aquating in a solution with $a_w = 1$, the SN1 pathway would account for ~6.4% of the aquation. Hydrogen azide is a good leaving group, and it is reasonable that an SN1 pathway would make a contribution to the aquation. Iodochromium(III) ion, which aquates more slowly[28] than hydrogenazidochromium(III) ion, does so predominantly by the SN1 mechanism.[29]

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(28) T. W. Swaddle and E. L. King, *Inorg. Chem.*, 4, 532 (1965).

(29) S. P. Ferraris and E. L. King, *J. Amer. Chem. Soc.*, 92, 1215 (1970).

Influence of Back Bonding on the Hydrate–Carbonyl Equilibrium for 4-Formylpyridine as Ligand

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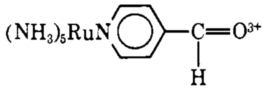
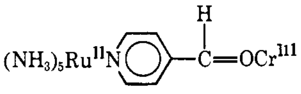
Abstract: Absorption spectra focusing on the πd–π* transition, infrared spectra, and nmr spectra agree in supporting the conclusion that at 25° the pentaammineruthenium(III) complex of 4-formylpyridine is largely (>90%) hydrated, while the corresponding Ru(II) complex is largely (>90%) in the carbonyl form. The effect on the extent of hydration of changing the oxidation state of the ruthenium is attributed to back bonding, which is greater for Ru(II) than for Ru(III) and greater when the ligand is in the carbonyl rather than in the hydrated form. Reduction of the Ru(III) complex by V^{2+} acting as an outer-sphere reducing agent produces the Ru(II) complex in the hydrated form (>95% at 6.5°). The dehydration of the complex was studied as a function of acidity, and Ru(II) is found to reduce the rate of dehydration, as compared to the free ligand, by a factor of 70. Ruthenium(III) increases the rate of dehydration of the Ru(II) complex, and its effect is attributed to electron-transfer catalysis.

The present study grew out of an interest in the reaction of *p*-formylbenzoatopentaamminecobalt(III) with Cr(II), in the course of which an intermediate product,[2] presumed to be the aldehyde complex of Cr(III), was encountered. We felt that by using the Ru(III) complex



as oxidant, we would have a ready means of following the decay of the intermediate aldehyde complex



which, by analogy with the other systems, was expected to form when Cr^{2+} was the reductant. It is known[3] that the πd–π* charge-transfer transitions for Ru(II)–pyridine complexes are very sensitive to substitution on the pyridine ring, and thus the release of Cr(III) from the aldehyde could easily be followed. Events showed that the Ru(II)-containing intermediate is a poor model for a simple aldehyde complex of a metal ion because Ru(II) exerts a profound and specific effect on the aldehyde function. Our interest then turned to exploring the effect of coordination to nitrogen on the behavior of the aldehyde in the para position. The results obtained from this study form the subject of this communication.

The major results deal with the degree of hydration of the ligand when it is coordinated to Ru(II), Ru(III), or H^+. Measurements of absorption spectra covering the visible region, infrared spectra, and nmr spectra have proved to be useful in estimating the equilibrium constant for the hydration reaction. Data on the rate of dehydration of the Ru(II) complex were obtained by using the reaction of $V(H_2O)_6^{2+}$ with the Ru(III) complex to generate the Ru(II) complex in an unstable state with respect to the aldehyde hydration equilibrium.

Related, but of secondary interest, are data on the rate of reduction of the Ru(III) complex. Those with Cr(II) as reductant show some special and unexplained features, undoubtedly related to the capacity of Cr(II) to reduce by "capturing" a ligand derived from the oxidant, but they also show features which correlate with the dehydration reaction observed for V(II) as reductant.

Experimental Section

Reagents. All common chemicals were of reagent grade and were used without further purification unless otherwise noted. Tap distilled water was redistilled from alkaline permanganate. Water-pumped, compressed nitrogen was deoxygenated by passing it through two gas-scrubbing bottles containing 0.1 *M* Cr(II) solutions in 4 *M* $HClO_4$ over zinc amalgam. Compressed hi-pure argon was similarly treated.

Lithium perchlorate was prepared by the reaction of lithium carbonate with perchloric acid, following Gaunder's procedure[4a]

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(1) Postdoctoral Fellow, Research School of Chemistry, Australian National University, Canberra.

(2) A. Zanella and H. Taube, unpublished results.

(3) P. C. Ford, D. F. P. Rudd, R. G. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, 90, 1187 (1968).

to eliminate an unknown oxidizing agent which was found to be present. Perchlorate analysis was done using the method described by Deutsch.[4b] Trifluoromethylsulfonic acid (HTFMS) was provided through the generosity of the 3M Corp.

Reducing Agents. Chromium(II) was prepared by reducing Cr(III) over zinc amalgam. Chromium(III) perchlorate was prepared by the hydrogen peroxide reduction of primary standard potassium dichromate in perchloric acid.[5] Total chromium was determined as chromate ion in alkaline solution.[6] Hydrogen ion concentration was determined according to the method of King and Neptune.[7] Chromium(III) solutions with chloride and trifluoromethylsulfonate (TFMS) as the counterions were prepared in an analogous manner.

Vanadium(II) was prepared by reducing vanadyl perchlorate with zinc amalgam. Solutions were used within 2 hr of preparation because V(II) is oxidized by perchlorate ion. Vanadyl perchlorate was prepared as described by Rossotti and Rossotti[8] and the total vanadium was determined by standard methods.[9] Hydrogen ion was determined from total vanadium and total perchlorate.

Hexaammineruthenium(II) was prepared by reducing hexaammineruthenium(III) trichloride over zinc amalgam. The hexaammineruthenium(III) trichloride was purified by recrystallization before using.

Ligand. *p*-Formylpyridine (hereafter referred to as PFP) was obtained from Aldrich Chemical Co. and was usually used without further purification. The ligand was kept over Drierite in a desiccator and stored in a refrigerator. In one instance the ligand was vacuum distilled under nitrogen at *ca.* 12 mm, bp 77°. Data obtained using this sample did not differ from that using the material as supplied, so routine purification was deemed to be unnecessary.

