Reduction of *p*- and *m*-Formylbenzoatopentaamminecobalt(III) by Metal Cations

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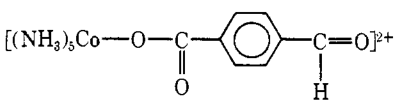
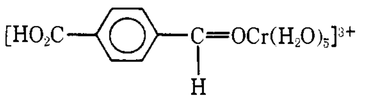
Abstract: In the reduction of *p*-formylbenzoatopentaamminecobalt(III) by Cr(II) an intermediate is produced, which on the basis of its absorption characteristics in the near uv (λ_{max} at ~290 nm with an extinction coefficient close to that of the free ligand) is assigned the structure [p-HO$_2$CC$_6$H$_5$CH=OCr(H$_2$O)$_5$]$^{3+}$ (I). The complex is quite labile, aquating to form free ligand and Cr(H$_2$O)$_6{}^{3+}$. The rate of aquation is insensitive to the concentration of acid in the range 0.40–1.00 *M;* the specific rate governing the reaction is ~24 sec^{-1} at 25°. The present results confirm the conclusion that the *p*-formylbenzoato complex is reduced by Cr(II) by remote attack, reached earlier on the basis of less direct evidence. The specific rate of the redox reaction at 25° is $(53 + 3.8 \times 10^2\ [\text{H}^+])\ M^{-1}$ sec^{-1}. When the *m*-formylbenzoato complex is reduced by Cr(II) at 25°, 55% of the ligand appears free and the remainder is bound to Cr(III) as a carboxylate complex. The specific rate for adjacent attack, 0.14 M^{-1} sec^{-1} at 25°, is in the range expected on the basis of measurements with related species. The portion of the reaction producing free ligand probably involves remote attack. The specific rate, 0.17 M^{-1} sec^{-1}, governing the rate by this path is much less than for the *p*-formylbenzoato complex (53 M^{-1} sec^{-1} at 25°) and, in contrast to the behavior of the latter system, the rate law for reducing of the *m*-formylbenzoato complex does not show a term first order in [H$^+$].

Early in the history of the study of oxidation–reduction reactions in which organic groups mediate in the electron transfer act, behavior was described[2] for *p*-formylbenzoate (PFB) which showed it to be unusual among the class of organic groups which had then been studied. In the reaction of Cr(II) with carboxylatopentaamminecobalt(III) complexes only for PFB as the carboxylate was the ligand found free in solution after electron transfer, rather than being contained in the Cr(III) product. The conclusion that PFB is not trapped in the course of the redox reaction was confirmed by LaFollette[3] and it was strengthened by the report[4a] that *p*-benzoylbenzoate as ligand shows like behavior. The special chemistry of ligands of this kind has been ascribed[2,3,4a] to attack by Cr(II) on the remote carbonyl function and to the resulting aldehydic or ketonic complex being labile.

The rate law for the reaction of Cr(II) and *p*-formylbenzoatopentaamminecobalt(III)



has been shown to feature prominently a term which is first order in [H$^+$] as well as a term independent of [H$^+$].[4a] The appearance in the rate law of the term first order in [H$^+$] and the unusually large value of the rate coefficient for the acid-independent term compared to that of the corresponding term when benzoate is the ligand have been cited as evidence supporting attack by Cr(II) on the remote carbonyl of the ligand.[4a] These arguments and the observations already mentioned, based on product identification, though suggestive of an inner sphere mechanism involving remote attack do not take the place of direct evidence on the mechanism of the redox reactions. We have undertaken a reinvestigation of the system, using the stopped flow technique, to search for the transient intermediate, I, which is expected to form if reaction takes place by remote attack. At the same time, we thought it worthwhile to devote some attention to the system with *m*-formylbenzoate (MFB) as the ligand, amplifying the work on this system which had previously been done by LaFollette. We also wished to extend our observations for both oxidizing complexes to include measurements with other reducing metal ions.



I

Experimental Section

Reagents. The purification of water used as solvent, the preparation of the reagents LiClO$_4$, Cr^{2+}, V^{2+}, and Ru(NH$_3$)$_6{}^{2+}$, and the associated analytical procedures have been described or referred to elsewhere.[4b]

Europium(II) was prepared by reducing dried Eu(III) oxide with zinc amalgam in perchloric acid solution. The reducing power was determined by the reaction of excess bromopentaamminecobalt(III) with Eu(II) followed by analysis for Co(II) produced.

p-Formylbenzoic acid (PFB) was obtained as the solid acid from Aldrich Chemical Co. and was used without further purification.

m-Formylbenzoic (MFB) acid was synthesized according to the method described by LaFollette[3] based upon a preparation of the para isomer.[5] *Anal.* Calcd for C$_8$H$_6$O$_3$: C, 64.0; H, 4.00. Found: C, 64.0; H, 4.01.

The immediate source of Co(III) was solid aquopentaamminecobalt(III) perchlorate which was synthesized from carbonatopentaamminecobalt(III) nitrate and perchloric acid according to Nordmeyer's procedure.[6] The carbonato complex was synthesized as described by Basolo and Murmann.[7] *Anal.* Calcd for [Co(NH$_3$)$_5$CO$_3$](ClO$_4$)$_2$: Co, 12.8; H, 3.73; N, 15.2; Cl, 23.1. Found: Co, 12.7; H, 3.50; N, 14.9; Cl, 22.5.

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[1] Postdoctoral Fellow, Australian National University, 1970–1972.

[2] (a) R. T. M. Fraser, *J. Amer. Chem. Soc.*, **83**, 2239 (1961); (b) R. T. M. Fraser, *ibid.*, **83**, 4920 (1961).

[3] D. J. LaFollette, M.S. Thesis, Stanford University, 1964.

[4] (a) E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964); (b) A. Zanella and H. Taube, *ibid.*, in press.

[5] R. H. Miller and O. Griswold, *J. Amer. Pharm. Ass.*, 42, 367 (1953).

[6] F. Nordmeyer, Ph.D. Thesis, Stanford University, 1967.

[7] F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1953).

All cobalt analyses were done by Kitson's method,[8] using Nordmeyer's modification which involves using perchloric in place of hydrochloric acid.

