ml of concentrated HCl plus 2 ml of a mixture of dioxane (3 vol.) and benzyl alcohol (1 vol.) in a 50-ml volumetric flask. The mixture was allowed to stand for a few minutes for complete destruction of ceric ion, and then the usual procedure¹⁴ was followed in which acetone, aqueous thiocyanate, and water were added up to the mark. The absorbance at 622 $m\mu$ (λ_{\max} for cobalt(II) thiocyanate) was used for spectrophotometric measurements. In routine analyses of reaction mixtures the above procedure was carried out in duplicate or triplicate, individual measurements never differing by more than 1%. That no species other than cobaltous thiocyanate were contributing to the observed absorption was demonstrated with each measurement by making up a "comparison solution" containing the same volume of reaction mixture and all the components except thiocyanate that were used for the spectrophotometric solution. The absorbance at 622 $m\mu$ of such "comparison solutions" never differed significantly from that of a freshly made up "blank solution" containing all the components except the aliquot of reaction mixture.

In the reactions in which Co^{3+} was used as the external oxidizing agent, the total cobalt (Co(II) + Co(III)) introduced by the cobaltic solution into reaction mixtures was determined as follows. The same volume of stock oxidant solution at 0° as was transferred to the reaction vessel to initiate the reaction was transferred to another vessel containing a volume of water at 0° so that the total volume became the same as that of the reaction mixture. Such comparison solutions were made up in duplicate alongside each run. Application of the above modified spectrophotometric thiocyanate method for cobalt(II) determination to aliquots of the comparison solutions gave the total cobalt content, the cobalt(III) being reduced quantitatively to cobalt(II) by the dioxane-benzyl alcohol mixture.

Determination of *p*-Formylbenzoic Acid. To an aliquot of the reaction mixture (containing 0.001–0.008 mmole of free *p*-formylbenzoic acid) diluted with ca. three times its volume of water was added 0.4 *M* NaOH until the pH of the mixture was near 4. The mixture was then passed down a column of 5 ml of purified (see above) Dowex Ag 50W-X4 cation-exchange resin in the sodium form which had been prepared immediately previously by passing distilled water until the effluent showed negligible absorption in the range 220–300 $m\mu$. The effluent was collected directly into a 250-ml volumetric flask, the sample being followed by washings from the beaker in which the pH adjustments had been made and then by distilled water until ca. 200 ml of effluent had been collected. The effluent was acidified with ca. 1 ml of 60% perchloric acid and then made up to volume with distilled water. The absorption spectrum in the range 220–300 $m\mu$ was recorded and from the absorbance at 254 $m\mu$ the concentration of *p*-formylbenzoic acid could be calculated using the extinction coefficient below. This procedure applied to a known mixture of *p*-formylbenzoic acid and ceric perchlorate gave the aldehyde content to within 2%.

For determination of extinction coefficients *p*-formylbenzoic acid as supplied by the Aldrich Chemical Co. was recrystallized twice from boiling water. Attempted further purification by sublimation *in vacuo* produced no improvement in the melting be-

havior (see Table I). Since our extinction coefficients were considerably higher than those quoted in the literature,¹⁵ the measurements and comparisons recorded in Table I were made. Since any nonacidic contaminants would increase the observed equivalent weight above the theoretical value of 150, we must conclude that our samples were contaminated by some acidic material of equivalent weight less than 150. The only likely contaminant of this nature which could be expected to resist selective removal by recrystallization and sublimation is terephthalic acid which has a higher melting point (360°) and lower extinction coefficients (ϵ_{254} (in acid) 10,600; ϵ_{258} (in alkali) 6000) than *p*-formylbenzoic acid. All the above evidence is consistent with contamination by terephthalic acid of both of our samples and also, to a larger extent, of those referred to in the literature. Therefore, although our figures are ca. 25% higher than those of LaFollette (in aqueous alkali) and ca. 15% higher than those quoted by Forbes (in hydrocarbon solvent), it seems likely that ours are still a little low.