Ruthenium Complexes. *p*-Formylpyridinepentaammineruthenium(II) ion was obtained both by generating it in solution and by dissolving solids containing the ion. At first we tried to prepare the perchlorate salt but the products were very impure. This difficulty, coupled with the hazards of the perchlorate salts[10] led us to generate the complex ion in solution without isolating a solid. Later in the study bromide and tetrafluoroborate salts were prepared.

The preparation in solution was a modification of that described by Gaunder.[11] In a typical case, 11 mg of silver oxide was dissolved in 2 ml of hot water by dropwise addition of trifluoroacetic acid. To this solution was added 15 mg of chloropentaammineruthenium(III) dichloride and a silver chloride precipitate formed immediately. The mixture was digested on a steam bath for about 10 min and then filtered. The resulting Ru(III) solution was deoxygenated in a serum bottle by passing argon through it. Several pieces of zinc amalgam were added to reduce the Ru(III) to aquopentaammineruthenium(II) ion. Then about 0.25 ml of deoxygenated PFP was injected into the solution. A purple color appeared at once, and the reaction was allowed to proceed for about 10 min. The product solution was separated from the zinc by decanting and rinsing the zinc with small volumes of water. Since excess ligand was used in most preparations, the kinetic studies were generally performed with free PFP present. The results agreed with those obtained in the absence of free ligand.

When solid preparations were desired, the above scheme was employed on a larger scale, using 200 mg of chloropentaammineruthenium(III) dichloride as starting material and using NaBr or $NaBF_4$ to precipitate solids. In several cases a stoichiometric amount of PFP was added, the reaction then being allowed to proceed for a longer time. The yields were small (the salts are very soluble) and the microanalyses were not particularly good. The band positions noted in the spectrum agreed exactly with those obtained from solution preparations, and the extinction coefficient at 544 was about 10^4 M^{-1} cm^{-1}, as was previously reported by Ford, *et al.*[3]

The Ru(III) species was always prepared in solution by oxidizing the Ru(II) complex with *ca.* 0.04 *M* Ce(IV) or Fe(III). The extent of reaction was estimated by the disappearance of the intense purple color of the Ru(II) species. The volume was kept small and the solution was made acidic. Both oxidants were kept in 1 *M* acid, since they are effective only in highly acidic media. It should be noted that silver oxide did not satisfactorily oxidize the Ru(II) complex. The reaction seemed to proceed very slowly; it required a large excess of silver oxide, and a red-brown solution was formed instead of the faintly yellow one expected.

Spectra. Visible spectra were run on a Cary 14 or Cary 15 recording spectrophotometer fitted with thermostated cell compartments. Infrared spectra were run on a Perkin-Elmer Model 421 grating double beam instrument. Irtran cells with a 0.1-mm path length were used to hold the sample dissolved in D_2O; a cell filled with D_2O was placed in the reference beam.

Nmr spectra were run on Model T-60 or HA-100 instruments manufactured by Varian Associates. For the runs at 10°, the HA-100 was used and the sample treated in a special manner. The Ru(II) salt was placed in a standard nmr tube and a serum cap was placed over the top of the tube. The tube was deoxygenated with dry argon by using a long syringe needle. Deoxygenated D_2O was injected; then the tube was placed in an ice-water bath and the spectrum was run within several minutes.

Kinetics. A. Stopped-Flow Experiments. The apparatus was constructed by Stritar[12] based on a design by Dulz and Sutin.[13] Reactions were followed at one wavelength during each run. The temperature of reactants and mixing chamber was controlled by a constant temperature bath (±0.1°). Reactant solutions including acid and supporting electrolyte were made up in 250-ml volumetric flasks and then transferred to special 500-ml round-bottom flasks which incorporated provision for deoxygenating the contents. Solutions used to generate reducing agents were deoxygenated for 1 hr before zinc amalgam was added (about 100 g of zinc for Cr(II) and V(II), 50 g for hexaammineruthenium(II)). Chromium(II) solutions were left to reduce for 4 hr when the expected Cr(II) level was 1.4×10^{-3} *M*. Vanadium(II) was produced more readily and 2 hr was allotted for the same concentration. At 10^{-4} *M* Cr(II) solutions were given at least 5 hr to reduce. The Ru(III) solutions were deoxygenated at least 1 hr before reaction was initiated by mixing. A blanket of nitrogen was kept over both solutions during the entire experiment.

B. Ordinary Mixing Experiments. Reactions were followed at one wavelength during each run. The Ru(III), supporting electrolyte, and acid were measured by pipet into 5-cm cells fitted with serum caps, and the solution was deoxygenated using nitrogen or argon. 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, 1–2 ml, with detachable stainless steel needles were used for the transfers. For reactions below room temperature, syringes were precooled to minimize uncertainty in reaction temperature.

For the experiments at 6.5° with the Ru(III) complex in excess, 0.0095 *M* V(II) was prepared by dilution of more concentrated solution. The amount of Ru(II) produced showed the handling and delivering of the reductant to be quantitative. The hydrogen ion concentration in these experiments was determined by measuring the pH of the product solutions.

Results

Visible Spectra. The spectra of PFP pentaammineruthenium(II) ion in aqueous acid and 50% aqueous methanol obtained in the course of this work were consistent with those reported previously.[3] In aqueous acid the complex yielded a purple solution which exhibited an intense band with a maximum at 544 nm and having a molar extinction coefficient of approximately 1.0×10^4 M^{-1} cm^{-1}. A minor band with a maximum near 420 nm was also observed. In aqueous methanol, the band at 544 nm decreased and that at

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(4) (a) R. G. Gaunder and H. Taube, *Inorg. Chem.*, 9, 2627 (1970); (b) E. A. Deutsch and H. Taube, *ibid.*, 7, 1532 (1968).