In a typical synthesis of *p*-formylbenzoatopentaamminecobalt(III) perchlorate, 0.020 mol of $[(NH_3)_5CoOH_2](ClO_4)_3$ and 0.060 mol of PFB were dissolved in 215 ml of dimethylformamide (DMF) (both compounds are readily soluble). Sodium carbonate (0.030 mol) was added and nitrogen was passed through to minimize oxidation of the aldehyde by molecular oxygen, and to provide for stirring. A hot water bath was used to maintain the temperature between 65 and 75°. As the reaction proceeded, the solution changed from deep red to violet and finally to purple.

In order to isolate the desired product, the mixture was cooled to room temperature, filtered, and placed on a rotary evaporator to remove the DMF. When the solution reached a consistency of viscous syrup, absolute ethanol (250 ml in 50-ml portions) was added with stirring to cause precipitation. The mixture was filtered. and the product, which was an amorphous pink solid, was washed with more ethanol and dissolved in 400 ml of water. Free ligand readily precipitated and was removed by filtration. The solution was then saturated with solid $LiClO_4 \cdot 2H_2O$ to precipitate the cobalt complex, which was washed with ethanol and then ether and dried in a vacuum desiccator overnight. The yield was about 50% based on the $[(NH_3)_5CoOH_2](ClO_4)_3$ used. *Anal.* Calcd for $[Co(NH_3)_5C_8H_5O_3](ClO_4)_2 \cdot H_2O$: Co, 11.6; C, 18.8; H, 4.32; N, 13.7. Found: Co, 11.6; C, 19.45, 19.28; H, 4.15, 4.38; N. 13.7, 14.1.

The analysis agrees somewhat better with a hydrated rather than an anhydrous form of the solid. The slightly high value for carbon is ascribable to a slight contamination by free ligand.

Ion exchange analysis showed a barely detectable trace of 3+ charged material, either aquopentaamminecobalt(III) or the corresponding DMF complex.

m-Formylbenzoatopentaamminecobalt(III) perchlorate was prepared from the aquo complex and MFB by the procedure described for the PFB complex. Because the ligand was not easily prepared, the synthesis of the complex was on a smaller scale. A typical preparation involved 0.0044 mol of aquopentaammine complex and 0.014 mol of MFB. The yield was about 71%. The complex salt was found to contain a considerable amount of free MFB. Ion exchange analysis showed that only one Co(III) species was present and that it was of 2+ charge. The spectral characteristics agreed with La Follette's description. Instead of repeated recrystallization, extraction with ether was used to remove free ligand. A concentrated solution of the complex in 100 ml of water was prepared and then extracted ten times with equal volumes of ether. Residual ether was removed by rotary evaporation. The concentrated cobalt solution was diluted to a convenient volume and used as stock. Cobalt analysis was performed to determine the concentration of complex.

In both systems, ligand is released during the reaction. No kinetic anomalies are noted which are attributable to the free ligand concentration increasing during the reaction. For this reason and the added one that the results were the same for different samples of starting material, we dismiss catalysis by free ligand as being a significant factor in our results.

Ion Exchange Methods. Dowex 50W-X2 cation exchange resin, hydrogen form, 200–400 mesh, sized and purified by Bio-Rad Co., was used. The resin was further purified as described by Deutsch[9] and stored under water in the dark until use. Small Pyrex columns, 1.2 cm in diameter, were used for analytical purposes. The resin was rinsed with copious amounts of water before being charged with an analytical sample. In particular, for analyses depending on uv spectra, the water rinses were monitored until the peak at 220 nm essentially disappeared. The usual eluent for cobalt and chromium species was lithium perchlorate ranging from 0.5 to 3.0 *M* and acidified to about pH 2. In testing for ionizable protons either an acetic acid–sodium acetate buffer at pH 4.6 and ionic strength of 0.6 *M* or a boric acid–sodium borate buffer at pH 7.3 containing 0.92 *M* chloride, 1 *M* sodium ion was used.

Analyses. Analyses for C, H, N, and Cl were done by the Microanalytical Laboratory, Chemistry Department, Stanford University.

In one experiment aldehyde group analysis was performed by conversion to the 2,4-DPNH derivative. The species analyzed by this method were *m*-formylbenzoic acid and its pentaaquochromium(III) complex. The method is a colorimetric one described by Lappin and Clark.[10] French[11] found that the analysis was valid for aldehyde species coordinated to a metal center.

Free PFB was analyzed in dilute aqueous mineral acid by using the maximum at 254 nm with an extinction coefficient of $1.93 \times 10^4\ M^{-1}\ cm^{-1}$ as determined by Robson.[12]

MFB was analyzed as the anion in aqueous NaOH or LiOH by using the maximum at 248 nm (ϵ $1.02 \times 10^4\ M^{-1}\ cm^{-1}$).

Spectra. Visible and ultraviolet spectra were taken on a Cary 14 or Cary 15 recording spectrophotometer fitted with thermostated cell compartments regulated by external constant temperature baths.

Nmr spectra were run on a Model T-60 or A-60, manufactured by Varian Associates. The ambient temperature was approximately 37°.

Kinetics. The apparatus was constructed by Stritar[13] based on a design by Dulz and Sutin.[14] The reactants and mixing chamber could be thermostated over a limited range, 12–35°, and either a visible or a uv light source was available. Reactions were followed at one wavelength during each mixing event. Reactant solutions including acid and supporting electrolyte were usually made up in 250-ml volumetric flasks and then transferred to special 500-ml, round-bottom flasks which incorporated provision for deoxygenating the contents using oxygen-free nitrogen. Chromium(III) solutions were deoxygenated for 1 hr before zinc amalgam was added (about 100 g). The solutions were left to reduce for at least 1 hr. The Co(III) solutions were deoxygenated for at least 1 hr before mixing with the reductant. The temperature was stabilized at least 1 hr before mixing. A blanket of nitrogen was kept over both solutions during the entire experiment.

Ordinary Mixing Experiments. Reactions were followed on the Cary 14 or 15 at one wavelength during each run. The Co(III), supporting electrolyte, and acid were measured by pipet into 5- or 10-cm cells fitted with serum caps, and the solution was deoxygenated using nitrogen passed through syringe needles. The cells and solutions were then thermostated at the selected temperature for at least 1 hr. The reducing agent solution was prepared in a serum bottle, thermostated, and transferred to initiate reaction. All-glass syringes with detachable stainless steel needles were used for the transfers. Immediately after mixing, the cells were placed in the spectrophotometer and the absorbance change was recorded. The stoichiometry experiments described below show that handling and delivering the reductant was quantitative.