Simultaneous Determination of *p*-Formyl- and *p*-Hydroxymethylbenzoatopentaamminecobalt(III). An aliquot of the reaction mixture containing a total of 0.005–0.02 mmole of +2 pentaamines diluted with three or four times its volume of distilled water was treated with an excess of sodium iodide to destroy the excess of oxidizing agent. Five milliliters of a 0.1 *M* aqueous solution of the disodium salt of ethylenediaminetetracetic acid was added followed by 0.4 *M* sodium hydroxide until the pH was 4.9–5.1. The mixture was made up to 100 ml with distilled water, and a 30-ml portion of the resulting solution was passed down a column of 1 ml of purified Dowex AG 50W-X2 in the sodium form. The mixture was followed up with 10 ml of 0.1 *M* EDTA disodium salt and then with distilled water until the effluent showed no absorption in the range 220–300 $m\mu$. By this procedure all species in the reaction mixture except substitution-inert cations were washed off the column. Fifty milliliters of 2 *M* HClO₄ was then passed down the column to remove the pentaamminecobalt(III) species, the effluent being collected and made up to the appropriate volume (usually 250 ml) with distilled water. From the absorbancies at 238 and 257 $m\mu$, the amounts of *p*-formyl and *p*-hydroxymethyl complexes could be calculated from the extinction coefficients given below on the assumption that these were the only species present (see Discussion section). These extinction coefficients at 238 and 257 $m\mu$ are 26.9×10^3 and 8.19×10^3 for the *p*-hydroxymethylbenzoato complex and 15.6×10^3 and 22.1×10^3 for the *p*-formylbenzoato complex.

The above procedure applied to a known mixture of *p*-hydroxymethyl complex, *p*-formyl complex, and a large excess of cerous ion gave the concentrations of both complex species to within 2.5%.

Determination of Unchanged Ceric Ion. The spectrophotometric method of Medalia and Byrne,⁶ based on the absorption in the 320–350- $m\mu$ region of ceric ion in the presence of 1 *N* H₂SO₄, was used. Beer's law plots at 320, 330, and 340 $m\mu$ gave good straight lines and the extinction coefficients: ϵ_{320} 5590 (cf. lit.⁶ ϵ_{320}), ϵ_{330} 5330, and ϵ_{340} 4770. It was demonstrated that large concentrations of cerous ion would not interfere in the above spectral range. In order to compensate for the absorption of pentaamminecobalt(III) species in reaction mixtures to be analyzed, comparison solutions were made up in exactly the same way as were the spectrophotometric solutions except that one drop of 30% H₂O₂ was added to destroy the ceric ion. Usually measurements were made at 330 $m\mu$, and spectrophotometric and comparison solutions were made up in duplicate.

(15) J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, 1362 (1958).

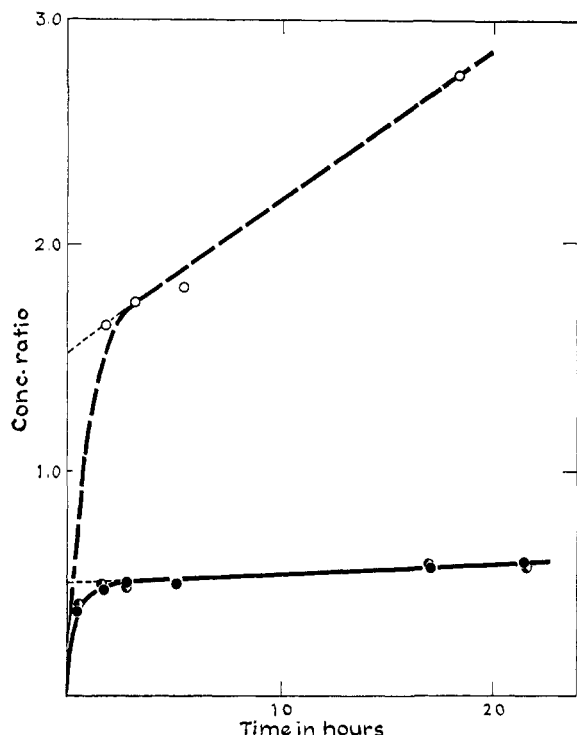


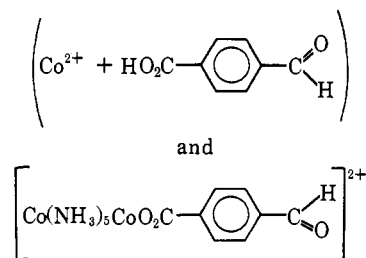
Figure 1. The stoichiometry as a function of time: - - -, ratio of Ce(IV) consumed to initial hydroxymethyl complex; —, ratio of Co^{2+} produced to initial hydroxymethyl complex. $[\text{Hydroxymethyl complex}]_0 = 6.9 \times 10^{-3} M$; $[\text{Ce(IV)}]_0 = 29.1 \times 10^{-3} M$, $[\text{HClO}_4] = 1 M$; ionic strength = 1.00; $25 \pm 0.1^\circ$.