(5) J. K. Hurst and H. Taube, *J. Amer. Chem. Soc.*, 90, 1178 (1968).

(6) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, 48, 414 (1952).

(7) E. L. King and J. A. Neptune, *J. Amer. Chem. Soc.*, 77, 3186 (1955).

(8) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, 9, 1177 (1955).

(9) L. Meites, "Handbook of Analytical Chemistry," McGraw-Hill, New York, N. Y., 1963, pp 3–73.

(10) Caution: perchlorates of ruthenium complexes have exploded on handling.

(11) R. G. Gaunder, Ph.D. Thesis, Stanford University, 1969. See also ref 2.

(12) J. Stritar, Ph.D. Thesis, Stanford University, 1967.

(13) G. Dulz and N. Sutin, *Inorg. Chem.*, 2, 917 (1963).

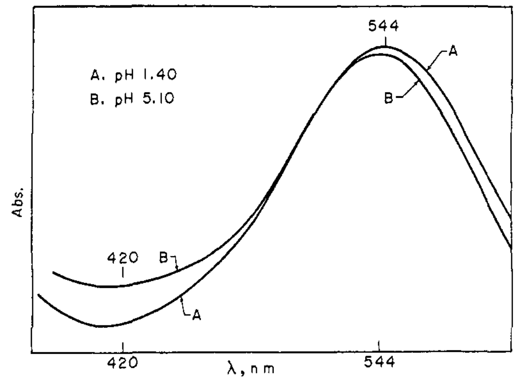

Figure 1. Visible spectrum of PFP pentaammineruthenium(II) as a function of pH (room temperature).

420 nm intensified. As concluded in the earlier work, these observations show that the Ru(II)-PFP complex exists in two forms, aldehyde and hydrate, with the former predominating when water is the solvent.

The spectrum of the complex is observed to be dependent on pH and temperature as shown in Figures 1 and 2. The ratio of the hydrate to the carbonyl form increases when the pH rises above ~5, and it decreases as the temperature increases.

The Ru(III)-PFP complex has no appreciable absorbance in the visible region. The free ligand in basic solution exhibits a band at 381 nm with a molar extinction coefficient of about 20 M^{-1} cm^{-1}. This band is quite pH dependent and becomes insignificant at pH values less than 3.

Infrared Studies. The carbonyl region 1650–1850 cm^{-1} was investigated for both oxidation states of the complex. The sensitivity of the ir technique was tested by running spectra of the free ligand first. Pocker and coworkers had shown that the degree of hydration of the formyl group of PFP is pH dependent.[14] A solution of PFP (*ca.* 0.1 *M*) in D_2O showed a strong band at about 1695 cm^{-1}. When the solution was acidified with DCl (pD 1), the band diminished in intensity from 0.4 to 0.1 absorbance units. This was the result expected on the basis of the earlier work[14] and it indicated that the method could be used for complexed PFP.

In the experiments with complexed PFP, compounds were used which had been prepared using stoichiometric amounts of ligand so as to avoid complication by free PFP. A solution approximately 0.08 *M* in the Ru(II) complex was prepared and charged into the Irtan cell. The remainder of the solution was oxidized to Ru(III) with 1 drop of a concentrated $FeCl_3$ solution in D_2O-DCl. The spectrum of the Ru(II) complex was scanned quickly and a reasonably good signal was found at 1660 cm^{-1}. In the Ru(III) spectrum this band was completely absent, and no other bands were observed in the carbonyl region. Heating by the light beam raised the temperature of the samples. By using a thermocouple, Nordmeyer[15] had estimated the temperature to be about 35° for conditions similar to ours.

Nmr Studies. Spectra of free PFP were run on the T-60 at 37° in D_2O. The sample was prepared by mixing 2 drops of PFP with 0.6 ml of D_2O in a standard nmr tube giving a solution about 1.5 *M* in PFP. The pD dependence of the spectrum was studied by adding 2 drops of concentrated D_2SO_4 to give pD 1.[16] The spectral features agreed well with those reported in the literature[14] at other temperatures. The spectrum in near-neutral solution showed the signals attributable to two sets of aromatic protons and two widely separated strong signals attributable to the aldehyde proton (10.0 ppm) and the hydrate proton (6.02 ppm), respectively. Upon addition of acid, the aldehyde proton signal disappeared and the hydrate proton signal increased and shifted slightly (to 6.23 ppm). The equilibrium quotient calculated from the data for the near-neutral solution was

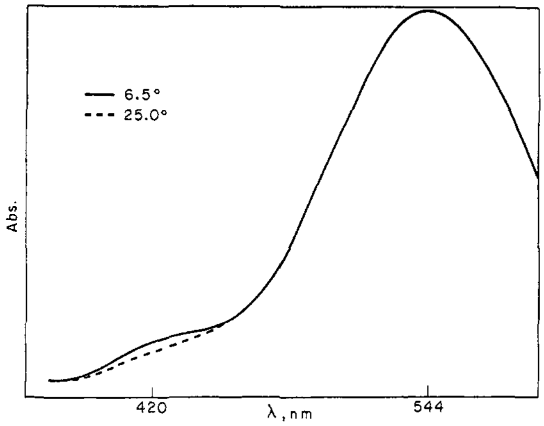

Figure 2. Visible spectra of PFP pentaammineruthenium(II) at 25 and 6.5°.

$$K = \text{aldehyde/hydrate} = 1.4 \pm 0.08 \text{ at } 37°$$

Spectra of the Ru(II)-PFP complex were run at 10° in D_2O on the HA-100 using the BF_4^- salt. The lower temperature was chosen in order to avoid aquation of the complex. Spectra were run first in neutral solution and then under acidic conditions by adding DCl to give pD <1. The spectra indicated that the distribution between aldehyde and hydrate changes with acidity, with the aldehyde concentration increasing as the pD decreases. The equilibrium quotient could not be accurately determined because no signal ascribable to the hydrate form was observed. As the pD was lowered, the aldehyde signal increased in intensity. This suggested that there was some hydrate in neutral solution which became aldehyde in acidic solution. An estimate of K = carbonyl/hydrate > 10 at 10° seems to accord with the data for neutral solution.