For the kinetic studies done at 4.0° involving the PFB complex, a special thermostating device as described by Barrett[15] was used. This allowed for immersion of the reaction cells in the cooling water.

Product Studies. In general, ion exchange methods were used for the separation of the components of product solutions. Organic acids such as PFB were washed through the resin with water, collected, and analyzed as already described. The various metal ion species retained on the resin were eluted, characterized, and analyzed as described above.

Stoichiometry of Redox Reactions. Several determinations of stoichiometry were performed with Cr(II) as the reductant and a Co(III) complex as the oxidant. A known amount of Cr(II) was mixed with an excess of oxidant and allowed to react completely. The product solution was then diluted and the Co(II) content was determined.

Treatment of Kinetic Data. Most kinetic experiments were done under first-order or pseudo-first-order conditions, but in several instances second-order conditions were used. For the stopped flow data a treatment was applied which is described by Stritar.[13] For the systems featuring a two-term rate law, namely an acid-dependent term and a term independent of acid concentration, the two rate constants were determined by a least-squares line fit of the second-order constant plotted against the hydrogen ion concentration. Activation parameters as defined by the transition-state theory were also calculated using a least-squares line fit.

A least-squares computer program was written by J. Malin in Basic and was operated from a remote time-sharing terminal linked to the IBM 360/67 at the Stanford University Computational Center. For the purpose of estimating errors, a 50% confidence limit was always assumed and the corresponding Student t value was inserted into the program.[16]

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[8] R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).

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

[10] G. R. Lappin and L. C. Clark, *Anal. Chem.*, **23**, 541 (1951).

[11] J. E. French, Ph.D. Thesis, Stanford University, 1968.

[12] R. Robson and H. Taube, *J. Amer. Chem. Soc.*, **89**, 6487 (1967).

[13] J. A. Stritar, Ph.D. Thesis, Stanford University, 1967.

[14] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

[15] M. Barrett, Ph.D. Thesis, Stanford University, 1967.

[16] H. A. Latimer, "Chemical Analysis," McGraw-Hill, New York, N. Y., 1960, p 546.

For the treatment of the data involving formation of the intermediate observed in the reduction of the PFB complex, a program designed to analyze consecutive first-order reactions, written by Stritar,[13] was used. The program was written in Algol and run on a Burroughs B5500 at the Computational Center.

Results

Spectra. The PFB complex shows a maximum at 503 nm (ϵ 83.5 M^{-1} cm^{-1}), a shoulder at 340 nm (105), and a maximum at 257 nm (22.5 × 10^3); for the MFB complex maxima are observed at 503 (78.1) and 344 nm (79.0). The absorption for the PFB complex at 257 nm is ascribable largely to the ligand (the values of ϵ for free ligand at the uv maxima for the free acid and anion are 19.3 × 10^3 and 16.2 × 10^3, respectively.)[12] The MFB complex undoubtedly would show corresponding absorption, but the measurements for it stopped short of the region in question.

MFB in the acid form shows maxima at 244 (9.9 × 10^3) and 218 nm (31.0 × 10^3) and in the anion form at 248 (10.2 × 10^3) and 288 nm (1.2 × 10^3). The values determined by us are some 15% higher than those recorded by LaFollette.[3] It appears that the ligands, PFB and MFB, as used by LaFollette, were contaminated by impurities, presumably the corresponding dicarboxylic acids.

Proton nmr measurements (temperature 37° in D_2O and in DMSO) were made to determine the extent of hydration of the aldehyde group in the complexes. In several cases D_2SO_4 was added to study the effect of acid on the spectra. The complexes as well as the free ligands in acid form are much more soluble in DMSO than in D_2O. The ligands in fact are so sparingly soluble in D_2O as to preclude nmr measurements on them in this medium.

The data are summarized in Table I. In no case was a signal ascribable to a hydrate form observed. Price[17] found the hydrate proton in glyoxylatopentaamminecobalt(III) at δ 5.2. If the integral recorded for MFB in DMSO is used as a calibration, it appears that less than 10% of the complexed ligand is converted to the hydrate form in water at ~37°. Adding acid broadened the CHO proton signals and, for the PFB complex, broadened also the ring proton signals significantly but did not produce a noticeable shift. The broadening is ascribable to exchange with a hydrate form. The fact that little shift occurs supports the view that only a small fraction of the complexed ligands is converted to hydrate in solution.

Table I. Summary of Pmr Results on Complexes and Ligands

Compd[a]	Solvent	CHO[c]	Integral of CHO[b]
PFB	DMSO-d_6	10.1	
MFB	DMSO-d_6	10.1	0.89
RoPFB^{2+}	DMSO-d_6	10.1	0.84
RoPFB^{2+}	D_2O	10.0	0.85
RoPFB^{2+}	D_2O/D^+	10.0	
RoMFB^{2+}	D_2O	10.0	0.83
RoMFB^{2+}	D_2O/D^+	10.0	

[a] Ro refers to the pentaamminecobalt(III) group. [b] Relative to ring proton integral, theoretical value is 1.00. [c] Relative to TMS or SDSS, in ppm.

Chromium(II)–*p*-Formylbenzoatopentaamminecobalt(III) Reaction. Stoichiometry. The experiments on redox stoichiometry were done at a twofold excess of Co(III). With the Co(III) complex at 1.5 × 10^{-3} M, the ratio ΔCo(II)/ΔCr(II) was observed as 0.97 and 0.99 at 1.00 and 0.037 M [H$^+$], respectively.

LaFollette[3] reported that ligand was quantitatively released during the reaction over a range of acid concentration and temperature. His experiments were all done with Cr(II) in excess, thus giving ample opportunity for ligand release catalyzed by Cr(II). If the reaction is done with Co(III) in excess, reorganization of a primary product by Cr(II) will be minimized, and it seemed important to check on the chemistry under such conditions. In a series of three experiments with [H$^+$] = 0.045 M and with the pairwise values of [Co(III)] and [Cr(II)] (×10^3) as (5.2, 3.3), (8.9, 4.2), and (8.9, 3.9), the percentage of ligand released on reduction was found to be 101, 101, and 104, respectively. Ion exchange experiments showed $Cr(H_2O)_6^{3+}$ to be the only form of Cr(III) product.