Results

Over-all Features of the Reaction with Ce(IV) as Oxidant. In Figure 1 are summarized the results of experiments in which the production of Co^{2+} and the consumption of Ce(IV) were measured as a function of time. Experiments were done both with air present and air removed, with no significant difference in the yield of Co^{2+} . A white solid begins to form at *ca.* 15 hr. It was collected after 21.5 hr, washed with water, and dried. The infrared spectrum (KBr disk) of the solid was found to be a composite of those of authentic *p*-formylbenzoic and terephthalic acids, and the band intensities suggest that the two components were present in roughly equal amounts. Application of the ion-exchange technique to a portion of the reaction mixture again after 21.5 hr yielded an eluate with an ultraviolet spectrum (λ_{max} 257 $m\mu$, λ_{min} 230 $m\mu$) almost identical with that of the *p*-formyl complex (λ_{max} 257 $m\mu$, λ_{min} 228 $m\mu$) and quite different from that of either the *p*-hydroxymethyl or *p*-carboxy complexes. The absorbance at 257 $m\mu$ indicated a yield of 34% of the *p*-formyl complex, but small quantities of other Co(III) complexes were undoubtedly present as well; thus note that the ratio of the optical densities at the maximum compared to the minimum was observed to be 1.8 as compared to 1.6 for the *p*-formyl complex.

The shape of the curves representing Co^{2+} production and Ce(IV) consumption suggests that the first step of the reaction, namely, the oxidation of the alcohol function to the aldehyde, is complete under the conditions of the experiment after *ca.* 2 hr. If the curves representing the progress of the reactions in the second

stages are extended to zero time, the stoichiometry corresponding to the first phase is 0.52 mole of Co^{2+} produced from each mole of the Co(III) complex and 1.58 moles of Ce(IV) consumed. If Ce(IV) is consumed only in producing



consumption of 1.48 moles of Ce(IV) would be expected. There is excess consumption of Ce(IV) even in the first stage, and this can reasonably be attributed to the process which gives rise to excess consumption in the later stage. The conclusions on the relative yields of Co^{2+} compared to the *p*-formyl complex were confirmed in an experiment at 25° with $[\text{Ce(IV)}]_0$ at $19.1 \times 10^{-3} M$, $[\text{Co(III)}]_0 = 2.44 \times 10^{-3} M$, $[\text{HClO}_4] = 1 M$, carried out with air present. After 63 min the concentrations of the initial complex, the *p*-formyl complex, Co^{2+} , and *p*-formylbenzoic acid were found to be 0.064×10^{-3} , 1.12×10^{-3} , 1.15×10^{-3} , and $1.11 \times 10^{-3} M$, respectively. In this case, however, the consumption of Ce(IV) was *ca.* 60% higher than corresponds to the production of the products as stated above.

Continued production of Co^{2+} and consumption of Ce(IV) in the second stage of the reaction take place much more rapidly than was expected on the basis of the report by Fraser and Taube² to the effect that there is no observable reaction between the *p*-formyl complex and cerium(IV) perchlorate after 3 days at room temperature. A direct experiment was performed to examine the reaction of Ce(IV) with the *p*-formyl complex, the results being shown in Table II. The

Table II. Reaction between Ce(IV) and *p*-Formylbenzoatopentaamminecobalt(III)^a

Time, hr	$\Delta[\text{Co}^{2+}]/[\text{Co(III)}]_0$	$-\frac{\Delta[\text{Ce(IV)}]}{[\text{Co(III)}]_0}$
2	0.79	0.57
5	0.138	2.06
23.5	0.292	6.03

^a $[\text{Ce(IV)}]_0 = 19.1 \times 10^{-3} M$, $[\text{Co(III)}]_0 = 2.68 \times 10^{-3} M$, $[\text{HClO}_4] = 1 M$; $25.0 \pm 0^\circ$; air present.

consumption of Ce(IV) is much in excess of that needed for the oxidation of the aldehyde to acid. Blank experiments showed that Co^{2+} catalyzes the oxidation of water by Ce(IV), but this reaction is too slow to account for the observed excess consumption of Ce(IV). It is likely that the excess consumption results from a partial process in the oxidation of the *p*-formyl complex or free *p*-formylbenzoic acid in which the aromatic ring is ruptured. Each such event could then account for the consumption of several molecules of Ce(IV).