The probe was allowed to warm and, as it approached ambient temperature, the aldehyde signal broadened. No signal due to the hydrate form appeared. The broadening may be due to exchange between aldehyde form and a small concentration of hydrate. It should be mentioned that the hydrate signal of free PFP was readily observable at 10° at pH 1 and at pH 7.

Reaction of PFP Pentaammineruthenium(III) with Vanadium(II). The principal interest was in the reaction

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[14] Y. Pocker, J. E. Meany, and B. J. Nist, *J. Phys. Chem.*, 71, 4509 (1967).

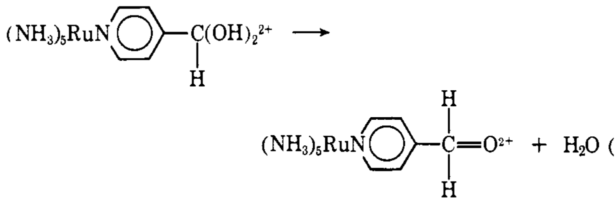
[15] F. Nordmeyer, Ph.D. Thesis, Stanford University, 1967.

[16] P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960), give the H_2O/D_2O correction as pD = pH + 0.4.

following electron transfer, and thus the kinetics of the redox reaction were not studied exhaustively. Only enough was done to ensure that the redox reaction which is dependent on [V(II)] can be gotten over quickly enough at reasonable levels of [V(II)] so that the observations on the subsequent reaction are not complicated by effects arising from the redox step.

Data on the rate of the redox reaction were obtained on the stopped-flow apparatus at two wavelengths, 420 and 460 nm. The latter is particularly useful because it is an isosbestic point for the species involved in the second reaction, and thus the observations at this wavelength on the rate of reduction are not complicated by the following reaction. In two experiments done at 460 nm, values of the specific rate of the electron transfer were measured as 3.2×10^4 and 3.0×10^4 M^{-1} sec^{-1} at $\mu = 0.11$, $(H^+) = 0.097$, 25°. Most of the experiments were done at 460 nm. At low acid, 0.002 M, k was observed to be 3.3×10^4 M^{-1} sec^{-1}. At higher acid, the specific rates calculated tend to rise, and this effect is reasonably attributable to interference by the succeeding reaction which, as will be shown presently, is acid catalyzed.

The wavelengths 420 and 540 nm which were chosen to monitor the second reaction correspond approximately to maxima in the absorption spectra for the hydrate and carbonyl form of the Ru(II) complex, respectively, and are therefore particularly useful in trying to understand the chemistry. Using the stopped-flow apparatus, both phases of the reaction could be followed. Making observations at 420 nm, a very rapid rise in absorbance is seen, corresponding to the change Ru(III) → Ru(II), followed by a decrease on a longer time scale ascribable to the dehydration reaction



(1)

At 540 nm, only a rise in absorbance is observed. This appears only in the phase corresponding to reaction 1 and on the same time scale as that observed for the reaction at 420 nm.

The changes in absorbance at λ 420 and 540 nm on reduction show that the Ru(II) produced from Ru(III) is virtually completely in the hydrate form. Unless electron transfer itself affects the distribution, we are led to conclude, consistent with the ir work, that the Ru(III) complex exists largely in the hydrate form. This conclusion is supported by the experiments, to be described presently, in which orthodox mixing procedures were used but at lower temperature and lower acid to reduce the rate of dehydration.

The rate constants observed for the rate of reaction 1 are summarized in Table I. A least-squares fit of the data leads to a large acid-dependent term and, within experimental error, to zero for the acid-independent term

$$k_{obsd} = k_0 + k_h[H^+]$$

Table I. k_{obsd} for the Net Dehydration of PFP Pentaammineruthenium(II) at 25.0° [a]

Expt	$[H^+]$, M	k_{obsd} (540 nm),[b] sec^{-1}	k_{obsd} (420 nm),[b] sec^{-1}	$k_{obsd}/[H^+]$, M^{-1} sec^{-1}
1	0.097	4.87 (10)	4.84 (7)	50.1
2	0.067	3.19 (9)	3.05 (3)	47.3
3	0.027	1.30 (6)	1.30 (4)	48.2
4	0.017	0.754 (6)	0.711 (4)	43.4
5	0.0070	0.326 (5)	0.316 (5)	45.8
6	0.0020	0.093 (7)	0.095 (5)	47.0
7	0.097	4.92 (9)	4.85 (4)	50.5
8[c]	0.0070	0.285 (2)	0.271 (5)	39.4
9[d]	0.10	5.21 (3)	5.17 (3)	51.9

[a] $\mu = 0.11$ M, perchlorate media. $[V(II)] = 1.40 \times 10^{-3}$ M, $[Ru(III)] = 7.0 \times 10^{-5}$ M. [b] Numbers in parentheses refer to the number of stopped-flow traces. The standard deviation was always 4% or less. [c] Fe(III) instead of Ce(IV) used to oxidize Ru(II) to Ru(III). [d] $[V(II)] = 2.00 \times 10^{-4} M$, $[Ru(III)] = 5.0 \times 10^{-5}$ M.

with $k_0 = 0.053 \pm 0.073$ sec^{-1} and $k_h = 49.6 \pm 1.5$ M^{-1} sec $^{-1}$ at 25.0° and $\mu = 0.11$. The spectra of the final product were identical with those obtained under the same conditions by preparing the Ru(II) complex by more direct means.