Rate Data. The measurements of rate at 4.0° were done by ordinary mixing techniques, using the Cary 14 spectrophotometer at 503 nm. In these experiments the concentration of Co(III) and Cr(II) were roughly equivalent. The data were found to conform to the rate law

$$d[\mathrm{Co(III)}]/dt = -k[\mathrm{Cr(II)}][\mathrm{Co(III)}] \qquad (1)$$

over at least 90% extent of reaction, and this provides a test of the validity of the rate law in describing the effect on the rate of changing [Cr(II)] and [Co(III)]. The results of the experiments at 4.0° are summarized in Table II.

Table II. Chromium(II) and *p*-Formylbenzoatopentaamminecobalt(III) at 4.0° and μ = 1.1 ($LiClO_4$)

[H$^+$], M	[Co(III)], M × 10^4	[Cr(II)], M × 10^4	k_7, M^{-1} sec^{-1}
0.0080	4.45	5.35	41.6
0.0080	4.45	5.28	38.5
0.051	4.00	4.83	45.9
0.051	3.99	5.14	53.9
0.150	3.88	4.68	90.8
0.150	4.29	5.19	88.8

The experiments at higher temperatures were done on the stopped flow apparatus under pseudo-first-order conditions with Cr(II) in excess and are summarized in Table III. Each experiment provides a stringent test of rate law (1) insofar as it describes the variation of rate with [Co(III)]. No systematic deviations from pseudo-first-order rate behavior were observed for observations extending to 95% consumption of Co(III). The results of the last experiment recorded in Table III at 25° and [H$^+$], in comparison with others obtained under the same conditions but at [Cr(II)] fourfold higher, provide a test of rate law (1) in respect to the dependence of rate on [Cr(II)] as a variable.

In agreement with the results of earlier work,[4a,18] the rate is observed to be strongly dependent on [H$^+$], the values of k conforming to the relation

$$k = k_0 + k_h[\mathrm{H}^+] \qquad (2)$$

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(17) H. J. Price and H. Taube, *J. Amer. Chem. Soc.*, **89**, 269 (1967).

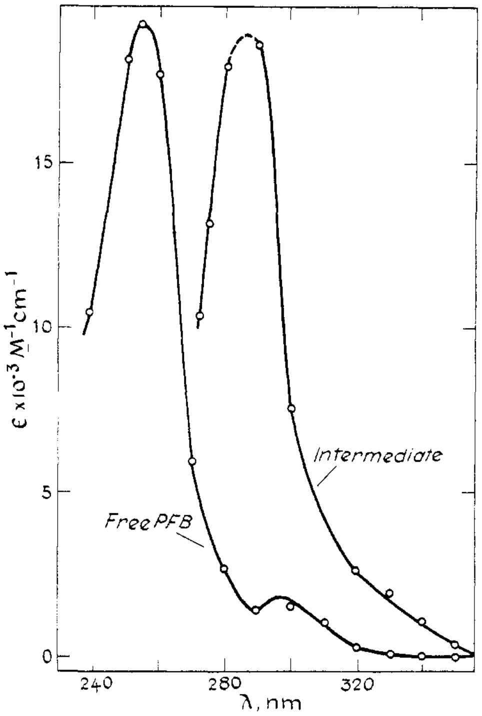

Figure 1. Absorption spectrum of the intermediate as determined using the stopped flow apparatus.

Table III. Kinetic Data on the Reaction of Cr(II) with *p*-Formylbenzoatopentaamminecobalt(III)[a]

[H$^+$], M	k, M^{-1} sec^{-1} 15.0°	25.0°	33.0°
0.015	55	58	65
0.067	76	75	84
0.166	107	104[b]	134
		125	
0.265	147	144	183
0.413		217	
0.513		268	
0.760	320	325	390
	344		389
0.91	359	389	438
1.00	426	418	471
1.00		448	487
1.00		430[c]	

[a] λ 503 nm; μ = 1.1 (LiClO$_4$); [Co(III)] = 6.0 × 10^{-4} M; [Cr(II)] = 1.20 × 10^{-2} M. [b] [Co(III)] = 6.7 × 10^{-4} M; [Cr(II)] = 1.30 × 10^{-2} M. [c] [Co(III)] = 3.0 × 10^{-4} M; [Cr(II)] = 0.30 × 10^{-2} M.

The values of the coefficients k_0 and k_h derived from the present work are summarized in Table IV. Those at 25° agree within experimental error with earlier results,[18] but there is disagreement on the variation of k_h with temperature. The present work covering a much wider range in temperature than the earlier shows k_h to be rather insensitive to changes in temperature.

Intermediate Species. When the reduction of the Co(III) complex is observed at 320 nm on the stopped flow apparatus, the absorbance is seen first to rise rapidly and then to fall. Since the final products have a lower absorbance at 320 nm than do the reactants, the behavior described shows that a reactive intermediate is produced in the course of the reaction. It was found possible to account for the observations by consecutive processes, one being the growth of the intermediate governed by the rate of reduction and the other its decay by a first-order process. The results obtained in analyzing the data according to this prescription are summarized in Table V, where k_i is defined by

Table IV. Summary of Rate Data for the Reaction of the PFB Complex with Cr(II) as a Function of Temperature

T, 0°C	k_0, M^{-1} sec^{-1}	k_h × 10^{-1} M^{-2} sec^{-1}
4.0	35 ± 4	36 ± 4
15.0	50 ± 13	36 ± 2
25.0	53 ± 14	38 ± 2
33.0	63 ± 9	42 ± 1
$\Delta H^{\ddagger}$, kcal mol^{-1}	2.7 ± 0.6	0.3 ± 0.3
$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	−42 ± 2	−46 ± 1

$$d[\mathrm{Int}]/dt = k_i[\mathrm{Int}] \tag{3}$$

Table V. Rate Constants for the Decomposition of the Intermediate Species, μ = 1.1

T, °C	[H$^+$], M	[Co(III)], M × 10^4	[Cr(II)], M × 10^3	nm	k_i, sec^{-1}
25.0	1.00	3.0	6.0	320	20.3[b]
25.0	1.00	3.0	6.0	310	17.6
25.0	1.00	3.0	6.0	300	22.9
25.0	1.00	3.0	6.0	320	35.1
25.0	1.00	3.0	3.0	320	24.9
25.0	1.00	3.0	3.0	320	25.4
25.0	1.00	3.0	3.0	290	28.5
25.0	0.76	6.0	12.0	320	16.8
25.0	0.76	6.0	12.0	320	20.6
25.0	0.51	6.0	12.0	320	27.0
25.0	0.41	6.0	12.0	320	29.6
15.0	1.00	3.0	6.0	320	26.5
12.0	1.09	3.0	100[a]	320	45.4
25.0	1.09	3.0	100[a]	320	71.3[c]
25.0	1.09	3.0	100	320	59.6

[a] Ionic strength = 1.6 M. [b] Average value at 25° and [Cr(II)] between 3.0 and 1.0 × 10^{-3} M is 24.4 sec^{-1}. [c] Average at 25° and [Cr(II)] = 0.100 is 60 sec^{-1}.