Table III. Dependence of Product Distribution upon Ceric Concentration^a

Initial Ce(IV)	Initial hydroxy-methyl complex	Concentration, mM					Reaction time	Cobalt ^b balance, %	Oxidant ^c balance, %	Product ratio ^d
		Final Ce(IV)	Co(II) produced	<i>p</i> -Formyl-benzoic acid produced	<i>p</i> -Formyl complex produced	Unchanged hydroxy-methyl complex				
2.28	3.60	0.24	0.958	0.958	0.470	2.07	~3 hr	2.7 low	93	0.49
2.30	3.54	0.19	0.868	0.854	0.408	2.12	~3 hr	3.5 low	80	0.47
8.29	3.54	4.48	1.21	...	1.10	1.26	60 min	1.0 high	90	0.91
25.8	3.55	20.9	1.23	...	1.49	0.962	25 min	3.7 high	86	1.21
31.4	3.56	26.7	1.21	...	1.49	0.889	23 min	0.5 high	89	1.23

^a Air excluded. $[\text{HClO}_4] = 1 \text{ M}$, $\mu = 1$, $25.0 \pm 0.1^\circ$. ^b Sum of observed cobalt(II) produced plus *p*-formyl complex produced plus *p*-hydroxymethyl complex unchanged compared with initial *p*-hydroxymethyl complex. ^c Ceric consumption theoretically required by observed cobalt(II) and *p*-formyl complex formed expressed as a percentage of the observed Ce^{4+} consumption. ^d The product ratio is defined as the ratio of the *p*-formyl complex formed to Co^{2+} formed, and the term will be used in the text with this meaning.

Dependence of Product Distribution upon Ceric Ion Concentration. The results of a study of the dependence of the product distribution upon oxidant concentration in the absence of air are summarized in Table III and diagrammatically in Figure 2.

In Figure 2 the results of the experiments are represented by horizontal lines, the lengths of which correspond to the range of ceric ion concentrations from the beginning to the end of each experiment. For convenience a curve is drawn through the midpoints of the horizontal lines.

Dependence of Product Distribution upon Acid Concentrations. The results of a study of the product ratio (*cf.* footnote *d*, Table III) as a function of acid concentration at ionic strength 2.0 in the absence of air are summarized in Table IV. Referring to the first four experiments of the table, it is clear that the product ratio is independent of acid in the range 1.0 to 2.0 *M*, but at lower acid concentration the product ratio increases somewhat. The increase though small must, in view of the precision of the results, be regarded as real. A significant comparison can be made of the data of Table IV with those of Figure 2. The product distribution is little affected by the change in ionic strength from 1 to 2; at ionic strength 2 in 1 *M* acid with a ceric concentration range of $1.89 \times 10^{-3} \text{ M}$ (initially)–0 *M*, the product ratio is 0.38, in accord with the data shown in Figure 2.

The last two experiments of Table IV were done using LiClO_4 solutions which had not been freed from SO_4^{2-} . The level of SO_4^{2-} as quoted by the manufacturer corresponds to approximately one SO_4^{2-} for each Ce(IV) ; the removal of SO_4^{2-} does have a small but significant effect on the product distributions.

Comparison of Product Distributions Obtained upon Oxidation of *p*-Hydroxymethylbenzoatopentaamminecobalt(III) Ion at 0° with Ceric Perchlorate, Aquocobalt(III) Perchlorate, and Aquocobalt(III) Sulfate. Effect of Radical Traps. The results of product distribution studies with three oxidants at low oxidant concentration are summarized in Table V. The main results which emerge from this study are the following.

(a) All three oxidants at low oxidant concentration in the absence of oxygen under comparable conditions of ionic strength and acidity produce roughly equal amounts of cobalt(II) and *p*-formyl complex.

(b) The product distributions in reactions with the cobalt(III) oxidants at low oxidant concentration and

at 0° show sensitivity to the presence of air. This was noted for ceric perchlorate at low ceric concentration and at 25°. Thus, at $1.9 \times 10^{-3} \text{ M}$ Ce(IV) in the pre-

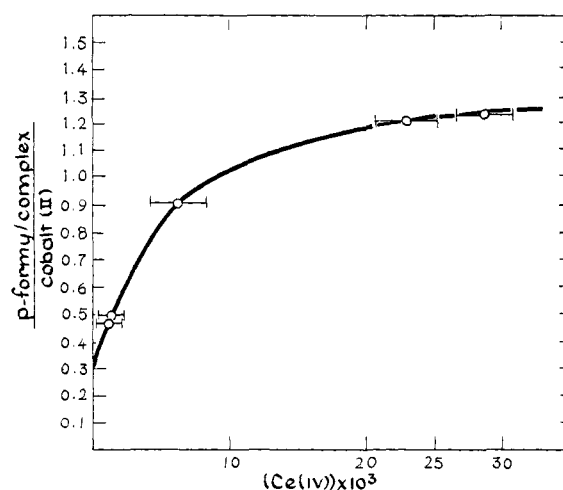


Figure 2. Dependence of product distribution on Ce(IV) concentration: $[\text{hydroxymethyl complex}]_0 = 3.5 \times 10^{-3} \text{ M}$; 25° ; $[\text{HClO}_4] = 1 \text{ M}$; $\mu = 1.0$.

sence of air, the product ratio was observed to be 0.81; according to the results of Table IV, under the same conditions in the absence of air, the ratio is 0.38.