To make it possible to follow the rate by conventional mixing methods, using the Cary spectrophotometer, the acidity was much reduced and the temperature was lowered to 6.5°. The electron transfer reaction is too rapid to be followed using ordinary mixing techniques, and only the dehydration reaction could be observed. The experiments done this way showed vividly that the Ru(II) produced on reduction is virtually quantitatively (~95%) in the hydrate form, thus supporting the conclusion that the Ru(III) complex is largely hydrated. Thus, for a solution with $[Ru(II)]_T = 2.5 \times 10^{-5}$, A_{540} immediately after reduction was measured as 0.021. Taking account of the values of ϵ_{540} for the carbonyl and hydrate forms as $\sim 1.0 \times 10^4$ and 5×10^2, respectively, the concentrations of these species as formed initially by reduction of Ru(III) are calculated as 0.1×10^{-5} and 2.4×10^{-5} M.

The data obtained using the Cary 15 method are summarized in Table II. Treatment by least squares yielded

$$k_h = 19.6 \pm 0.9\ M^{-1}\ \text{sec}^{-1}$$

$$k_0 = (0.81 \pm 1.9) \times 10^{-3}\ \text{sec}^{-1}$$

at $\mu = 0.11$ and 6.5°.

Table II. k_{obsd} for the Net Dehydration of PFP Pentaammineruthenium(II) at 6.5° [a]

$[H^+]$, $M \times 10^3$	k_{obsd}, sec^{-1}	$k_{obsd}/[H^+]$, M^{-1} sec^{-1}
3.09	0.0623	20.2
2.30	0.0444	19.3
1.49	0.0290	19.5
1.06	0.0222	20.9

[a] $\mu = 0.11$ M, perchlorate media. $[V(II)] = 1.93 \times 10^{-3}$ M, $[Ru(III)] = 2.4 \times 10^{-5}$ M.

The data in Table I show that changing [V(II)] does not influence the rate of dehydration of the Ru(II) complex. This implies that neither V^{2+} nor Zn^{2+} significantly catalyzes the dehydration. It nevertheless seemed desirable to test the possibility that vanadium ions were exerting a specific influence by using another outer-sphere reductant and, accordingly, an experiment was done with $Ru(NH_3)_6^{2+}$. Using the values[3] of $E°$ for related systems, the equilibrium constant for the reduction is expected to be of the order of 10^5.

In a chloride medium ($\mu = 0.11$), $[H^+] = 0.097$, $[Ru(III)] \times 10^4 = 0.30\ M$, $(Ru(NH_3)_6^{2+}) \times 10^4 = 1.39\ M$, and at 25°, k_{obsd} was found to be 4.6 sec^{-1} (using λ 540 nm) and 4.3 sec^{-1} (using λ 420 nm). In the comparison experiment with V(II), k_{obsd} would be measured as 4.8 sec^{-1}. The results agree within experimental error.

In the experiments described thus far, the reducing agent has been used in excess. A remarkable catalytic effect is observed if Ru(III) is left in excess. Two series of experiments were done under conditions of excess Ru(III), one at 6.5° using the Cary 15 and the other on the stopped-flow apparatus at 25°. The results are shown in Table III.

Table III. Net Dehydration of PFP Pentaammineruthenium(II) in the Presence of Ruthenium(III)[a]

T, °C	$[H^+]$,[b] $M \times 10^3$	$[V^{2+}]_0$, $M \times 10^5$	Excess $[Ru^{III}]$, $M \times 10^5$	k_{obsd}, sec^{-1}	k_{expt},[c] sec^{-1}
6.5	0.50	3.0	1.0	0.038	0.0098
	0.56	3.0	1.0	0.042	0.011
	0.50	1.5	2.5	0.14	0.0098
25.0[d]	1.0	3.8	6.2	0.31	0.050

[a] $\mu = 0.11\ M$ perchlorate. [b] Determined by measuring pH of product solutions. [c] Calculated from results with excess V(II). [d] Average of four runs done on stopped-flow apparatus.

Comparing the last two columns shows clearly a dramatic effect on the rate exerted by Ru(III) and shows moreover that the rate enhancement increases with [Ru(III)].

Chromium(II) as Reductant. Though it was our original purpose to emphasize the reaction of Cr(II) with the Ru(III) complex, our studies on this system have not been carried to a satisfactory conclusion. The redox reaction is apparently complicated by an intermediate which forms rapidly and which has a high extinction coefficient. In trying to study the electron transfer phase of the reaction using the stopped-flow apparatus, instead of the increase in extinction expected, corresponding to the formation of a Ru(II) species, only a decrease was observed, whether the reaction was followed at 420 or 460 nm. This suggests that electron transfer is very rapid indeed and that we are observing the decay of an intermediate (presumably containing Cr(III)) in the first observable phase of the reaction. When a chloride rather than a perchlorate medium was used, the intermediate was not observed.

On following the reaction on a more extended time scale, its course was found to correspond reasonably well to that observed for the dehydration reaction with V(II) or $Ru(NH_3)_6^{2+}$ as reductant. The value of k_{obsd} was found to vary directly with $[H^+]$ and to be independent of $[Cr^{2+}]$ over the range 2×10^{-4}–$28 \times 10^{-4}\ M$. Experiments covering a range in acidity from 7.0×10^{-3} to 0.097 led to $k_h = 46.6 \pm 2\ M^{-1}\ sec^{-1}$ ($\mu = 0.11$, ClO_4^- or Cl^-, 25°). However, it is clear that some reactions characteristic of Cr(II) as reducing agent play a role even at longer time intervals. The data quoted were obtained at 540 nm and do not agree well with those at 420 nm.

Other Reactions. The reaction between free PFP and Cr(II) in acidic solution is quite rapid. With each reagent at about 0.05 *M*, and with H^+ in excess (*i.e.*, at least one H^+ for each Cr(II)), a dark green color appears on mixing and continues to develop for about 1 min. The major chromium-containing product was found by cation exchange chromatography to be a "dimer," with $Cr(H_2O)_6^{3+}$ comprising the remaining one-third of the Cr(III). The organic product was not identified, but the experiment to be described shows that the ring had been reduced. When a solution of aquopentaammineruthenium(II) was injected into the product solution, no color was produced; N heterocyclic species such as pyridine are known[3] to associate with Ru(II), the complexes showing strong charge-transfer absorption in the visible region of the spectrum.