The decay rate of the intermediate is independent of the concentration of acid and of [Cr(II)] over a limited concentration range, but acceleration in the decay reaction is noted at high values of [Cr(II)]. It is very unlikely that the increase in ionic strength, occasioned by increasing [Cr(II)] to 0.10 M, can account for the acceleration in question. The rate of decay of the intermediate is rather insensitive to temperature, either at high or at low values of [Cr(II)].

An approximate spectrum of the intermediate was gotten by changing the wavelength at which observations were made on the stopped flow apparatus. For these experiments, the concentrations of H$^+$ and Cr(II) were made high, 1.09 and 0.100 M, so as to produce the intermediate at the highest, convenient concentration. Under these conditions, the maximum concentration of intermediate appeared after 1 half-life in the redox reaction. Approximate graphical methods were used to extrapolate the observations for the decomposition of the intermediate back to zero time. The spectrum of the intermediate is shown in Figure 1. The maximum appears at *ca.* 290 nm and the maximum extinction coefficient in this region is close to that observed for the free ligand, being approximately 1.9 × 10^4 M^{-1} sec^{-1}.

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(18) E. S. Gould, *J. Amer. Chem. Soc.*, 87, 4730 (1965).

Vanadium(II)-*p*-Formylbenzoatopentaamminecobalt(III). The reaction was studied over a range of acidity at a single temperature (25.0°) and ionic strength = 1.1, with V(II) in excess. The results are summarized in Table VI.

Table VI. Reduction of *p*-Formylbenzoatopentaamminecobalt(III) by V(II)[a]

$[H^+]$, M	k, M^{-1} sec^{-1}	$[H^+]$, M	k, M^{-1} sec^{-1}
1.00	1.11	0.30	0.96
1.00	1.11	0.30	0.93
0.70	1.07	0.10	0.93
0.70	1.05	0.097	0.87

[a] [Co(III)] = 1.1×10^{-3} M; [V(II)] = 2.5×10^{-3} M; temperature = 25.0°; ionic strength ($LiClO_4$) = 1.1 M; λ = 503 nm.

The variation of rate with $[H^+]$ is represented by the equation $k = 0.88 \pm 0.03 + (0.24 \pm 0.04)[H^+]$. The results are in reasonable agreement with those of Fraser,[16] who reports k at 25°, $\mu = 1.0$ ($NaClO_4$), to be $(0.57 + 0.17)[H^+]$.

Eu(II)-*p*-Formylbenzoatopentaamminecobalt(III). The results for this system are summarized in Table VII.

Table VII. Reduction of *p*-Formylbenzoatopentaamminecobalt(III) by Eu^{2+} [a]

$[H^+]$, M	k, M^{-1} sec^{-1}	$[H^+]$, M	k, M^{-1} sec^{-1}
0.11	1.12	0.98	1.39
0.11	1.12	0.98	1.40
0.50	1.21	0.98	1.39
0.50	1.21		

[a] Temperature = 25°; λ 503 nm; μ = 1.1; [Co(III)] = 1.0×10^{-3} M; [(Eu(II)] = 1.7×10^{-3} M.

The variation of k with $[H^+]$ conforms to the equation $k = 1.08 \pm 0.02 + (0.31 \pm 0.03)[H^+]$.

$Ru(NH_3)_6^{2+}$-*p*-Formylbenzoatopentaamminecobalt(III). The complex $Ru(NH_3)_6^{2+}$, unless oxidation is slow compared to loss of NH_3, is constrained to react by an outer sphere mechanism, and for this reason it seemed of interest to examine the rate of reduction by this reagent as a function of $[H^+]$. Unfortunately, the kinetic behavior was complicated, the values of k increasing with time, and as a result hope of dealing effectively with the point of interest was given up. In one experiment with $[H^+]$, $[Cl^-]$, [Co(III)], and [Ru(II)] at 0.050, 0.10, 1.0×10^{-3}, and 1.96×10^{-3} M, respectively, k as determined from initial rates was 0.035 M^{-1} sec^{-1}; in a second, with the same variables at 0.076, 0.018, 3.9×10^{-3}, and 3.0×10^{-3} M, k was determined as 0.015 M^{-1} sec^{-1}. The acceleration of the rate may be a result of acid-induced aquation of the ruthenium complex.[19]

Chromium(II) *p*-Formylbenzoate. Gould[18] reported that the reaction of Cr(II) with free PFB is slow. To make possible comparisons of the rate of reduction of free ligand and the cobalt complex, we undertook a study of the kinetics of free ligand reduction. The reaction was followed at 320 nm, where the extinction coefficient of the ligand is 330 M^{-1} cm^{-1} and where the reaction products have much weaker absorption.

For all the experiments, the initial concentration of the organic ligand was 4.5×10^{-4} M and the temperature 25°. In a series of experiments with $[H^+]$ in the range 0.50–0.56 M, k ($\equiv -d \ln [Cr(II)]/dt$) at $[Cr(II)]_0$ = 0.10, 0.050, and 0.0085 was observed as 3.5×10^{-4}, 2.2×10^{-4}, and 1.4×10^{-4} sec^{-1}, respectively. If the data are regarded as reflecting the rate law

$$-d[Cr(II)]/dt = [Cr(II)][PFB](k_1 + k_2)[Cr(II)] \quad (4)$$

k_1 is calculated to be 2.8. In another series of experiments with $[Cr(II)]_0$ = 0.10 and with $[H^+]$ varying from 0.090 to 1.0 M, k was found to decrease from 4.7×10^{-4} to 3.0×10^{-4}. No supporting electrolyte was used, and in the series the ionic strength increased from 0.70 to 1.6. The data, though imperfect, do show that the reduction of the ligand in the acid form is much less sensitive to $[H^+]$ than is the reduction of the cobalt complex.