(c) By comparison with the appropriate data in Table III it can be seen that the product ratio in the case of ceric ion at low concentration is quite sensitive to temperature (1.0 at 0°, ~0.5 at 25°).

An experiment was also done with $\text{Hg}(\text{ClO}_4)_2$ as a possible radical trap¹⁶ but, unfortunately, before the sensitivity of the product ratio to the presence of air at low Ce(IV) concentration was appreciated. For the experiment, $[\text{Co(III)}]_0 = 4.20 \times 10^{-3} \text{ M}$, $[\text{Ce(IV)}]_0 = 1.94 \times 10^{-3} \text{ M}$, $[\text{HClO}_4] = 1 \text{ M}$, $[\text{Hg}^{2+}] = 0.2 \text{ M}$, at 25°, while for the comparison experiment all conditions were the same except that the mercuric salt was omitted. For the blank after 21 hr, at which time Ce(IV) is completely consumed, 17.9% of the cobaltic complex was found as Co^{2+} , 14.5% as the *p*-formyl complex, and

(16) W. A. Waters and J. S. Littler, *J. Chem. Soc.*, 1299 (1959); A. F. Drummond and W. A. Waters, *ibid.*, 2836, 3119 (1953).

Table IV. Dependence of Product Distribution on Acid Concentration^a

HClO ₄ , M	Sulfate, M	Concentration, mM							Unchanged hydroxy- methyl complex	Cobalt complex, ^{b,c} %	Oxidant balance, ^b %	Product ratio ^d
		Initial Ce ⁴⁺	Final Ce ⁴⁺	Initial hydroxy- methyl complex	Co(II) produced	<i>p</i> -Formyl- benzoic acid	<i>p</i> -Formyl complex					
2.0	0	1.892	0	4.05	1.080	...	0.414	2.414	2.0	101	0.38	
1.5	0	1.892	... ^e	4.07	0.938	0.920	0.356	2.712	1.5	... ^e	0.38	
1.0	0	1.892	... ^e	4.06	1.028	1.022	0.384	2.624	0.8	... ^e	0.38	
0.5	0	1.892	... ^e	4.05	0.870	0.856	0.394	2.774	0.3	... ^e	0.45	
0.5	~2 × 10 ⁻³ ^f	1.894	0.25	4.10	0.67	...	0.414	2.852	1.5	97	0.54	
0.5	~2 × 10 ⁻³ ^f	1.894	0.28	4.06	0.77	0.734	0.404	2.862	0.5	98	0.53	

^a Initial ceric concentration = 1.89 × 10⁻³ M; initial hydroxymethyl complex = 4.06 × 10⁻³ M; reaction time ~3 hr; 25 ± 0.1°; μ = 2.0; air excluded. ^b As for Table III. ^c All values low. ^d See footnote d, Table III. ^e Slight excess of Ba²⁺ interfered with spectrophotometric determination of Ce⁴⁺ as sulfato complex by producing milkiness. ^f Sulfate added as impurity in LiClO₄ solution.

Table V

Oxidant		Concentration, mM										Product ratio
		Initial oxidant	Final oxidant	Initial hydroxy- methyl complex	Re- action time	Co(II) ^a pro- duced	<i>p</i> -Formyl- benzoic acid	<i>p</i> -Formyl complex	Un- changed hydroxy- methyl, complex	Cobalt ^b bal- ance, %	Oxi- dant ^c bal- ance, %	
Cobalt(III) perchlorate in 1 M HClO ₄	Air present	2.85	0	4.22	1.5 days	0.64	0.70	1.32	2.17	2.1 low	115	2.1
	Air excluded	2.99	0	4.10	16.5 hr	1.17	1.06	1.00	1.99	1.5 high	105	0.85
Cobalt(III) sulfate in 0.94 M H ₂ SO ₄	Air present	2.27	0	4.22	16.5 hr	0.7 ^d	...	1.13	2.58	... ^d	...	~2.5
	Air excluded					-0.5						
	(1)	2.47	0	4.05	37 hr	0.85	0.80	0.94	2.21	1.2 low	111	1.1
	(2)	2.49	0	4.25	18 hr	0.83	0.78	0.93	2.44	1.9 low	108	1.1
Ce ^{IV} (ClO ₄) ₄ in 1 M HClO ₄	Air excluded	2.28	0.46	3.59	2 days	0.53	0.51	0.55	2.38	3.6 low	89	1.0