By contrast, when PFP is coordinated to Ru(II), reduction by Cr(II) is very slow. A solution $2 \times 10^{-4}\ M$ in the Ru(II) complex, with Cr(II) at 0.01 *M* and HCl at 0.1 *M*, showed no diminution in the charge-transfer absorption even after 3 hr, and this sets an upper limit of $5 \times 10^{-4}\ M^{-1}\ sec^{-1}$ on the bimolecular rate constant for the reaction (the corresponding rate constant for the free ligand is in the range 1–10 $M^{-1}\ sec^{-1}$).

Discussion

The nmr studies by Pocker, *et al.*,[14] have shown that PFP is mostly (>95%) hydrated at 0° in D_2O at pD below 4. In a previous report[3] from this laboratory, also dealing with nmr results, it was claimed that at 37° in acidified D_2O only about one-half of the aldehyde is hydrated. The present reinvestigation of the system shows that, in agreement with the findings of Pocker and coworkers at 0°, at 37° the free ligand in acid solution is virtually all in the hydrate form (carbonyl/hydrate <0.10). Since the results obtained by Ford, *et al.*,[3] for the extent of hydration at higher pH appear to be correct, we must conclude that an error was made by them in acidifying the solution for the determination at lower pH.

Our measurements show the ratio carbonyl/hydrate in near neutral solution at 37° to be 1.4 ± 0.04. Pocker and coworkers[14] report a value for this ratio of 0.50 at 0°. They extended their measurements to somewhat higher temperatures and determined the value of $\Delta H°$. The extrapolation of their results to 37° yields a value of 1.25 for the ratio carbonyl/hydrate; we consider the agreement with the value we report to be satisfactory.

When PFP is coordinated to Ru(II), the hydration equilibrium constant is drastically changed. The visible absorption spectrum provides evidence that in the Ru(II) complex the carbonyl is the dominant form. In contrast to the behavior of most complexes of Ru(II) with pyridine derivatives, which give evidence for only a single absorption band associated with the dπ–π^* transition, when PFP is the ligand, in addition to a prominent maximum at 544 nm, there is a minor maximum at 420 nm. In harmony with the conclusion reached by Ford, *et al.*,[3] it is reasonable to ascribe the maximum at 544 nm to the carbonyl form of the complex and that at shorter wavelength to the hydrate (it should be noted that the maximum for the 4-methylcarbinol complex appears at ~412 nm). Our studies show the peak at 420 nm in slightly acidic solution to be less prominent than that in the spectrum reported in the earlier work,[3] which was obtained at an uncontrolled acidity, and thus may well have displayed the enhancement of the shorter wavelength absorption by increasing pH (*cf.* Figure 1).

The nmr spectrum of the Ru(II) complex shows that the C–H proton characteristic of the hydrate form is not observable at 10°, and we conclude that at this temperature the hydrate represents less than 10% of the total complex. The nmr measurements show, as is true also for the free ligand, that the extent of hydration increases as the temperature decreases, so that at 25° the ratio carbonyl/hydrate is considerably greater than 10, while at 6.5° the ratio is less than 10. It should be noted that the infrared experiments also show that the Ru(II) complex is predominantly in the aldehyde form at ~35°.

Turning now to the Ru(III) complex, the infrared measurements indicate that in this species the ligand at 35° is largely hydrated. Hexaaquovanadium(II) reacts so rapidly with Ru(III) that it must be reacting as an outer sphere reductant. If the reasonable assumption is accepted that reducing the Ru(III) complex does not affect the equilibrium between hydrate and carbonyl form, the observations on the absorption spectrum of the initial product show that at most 5% of the Ru(III) complex is present in the aldehyde form at 6.5°. We note then that changing the oxidation state of ruthenium in the complex from +2 to +3 decreases the equilibrium ratio aldehyde/hydrate by a factor of at least 100.

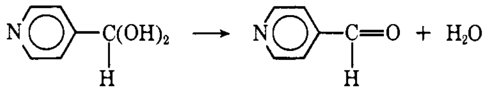
The effect of Ru(II) compared to Ru(III) in stabilizing the carbonyl form over the hydrate is attributable mainly to the greater capacity of Ru(II) to enter into a back-bonding interaction. In the carbonyl form, an additional double bond is included in the conjugated bond system and as a result, the π^* orbital lies at lower energy than it does for the hydrate. (The difference in the energy of the π^* orbital is attested to by the fact that the πd–π^* transition for the carbonyl form of the complex takes place at lower energies than for the hydrate.) The back-bonding interaction with Ru(II) is therefore greater for the carbonyl form than for the hydrate, leading to stabilization by Ru(II) of the former over the latter. The destabilization of the hydrate by Ru(II) is in part attributable to the smaller inductive capacity of Ru(II) compared to Ru(III). However, it should be noted that Ru(II) stabilizes the aldehyde over the hydrate by a factor of at least 14, as compared to the *free ligand* where the only inductive effect is that provided by water dipoles associating with the pyridine nitrogen.

The results just discussed constitute the second effect on the equilibrium behavior of a ligand which has been described and which is attributable to back bonding by Ru(II), the first being the increase in affinity for protons of pyrazine[3] and related molecules[17] when coordinated to Ru(II). In the system under present consideration, a marked effect on the reaction rate is also observable. The change being followed in the experiments in which the hydrate was generated by reduction is approach to equilibrium in reaction 1. The first-order specific rate, therefore, k_{obsd}, is given by $(k_f + k_r)$ and

$$k_f = k_{\text{obsd}}\frac{K_{\text{eq}}}{1 + K_{\text{eq}}}$$

where k_f is the specific rate for dehydration and k_r for the reverse. We take K_{eq} to be 10 or greater at 25° and thus k_f at this temperature lies in the range 45–50 M^{-1} sec^{-1}. At 6.5° where K_{eq} lies in the range of 5–10, k_f is in the range 16–18 M^{-1} sec^{-1}.