Chromium(II)-*m*-Formylbenzoatopentaamminecobalt(III). Stoichiometry. In five experiments, three at 1.00 M $[H^+]$ and two at 0.05 M $[H^+]$, and with $[Co(III)]_0$ and $[Cr(II)]_0$ for the series 2.8×10^{-3} and 1.8×10^{-3} M, respectively, the ratio of Co(II) produced to Cr(II) consumed was measured as 0.97, 0.92, 1.00, 1.00, and 1.00.

LaFollette[3] found that at 25° about 55% of the ligand was set free in the course of the redox reaction. This feature of the stoichiometry is especially significant, and it seemed important to investigate it further, varying the concentration of H^+, Co(III), and Cr(II) as well as the temperature. Our results are summarized in Table VIII; those at 25° are in excellent agreement with those obtained by LaFollette. They go beyond his in demonstrating that release of ligand is insensitive to the concentrations of Co(III) and Cr(II) used in the experiments, showing that the observations are not affected significantly by processes involving catalysis by Cr(II). Other experiments, which are not reported in detail,

Table VIII. Release of MFB in the Reduction of *m*-Formylbenzoatopentaamminecobalt(III) by Chromium(II)

$[H^+]$,[a] M	[Co(III)], $M \times 10^3$	[Cr(III)], $M \times 10^3$	% MFB released
	T = 25°		
1.00	1.92	7.06	55.3
1.00	1.92	35.4	57.2
1.00	1.66	35.4	62.0
1.00	1.66	17.7	59.2
1.00	2.01	15.2	55.8
0.156[d]	4.32	7.35	55.5
0.086[e]	4.80	4.10	56.5
0.050	1.66	2.65	50.2
0.050	1.66	35.4	55.5
			Av +56.4 ± 3.0
	T = 45°		
1.00	5.52	3.28[b]	48[c]
1.00	5.52	3.11	48
	T = 5°		
1.00	5.52	3.05[b]	78
1.00	5.52	3.39	80

[a] Maintained at 1.0 M unless otherwise noted. [b] Determined by cobalt(III) analysis. [c] Runs at 45° were corrected for the significant amount of MFB from aquation of cobalt complex. [d] μ = 0.23 M. [e] μ = 0.13 M.

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(19) P. C. Ford, J. Retz, J. R. Kuempel, and H. Taube, *Inorg. Chem.*, 7, 1976 (1968).

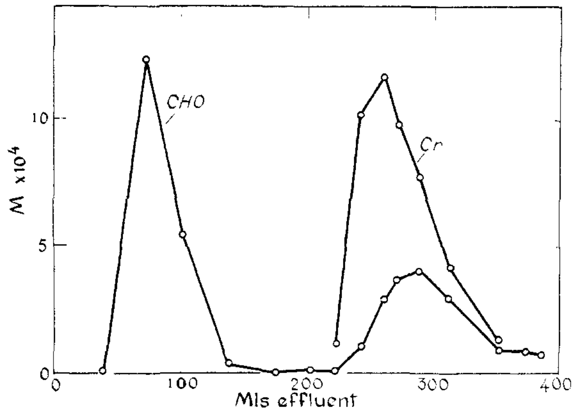

Figure 2. Elution characteristics of the products of the reaction of Cr(II) with the MFB complex.

showed that spontaneous loss of ligand under the experimental conditions is so slow (*e.g.*, in 1 *M* [H$^+$] at 25° the free ligand increases from 55% at the end of the redox reaction to 81% after 1.5 months) as not to affect the observations.

An effort was made to separate the Cr(III) products using cation exchange resins with little success, the Cr(III) bearing the organic ligand being found to move at about the same rate as does $Cr(H_2O)_6^{3+}$ despite the fact that the charge on the species is 2+. The method of Connick and Cady[20] was used to determine the charge per chromium in the colored band eluted from the column. Values of +2.40 and +2.65 were obtained, indicating that a roughly equimolar mixture of $Cr(H_2O)_6^{3+}$ and carboxylate-bound MFB complex was being eluted. In other experiments, analyses for aldehyde and for total chromium were done on successive volumes of column eluent. The results are shown graphically in Figure 2. They demonstrate that some aldehyde washes through early in the elution process and that the remainder is retained, emerging from the column together with Cr(III). In this particular experiment, 61% appeared as free aldehyde and most of the remainder is accounted for in the Cr(III) band. Recovery is not quite quantitative owing to tailing in the recovery of the Cr(III) complex. The maximum in the bound aldehyde peak appears somewhat later than the maximum in the Cr(III) peak, indicating that the MFB complex moves somewhat slower than does $Cr(H_2O)_6^{3+}$.

Kinetics. The results on the variation of the rate of reduction of the MFB complex by Cr(II) as a function of the concentration variables and temperature are summarized in Table IX.

Our results are in good agreement with LaFollette's at 25°, who reported *k* as 0.27 M^{-1} sec^{-1}, using $NaClO_4$ to maintain the ionic strength. The average of our values at this temperature is 0.310 ± 0.013.

The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ calculated from the values of *k* for the composite reaction are 4.2 ± 0.2 kcal mol^{-1} and −48 ± 2 cal mol^{-1} deg^{-1}. An examination of the product distribution as a function of temperature shows that the reaction leading to ligand release becomes a smaller fraction of the total as the temperature increases, and thus must have a smaller activation energy than does the reaction leading to ligand capture. Using the values of product distribution as a function of temperature, the values of k_a (*i.e.*, reaction at the adjacent carboxyl leading to formation of the MFB-Cr(III) complex) and k_r (reaction leading to ligand release) at each temperature can be calculated. At 25°, these values are 0.14 and 0.17 M^{-1} sec^{-1}, respectively. The Eyring plots for the separate paths are not as nicely linear as are those for the composite reaction. As deduced from such plots using the best straight lines, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the k_r path are 2.2 kcal mol^{-1} and −56 cal mol^{-1} deg^{-1}, and for the k_a path, 8.3 kcal mol^{-1} and −38 cal mol^{-1} deg^{-1}. It may be noted that the values for the k_a path are quite similar to those for the benzoato complex (9.0 and −33).