^a The cobalt(III) referred to in this column is that in excess of the total cobalt introduced with the oxidant solution, *i.e.*, only the cobalt(II) liberated from the initial hydroxymethyl complex. ^{b,c} See corresponding footnotes in Table III. ^d In this experiment it was found that the apparent cobalt(II) produced (see footnote a) decreased from *ca.* 0.7 mm/l. after 13-hr reaction time to *ca.* 0.5 mm/l. after 22 hr. After a further day it was unaltered. A possible explanation for this behavior is that the oxidizing solution which was prepared by electrolysis of a cobalt(II) solution (rather than *via* solid cobalt(III) sulfate as in the air-free reactions) may have contained some persulfate (D. G. Hoare and W. A. Waters, *J. Chem. Soc.*, 971 (1962)). The persulfate then decayed slowly in the reaction mixture requiring ~20 hr for total destruction, and any unchanged persulfate interfered with the thiocyanate determination of cobalt(II) giving high results. Moreover, the difference between initial pentaammine and the sum of the observed *p*-formyl and *p*-hydroxymethyl complexes (after 16.5 hr) was 0.51 mm/l. which agrees well with the above assumption that 0.5 mm/l. was the "true" cobalt(II) concentration. In any case the important result is clear merely from consideration of the *p*-formyl complex produced, namely, that in the presence of oxygen a considerably higher proportion of *p*-formyl complex is produced than in the absence of oxygen.

62.5% was the original form, and the product ratio was 0.81. In the experiment with Hg²⁺ present, the conversion to Co²⁺ was significantly less and corresponded to 15.2% of the original complex. It is likely that if oxygen had not been present, the sensitivity of the products to Hg²⁺ would have been found to be considerably greater.

Attempted Reactions with Other Oxidizing Agents. In an attempted reaction between ceric sulfate (17.6 mM) and the hydroxymethyl complex (2.98 mM) in 0.5 M H₂SO₄, no hint of cobalt(II) production was observed after 24 hr at 25°.

In an attempted reaction between vanadium(V) perchlorate (40 mM) and the hydroxymethyl complex (2.0 mM) in perchloric acid (~0.8 M), no cobalt(II) production and no diminution in vanadium(V) were observed after 1 day at 25°.

Discussion

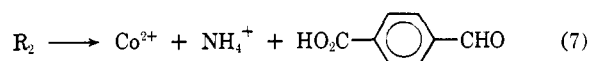
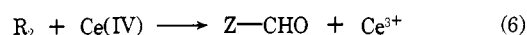
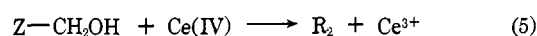
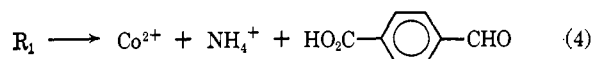
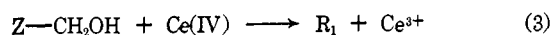
The most striking feature of our data is that although the product ratio (*p*-formylbenzoate)/(CO²⁺) does increase with [Ce(IV)] in the low range of [Ce(IV)], the ratio does not increase indefinitely, but reaches a limiting value of *ca.* 1.2–1.3 (*cf.* Figure 2). Consistent with this is the observation that the presence of air increases the product ratio when [Ce(IV)] is low but not when it is high. The simple mechanism involving a single intermediate and represented by reactions 1 and 2 thus needs to be modified to explain the results.

The results can be accounted for if two intermediates are invoked. It is assumed that for one of these, external oxidizing agents such as Ce(IV), O₂, or Hg²⁺ can compete effectively against internal electron transfer, and for the reaction of this intermediate the product ratio increases with the concentration of the external

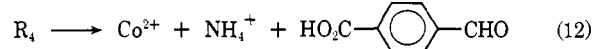
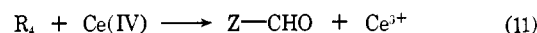
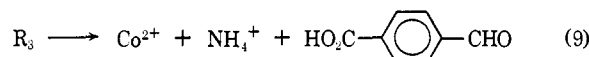
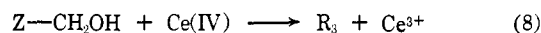
oxidizing agent as required by reactions 1 and 2. For the other intermediate we require that further reaction with external oxidizing agent does not compete effectively against internal electron transfer. The fraction of the reaction which proceeds by way of the second intermediate can be calculated from the limiting value of the product ratio at high Ce(IV), and for the conditions of the experiments summarized in Figure 2, it is 0.44.

An important question to settle before we inquire into the nature of the two intermediates is the following: are they formed by independent parallel processes as in Scheme I or do they have a common origin as in Scheme II?