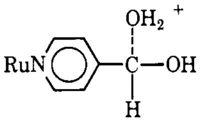
In considering the rate of dehydration of the free ligand, we note first that the dominant form of the ligand in the pH range covered by Pocker and coworkers[14] is the nonprotonated form, and k_f as reported by them then refers to the process



(2)

The specific rate for this reaction as catalyzed by H$^+$ is recorded at 700 M^{-1} sec^{-1} at 0°. By extrapolating our data, we obtain a value of ~10 M^{-1} sec^{-1} for the acid-catalyzed dehydration of the Ru(II) complex at 0° (it should be noted that the term in the rate law zero order in [H$^+$] could not be extracted from our data, which thus provide no basis for comparison with the value of 4.3 × 10^{-3} sec^{-1} reported for the acid independent term[14] in the dehydration of the free ligand).

It should be stressed that the 70-fold decrease in the rate of dehydration when Ru(II) coordinates to the ligand is registered despite the fact that the thermodynamic stability of the hydrate is thereby decreased. To understand the effect of Ru(II) on the rate of dehydration, we must suppose that the mechanism is such that the extra stabilization realized in the final state by πd–π^* back bonding cannot play a role in the activated complex. Let us consider the intermediate complex which results from the association of the hydrate with the proton, as suggested by the form of the rate law. If the rate-determining step were removal of the water molecule, with subsequent dissociation of the proton, the effect of Ru(II) would be difficult to understand



since an orbital is being opened on C which can take advantage of back bonding. But if the rate-determining step is proton removal (with subsequent dissocia-

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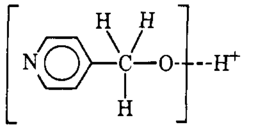
(17) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, 9, 495 (1970).

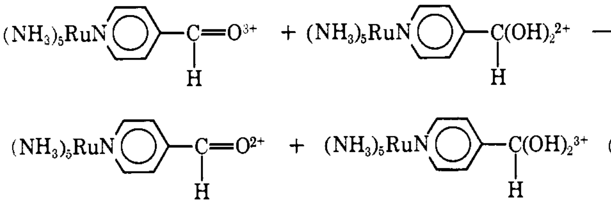
tion of H_2O), the influence of Ru(II) can be rationalized.



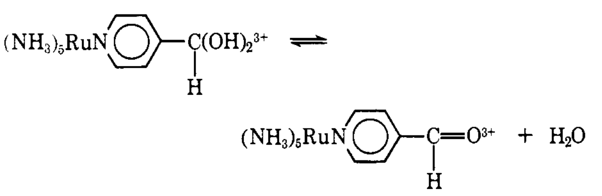
In this case back bonding does not play a role, and we can invoke the electron-releasing effect of Ru(II) as making the oxygen more basic and decreasing the rate of proton removal.

Pocker and coworkers[18] noted a marked effect of dipositive metal ions, *e.g.*, Cu^{2+}, Co^{2+}, Ni^{2+}, etc., on the rate of dehydration of 2-formylpyridine, and noted also that the effect on the 4-formyl derivative was much less. Their work, though related to ours in a general way, does not appear at this stage to afford instructive comparisons with the results we have obtained but will when our studies are extended to the 2-formyl derivative.

The effect of the change in oxidation state of ruthenium when it is coordinated to the ligand on the hydration equilibrium has already been commented on. The catalysis of the dehydration of the Ru(II) complex by the Ru(III) form indicates that the change in oxidation state affects also the lability at the aldehyde function, the lability being much greater for the complex of Ru(III) than of Ru(II). Numerous instances are known of the catalysis of substitution at metal ion centers by adjacent oxidation states of the metal, the catalysis depending on the greater lability of these states and on electron transfer to provide turnover. Much the same kind of mechanism probably operates in the present system, the only difference being that the effect of the metal ion extends also to a functional group on the ligand. The suggested mechanism is incorporated in eq 3 and 4. Reaction 3, on the basis of experience with related reactions[19] takes place with a specific rate of 10^5–10^6 M^{-1} sec^{-1}.



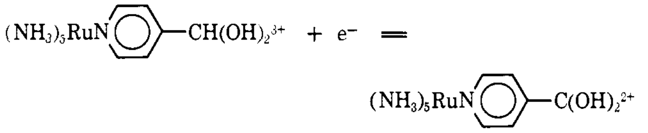
(3)



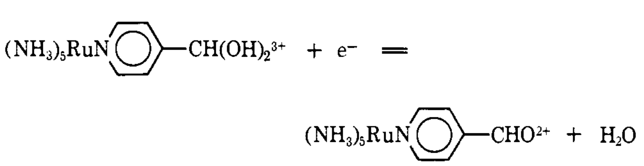
(4)

At equilibrium the hydrate is much favored over the carbonyl form; thus reaction 4 must be regarded as a relaxation toward equilibrium; *i.e.*, the relevant specific rate is $(k_4 + k_{-4})$ with the second term being the dominant one. Despite the unfavorable value of the equilibrium constant for the reaction, it can lead to catalysis if the relaxation time is short enough. A more thorough investigation will be required to obtain specific rates for the individual reactions.

A few comments on the reduction process itself are in order. The results with V^{2+} as reducing agent are quite straightforward, and the specific rate measured, 3.2×10^4 M^{-1} sec^{-1} at 25° and $\mu = 0.11$ M, is reasonable in comparison with that reported[16] for the pyridine complex as oxidizing agent, namely 11.9×10^4 M^{-1} sec^{-1}, also at 25°, but with $\mu = 1.0$. It should be noted that since the complex we studied is largely in the hydrate form when ruthenium is in the +3 oxidation state, the value of the redox potential is likely very close to that for the pyridine complex. The "instantaneous" redox potential applies to the reaction

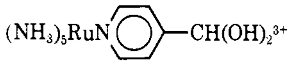


while the equilibrium value applies to the reaction

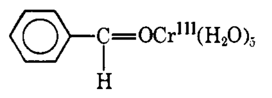


and the two values differ by at least 0.06 V.