Table IX. Kinetic Data on the Reduction of *m*-Formylbenzoatopentaamminecobalt(III) by Chromium(II)[a]

T, °C	[H$^+$], *M*	[Cr(II)] × 10^2	*k*,[b] M^{-1} sec^{-1}
25	1.00	1.95	0.316
25	1.00	3.54	0.292
25	1.00	3.54	0.301
25	1.00	3.72	0.325
25	1.00	3.54	0.322
25	1.00	0.265	0.306
25	1.00	0.396	0.298
25	0.50	3.54	0.302
25	0.50	3.54	0.288
25	0.050	3.54	0.307
25	0.050	3.54	0.330
25	0.050	3.54	0.322
25	0.050	3.54	0.313
9.5	1.00	3.53	0.210
9.5	1.00	3.28	0.190
38.5	1.00	3.53	0.434
38.5	1.00	3.28	0.462

[a] λ 503 nm; μ = 1.10 ($LiClO_4$); [Co(II)]$_0$ ~ 1.8 × 10^3 *M*. [b] *k* defined by −d[Cr(II)]/d*t* = *k*[Cr(II)][Co(III)].

Several experiments were done to estimate the rate of reduction of *m*-formylbenzoic acid by Cr(II). In 5 days at 25° with [H$^+$] = 0.025 and [Cr(II)] = 3.5 × 10^{-2} *M* and [MFB] = 1.9 × 10^{-3} *M*, 21% of the ligand was found to be reduced. The second-order specific rate for the reduction calculated from this result is 1.5 × 10^{-5} M^{-1} sec^{-1}. This is an upper limit on the specific rate of the path first order in [Cr(II)] and first order in [MFB] because a path order other than that assumed may be contributing to reaction.

Vanadium(II)-*m*-Formylbenzoatopentaamminecobalt(III). Four experiments were done for the purpose of measuring the rate of reaction. For all, the temperature was 26.0°, the wavelength was 503 nm, the ionic strength was 1.1, [Co(III)]$_0$ was 1.7 × 10^{-3} *M*, and [V(II)]$_0$ was 3.5 × 10^{-2} *M*. At 1.02 *M* H$^+$ *k* was recorded as 0.85 and 0.82, and at 0.070 *M* H$^+$ as 0.88 and 0.88 M^{-1} sec^{-1}.

Discussion

The most significant of the new results recorded for the Cr(II)-*p*-Formylbenzoatopentaamminecobalt(III) system is that an intermediate is observed. The absorption maximum as shown in Figure 1 can be ascribed to the π–π* transition, the band being shifted by interaction of carbonyl with Cr(III) to 290 nm from its position for the free ligand at 254 nm. Polar solvents[21] are

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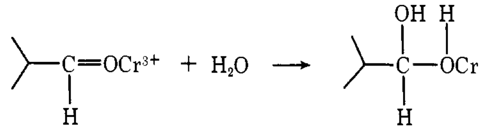
(20) R. E. Connick and H. H. Cady, *J. Amer. Chem. Soc.*, 80, 2646 (1958).

(21) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 8.

known to cause shifts to longer wavelength, and the shift by Cr(III), though extreme, is therefore simply an example of a recognized effect. The fact that the maximum extinction coefficient for the intermediate as calculated from the data is close to that for the free ligand shows that the major portion of the reaction proceeds through the intermediate, and further shows that in the intermediate the aldehyde is in the carbonyl rather than in the hydrate form (*cf.* structure I). The observations cited confirm the conclusion as to the site of attack by Cr(II) reached on the basis of the arguments outlined in the introduction.

The intermediate is quite labile as was expected on the basis of qualitative observations made by Nordmeyer[22] for the acetone complex of pentaamminecobalt(III), as well as on the basis of the fact that the hydrate–carbonyl equilibrium for aldehydes is established rapidly. Less expected was the observation that the rate of decomposition of the intermediate does not depend on the concentration of acid, it being known that the rate at which the hydrate–carbonyl equilibrium is established is markedly increased by acid. The observation can be understood if Cr(III) is regarded as being an acid, and the reaction being followed is taken to be



Release of $Cr(H_2O)_6^{3+}$ from the hydrate form may in fact be assisted by H^+, but on the interpretation advanced, it is the rate of formation of the hydrate rather than its decomposition that is being followed by observing the decay of the absorbance at *ca.* 320 nm. The hydrate will of course not show π–π^* transition and the region of strong absorption for it will be shifted to much shorter wavelengths.

Under the conditions used to generate the data on which Figure 1 is based, the H^+ dependent path accounted for *ca.* 90% of the total reaction, and the conclusions reached therefore apply strictly to this path only. But since ligand release is essentially quantitative over the whole range of acidity, and since outer-sphere reduction by Cr(II) of a carboxylatopentaammine complex at a rate as high as 53 M^{-1} sec^{-1} (k_0 at 25°) is unprecedented,[23] it seems safe to conclude that the acid-independent reaction also takes place mainly by remote attack. There is undoubtedly a contribution by adjacent attack. If the fact of quantitative ligand release when $[H^+] = 0.045$ *M* with [Co(III)] in excess is taken as a basis for setting an upper limit to this rate, the value thus calculated is $\sim$2 M^{-1} sec^{-1}. Pendent groups are known to affect the rate of reduction by adjacent attack[4a] and any value in the range 0.15 M^{-1} sec^{-1} (*k* for the reduction of benzoatopentaamminecobalt(III) at 25°) to the upper limit mentioned, $\sim$2 M^{-1} sec^{-1}, can be considered to be reasonable for the specific rate of adjacent attack.

Strong arguments have been advanced[24] in support of the conclusion that when isonicotinamide mediates in electron transfer from Cr(II) to either Cr(III) or Co(III), the reaction is stepwise and involves as an intermediate step the $1e^-$ reduction of the ligand. These conclusions have been bolstered by more recent work which demonstrates that the $1e^-$ reduction of free isonicotinamide by Eu(II) takes place at much the same rate as does the reduction by Eu(II) of isonicotinamidepentaamminecobalt(III).[25] The rate constant extracted from our cursory examination of the kinetics of reduction of *p*-formylbenzoic acid by Cr(II), $\sim$2.5 M^{-1} sec^{-1} at 25°, is close enough to the value of k_0 at 25°, 53 ± 14 M^{-1} sec^{-1}, to suggest that the mechanism of electron transfer by the k_0 path is also stepwise. Exact correspondence of rates for the two processes is not to be expected in general. The requirements on the product of the $1e^-$ reduction of the ligand which, on the one hand, prepare it for further net reduction and, on the other, make it sufficiently reactive to reduce the Co(III) center, may well be different. A difference is expected particularly in the present instance where net reduction calls for marked changes in geometry about the oxidizing carbon atom, whereas formation of a radical capable of reducing Co(III) would not seem to require distortion at this point.