Scheme I



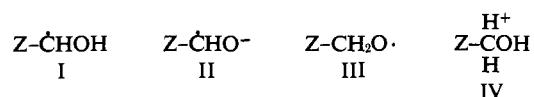
Scheme II



The fact that the product ratio is relatively insensitive to the identity of the oxidizing agent (*cf.* Table V) argues strongly in favor of Scheme II. In Scheme I the ratio in which the two intermediates are formed should depend on the nature of the oxidizing agents; Ce(IV) in ClO_4^- , Co^{3+} in ClO_4^- , Co^{3+} in SO_4^{2-} acting by this scheme yielded nearly the same product ratios. In Scheme II, the ratio in which the two intermediates is formed is independent of the oxidizing agent. Scope is left in this scheme for some effect on the product ratio of the chemical individuality of the oxidizing agent as in the competition between reactions 11 and 12, but, since reaction 11 may well take place almost at the diffusion-controlled rate, the influence is expected to be small. Though we can hardly claim that we have proven that Scheme II operates, it is strongly favored by the evidence which has been cited. In the following, we will therefore assume that Scheme II operates. Many of the suggestions which will be made as to the identity of the two intermediates are independent of whether Scheme I or II is assumed.

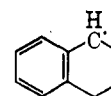
We are unable, on the basis of present evidence, to propose a unique or perhaps even satisfactory assign-

ment of structures to the radicals. Four candidates which might come up for consideration are



It is unlikely that III can be either R_3 or R_4 . R_3 must undergo rapid internal electron transfer, to the virtual exclusion of reacting further with external oxidizing agents. The internal electron-transfer process is not expected to be rapid for III both because the odd electron is isolated from the conjugated system by the carbon and because the process is likely not favored energetically (note that it would lead to highly oxidized oxygen). Acting in the role of R_4 , III would be required to act rapidly with O_2 , in competition again with internal electron transfer. Neither reaction is reasonable for III compared to the alternative that this high-energy radical would be converted to a carbon radical by inter- or intramolecular H-atom transfer. We conclude, therefore, that the alkoxy radical does not play a role in the processes we are considering.

A reasonably consistent description of the observations can be given if II is assigned the role of R_3 and I the role of R_4 . Internal electron transfer is expected to be more rapid for II than for I (note that internal transfer in I leaves the positive charge behind). Conversely I is expected to react more rapidly with O_2 than does II. Carbon radicals, unless they are already very highly oxidized, are known to react rapidly with O_2 . The radical



has been shown¹⁷ to react with O_2 in a hydrocarbon solvent at a specific rate of $6.8 \times 10^{-7} M^{-1} sec^{-1}$. The radical $C_6H_5\dot{C}HOCH_2C_6H_5$ is closely related to I; though the rate of reaction with oxygen is not known, the kinetics do require¹⁸ a very high specific rate for the process. By contrast, the available evidence suggests that ketyl-type radicals related to II react much more slowly than the corresponding radicals protonated in oxygen. No reference has been found to thorough kinetic measurements on such systems, but we have noted that in a qualitative study it was found¹⁹ that the reaction between the benzophenone radical anion and oxygen in tetrahydrofuran solution is observably slow.

The scheme is wanting, however, in an important respect. It does not appear entirely reasonable that two protons will be lost when one-electron oxidizing agent attacks the alcohol function, as is required if we select II for R_3 . If IV is chosen as the primary product of the electron-transfer process, although we now have a species which is expected to be resistant to attack by external oxidants, it is expected to be resistant also to internal electron transfer. Proton loss must be

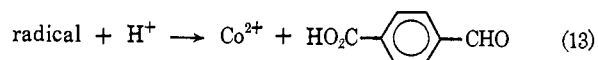
(17) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc. (London)*, **A198**, 252 (1949).

(18) L. Debiais, P. Horstman, M. Niclaude, and M. Letort, *Compt. Rend.*, **239**, 587 (1954).

(19) A. Le Berre and P. Goasguen, *Bull. Soc. Chim. France*, 1840 (1963).

assumed either to make internal transfer possible or to form R_4 . If we let proton loss from carbon represent the formation of R_4 , the only alternative is proton loss from oxygen to form III. Arguments have already been presented which tend to rule out the alkoxy form as an intermediate. These arguments may, however, not be entirely valid. It is perhaps possible that the alkoxy form undergoes proton loss, this being coupled to electron transfer. If this is so, it could play the role of R_3 .