The reaction of V^{2+} with the Ru(III) complex is certainly of the outer-sphere type, it being much too rapid to involve substitution on V^{2+} as a step. The situation when Cr^{2+} is the reducing agent is much less clear. Certainly some free hydrated Ru(II) complex is produced by the redox process; note that the changes in absorptivity after extended time periods are interpretable as caused by dehydration of the Ru(II) complex. At short time intervals, effects are seen which do not appear when V^{2+} (or $Ru(NH_3)_6{}^{2+}$) is the reductant, and it seems, therefore, that at least some inner-sphere attack occurs. Inner-sphere attack on



does not seem likely, the remote carbon being saturated,[20] and the highly colored intermediate therefore probably arises from reaction with Cr^{2+} of the small amount of the Ru(III) complex which is present in the carbonyl form. The extinction coefficient must be very high to account for the fact that the production and then decomposition of this species dominates the changes in absorptivity at short time intervals. A species such as



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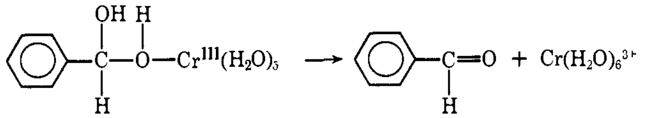
(18) Y. Pocker and J. E. Meany, *J. Phys. Chem.*, 72, 655 (1968).

(19) M. Abe and H. Taube, unpublished results.

(20) In no case thus far has reduction of a complex by remote attack involving electron transfer through a saturated carbon atom been observed.

probably reacts by hydrating and then decomposing to the carbonyl for (*via* C–O bond cleavage)



At present these ideas are at best reasonable conjectures, and further work will be necessary before the system is understood. The most useful evidence for diagnosis would be the absorptivities over a range of wavelength as a function of time.

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Proton and Deuteron Nuclear Magnetic Resonance Isotope Shifts in Partially Deuterated Tris(2,4-pentanedionato)vanadium(III)

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Contribution from the Department of Chemistry, The University of Kansas, Lawrence, Kansas 66044. *Received May 17, 1971*

Abstract: The proton and deuteron nmr spectra of tris(2,4-pentanedionato)vanadium(III) show three signals in the methyl resonance region when the ligand is partially deuterium substituted. The relative areas of these signals vary with the extent of deuteration. A series of complexes has been investigated in which the extent of deuteration at the ligand methyls ranges from 0 to 93%. For each complex the relative abundances of the four possible methyl groups CH_3–, CH_2D–, CHD_2–, and CD_3– were determined from mass spectra. A good correlation is found between the relative abundances of these groups and the relative nmr signal areas for each complex. It is concluded that the three proton resonance signals may be attributed to CH_3–, CH_2D–, and CHD_2–, and that the three deuteron resonance signals arise from CD_3–, CHD_2–, and CH_2D– groups on the ligands. Possible origins of the observed isotope shifts are discussed.

The shift of a nuclear magnetic resonance signal resulting from isotopic substitution at a neighboring site was first observed by Wimett in 1953 upon comparing the proton and deuteron spectra of H_2, D_2, and HD.[2] Several years later Tiers discovered a chemical shift difference in the ^{19}F resonances of *n*-C_3F_7H and *n*-C_3F_7D and subsequently observed a much smaller chemical shift difference in the methyl proton resonances of $C_6H_5CH_3$ and $C_6H_5CH_2D$.[3] Since that time "isotope shifts" have been reported for a number of compounds, utilizing ^{1}H, ^{59}Co, ^{19}F, and ^{13}C nmr, and several attempts have been made to explain the origin of the effect. The literature up to 1967 has been reviewed.[4]

In a recent report from this laboratory, which compares the resolution of proton nmr (pmr) and deuteron nmr (dmr) for several paramagnetic transition metal acetylacetonate complexes and their deuterated analogs, an unexpected splitting of methyl resonance signals for the V(III) and Mo(III) complexes was mentioned.[5] The splitting has now been examined in detail for the V(III) complex. Results of this investigation are presented along with arguments supporting our conclusion that the observed splittings are isotope shifts arising from incomplete deuteration of the ligand methyls. The shifts reported here for the paramagnetic V(III) complex are an order of magnitude larger than those generally found upon deuterium substitution in diamagnetic compounds.

Experimental Section

Deuteration of Ligands. 2,4-Pentanedione (Matheson Coleman and Bell) was deuterated by the following procedure. A mixture of the diketone and deuterium oxide, in a 1:8 mole ratio, respectively, is refluxed over a period of 24 hr in the presence of a small amount of Na_2CO_3. The mixture is then extracted with diethyl ether, and the product is recovered from the ether solution by evaporating the solvent. Fresh deuterium oxide is added to this product, and the above procedure is repeated a number of times sufficient to attain the desired extent of deuteration. A rough estimate of the degree of deuteration may be made from the pmr spectrum of the crude product. Six repetitions were necessary to obtain the 93% deuterated ligand. At the end of the final deuteration cycle, the product is distilled. An accurate measure of the extent of deuteration may be obtained from the mass spectrum of the final product.

Tris(2,4-pentanedionato)vanadium(III). Since the V(III) complexes in solution are susceptible to oxidation by air, all solvents were thoroughly degassed, and solutions of the complexes were handled under a nitrogen atmosphere or *in vacuo* using apparatus

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[1] NASA Predoctoral Trainee, 1969–present.

[2] T. F. Wimett, *Phys. Rev.*, 91, 476 (1953).

[3] (a) G. V. D. Tiers, *J. Amer. Chem. Soc.*, 79, 5585 (1957); (b) G. V. D. Tiers, *J. Chem. Phys.*, 29, 963 (1958).

[4] H. Batiz-Hernandez and R. A. Bernheim, *Progr. Nucl. Magn. Resonance Spectrosc.*, 3, 63 (1967).

[5] A. Johnson and G. W. Everett, Jr., *J. Amer. Chem. Soc.*, 92, 6705 (1970).