The most interesting feature of the kinetic results is the prominence of the path which calls for external H^+. Such paths have been observed in other instances, and selected data for these and related systems are summarized in Table X.

Table X. Rate Data for Selected Cr(II) and $(NH_3)_5CoL^{n+}$ Reactions

L	k^a	Ref
Terephthalate	0.20	18
o-Formylbenzoate	46	18
m-Formylbenzoate	0.31	This work
p-Formylbenzoate	$53 + 3.8 \times 10^2 [H^+]$	This work
o-Benzoylbenzoate	5.4	4a
p-Benzoylbenzoate	$0.32 + 1.5 [H^+]$	4a
Isonicotinamide	17.4	24
Fumarate	$1.6 + 4.0 [H^+]$	26
trans,trans-Muconate	$2.2 + 15 [H^+]$	18

[a] $-d[Cr(II)]/dt = k[Cr(II)][Co(III)]$. [b] Temperature = 25°; $\mu = 1.0$ or 1.1 *M*, except for *o*- and *p*-benzoylbenzoate when it is 3.0 *M*.

The demonstration that Cr(II) attacks the carbonyl oxygen when PFB is the bridging ligand seems to require that the proton in the activated complex is not located on the remote polar group. The fact that PFB as bridging ligand for remote attack shows the $[H^+]$ dependent term, but isonicotinamide does not, suggests that the proton in the activated complex is not situated on the aromatic ring. The relevant difference between the ligands would seem to be that PFB but not isonicotinamide has a suitable adjacent polar group to accommodate the proton. The conclusion is supported by the fact that when *o*-formylbenzoate is the bridging ligand, the $[H^+]$ dependent term does not appear.

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(22) F. Nordmeyer, unpublished observations.

(23) M. Barrett, J. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971). The rate constant for the outer-sphere component to the reduction of acetatopentaamminecobalt(III) by Cr(II) is estimated not to exceed 0.017 M^{-1} sec^{-1}.

(24) F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1162 (1689).

(25) C. Norris and F. Nordmeyer, *ibid.*, **93**, 4044 (1971).

When Cr(II) engages the adjacent polar group, as is probable when *o*-formylbenzoate is the bridging ligand, it is reasonable to suppose that attack by the proton at the same site is excluded. The significance of the difference between terephthalate and PFB acting as bridging ligands has been emphasized earlier,[18,26] the latter ligand being more easily reducible than the former, but it is perhaps worth mentioning that for the k_h path as well as the k_0 path the "reducibility" of the ligand is an important factor determining its capacity to mediate in electron transfer.

Though the present study leads to some rather definite conclusions on the position of the proton in the activated complex, it does not settle the question of its mode of action. The results are compatible with the view that it promotes a stepwise mechanism (or "radical ion mechanism"), positive charge on the ligand should make it more easily reducible, as well as with the view that it facilitates "resonance transfer." The fact that a [H$^+$] dependent term is not observed in the reduction of the free ligand in the acid form, though suggestive that the second type of mechanism operates, by no means provides proof.

Where our results for the *m*-formylbenzoatopentaamminecobalt(III) system overlap those of LaFollette,[3] the agreement is good. In this system adjacent attack leading to ligand transfer takes place at the usual rate, *i.e.*, at about the same rate as it does when benzoate or terephthalate is the ligand. This being so, it is highly unlikely that the portion of the reaction which leads to ligand release, governed by a value of k at 25° of 0.17 M^{-1} sec^{-1}, represents outer-sphere reduction. Even in the absence of direct evidence for remote attack, on the basis of the specific rate governing reaction by ligand release, it seems safe to conclude that a major part of the reaction takes place by this mechanism. If this conclusion is accepted, we are faced with the striking difference between PFB and MFB acting as bridging groups for reduction of Co(III) by remote attack, not only in the matter of rates ($k_0 = 53$ for the former and 0.17 M^{-1} sec^{-1} for the latter) but in the fact that a [H$^+$] dependent path is observed for the former but not for the latter.

For the MFB complex, a radical ion path, at least for the portion of the reaction which proceeds by remote attack, seems a more reasonable possibility than does resonance transfer. This view is based on the fact that conjugation between meta positions involves states at very high energy. Even for the para isomer, where conjugation is direct, a stepwise process seems to be preferred, at least for the k_0 path. The observations are consistent with the conclusion that a stepwise mechanism operates, though it must be admitted that they do not strengthen the conclusion significantly. As is true also for the para isomer, net reduction of the free acid is much slower than is electron transfer through the ligand, but as before, this does not disprove a stepwise mechanism being operative. The insensitivity of rate of reduction of the complex to [H$^+$] is understandable on the basis of the mechanism being considered. When the carbonyl is located meta to the carboxyl group, protonating the carboxyl would exert only a weak effect in influencing the reducibility of the ligand.

The experiments with V(II), Eu(II), and $Ru(NH_3)_6{}^{2+}$ acting on the PFB complex were done so as to learn whether the rate laws for these reagents would also feature the acid-dependent path. The variation of rate with [H$^+$] is so slight for V(II) and Eu(II) that we cannot be certain that the acid-dependent path is real.[27] Until more is known about the variation of rate with [H$^+$] for outer-sphere reduction of complexes such as have been studied, it seems unprofitable to speculate on the meaning of the results. Unfortunately, owing to complications already mentioned, the experiments with $Ru(NH_3)_6{}^{2+}$ did not help to clarify the point at issue.

Acknowledgment. Financial support for this research, both for Grant No. GM 13638 and for predoctoral Fellowships for A. Zanella, 1967–1970, National Institutes of Health, is gratefully acknowledged.

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(26) H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969).

(27) The possibility exists that the acceleration by H$^+$ is a salt effect, arising from the change in ionic composition as [H$^+$] is increased. A noteworthy example of a spurious rate term produced by salt effects has recently been disposed of [D. L. Toppen and R. G. Linck, *Inorg. Chem.*, **10**, 2635 (1971)].