Irrespective of the nature of the intermediate which shows competition between internal electron transfer and further reaction with external oxidant, the data do lead to an estimate of the specific rate of the internal electron-transfer act. If the specific rate for the reaction of O_2 with R_4 is assumed to be $10^7 M^{-1} \text{sec}^{-1}$ (i.e., of the order of that observed for the tetralin radical with O_2), for reaction 12 to be competitive with it its specific rate must be $\sim 10^4 M^{-1} \text{sec}^{-1}$ (note that the solubility of oxygen in air-saturated water at 25° is ca. $10^{-3} M$). Even if the reaction of O_2 with the radical is assumed to be diffusion controlled, or ca. $10^{10} M^{-1} \text{sec}^{-1}$, the specific rate for reaction 13 would be of the order only of $10^7 M^{-1} \text{sec}^{-1}$, and the lifetime of the



radical, when the external oxidant does not intervene, would therefore be ca. 10^{-7} sec. The internal electron-transfer process is therefore not extremely rapid and requires some activation of the intermediate radical. This feature makes it likely that $(\text{NH}_3)_3\text{Co}^{(\text{III})}$ or some similar group can be a very useful probe in exploring the mechanism of oxidation of functions suitably connected to the polar group bearing the oxidizing center. It is likely that the Co(III) group, at least when the function being oxidized is several bonds removed, affects the oxidation processes at that group only by virtue of its charge, and not by acting as an oxidizing agent in concert with the external oxidizing agents. The effect of the charge on the rates can be explored by kinetic studies, and the suggestion made can be tested by substituting for Co(III) a substitution-inert ion which cannot readily undergo reduction in the way Co(III) does.

Acknowledgment. Financial support by the National Institutes of Health, Grant GM 13638-01, is gratefully acknowledged.

The Mechanism of Electrophilic Reactions of Carbon-Metal Bonded Platinum(II) Complexes. A Comparison between Transition and Post-Transition Organometallic Compounds

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Contribution from the Istituto di Chimica Generale dell'Università di Padova, Padua, Italy. Received June 19, 1967

Abstract: Kinetic data for the reactions of *trans*-[Pt{P(C₂H₅)₃}₂(CH₃)X] (X = Cl or I) with hydrogen chloride in methanol to give *trans*-[Pt{P(C₂H₅)₃}₂ClX] are reported. The reactions obey the following rate law: rate = $(k_2[\text{H}^+] + k_3[\text{H}^+][\text{Cl}^-])[\text{complex}]$. A two-step mechanism is proposed involving the formation of labile platinum-(IV) intermediates of the type [Pt{P(C₂H₅)₃}₂(CH₃)(H)XY] (X = Cl or I; Y = Cl or solvent) followed by slow elimination of methane and rearrangement to *trans*-[Pt{P(C₂H₅)₃}₂ClX] in the rate-controlling step. A comparison of electrophilic reaction mechanisms of post-transition and transition metal-carbon compounds is presented.

It is known that d^8 transition metal ion complexes (e.g., of Rh(I),¹ Ir(I),² and Pt(II)^{3,4}) are active catalysts in the homogeneous hydrogenation of unsaturated compounds containing olefinic and acetylenic linkages,⁵⁻⁸ and labile species with metal-to-hydrogen

(1) J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Commun.*, 131 (1965).

(2) L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.*, **87**, 4970 (1965).

(3) R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stober, *ibid.*, **85**, 1691 (1963).

(4) J. C. Bailar and H. Itatani, *ibid.*, **89**, 1592 (1967).

(5) M. F. Sloane, A. S. Matlack, and D. S. Breslow, *ibid.*, **85**, 4014 (1963).

(6) J. Halpern, *Ann. Rev. Phys. Chem.*, **16**, 103 (1965).

(7) R. S. Nyholm, "Proceedings of the 3rd International Congress on Catalysis, Vol. 1, North Holland Publishing Co. Amsterdam, 1965, p 25; see also J. Halpern, *ibid.*, p 146.

(8) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., Sect. A*, 1711 (1966).

bonds have been postulated as intermediates in these processes. These catalytic reactions, in fact, quite often involve transfer of hydrogen to an olefin via a metal-hydrido species. For example, the activation of RhCl_3 , which occurs during rhodium-catalyzed olefin addition reactions, is claimed to proceed through a process which consists of an oxidation of the Rh(I) (obtained from Rh(III) in a preliminary step) by a proton (especially from HCl) to a hydridorhodium(III) complex which then coordinates an olefin to give a alkylrhodium(III) species.⁹ This process, as well as other d^8 -catalyzed reactions, involves an oxidative addition of hydrogen chloride to a four-coordinated planar complex followed by a coordination of the

(9) R. Cramer, *J. Am. Chem. Soc.*, **87**, 4717 (1965); **89**, 1633 (1967).