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The Ruthenium(II) Center and the Phosphite-Phosphonate Tautomeric Equilibrium

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The second-order specific rate constant for the reaction between $[Ru(NH_3)_5(H_2O)]^{2+}$ and $P(OEt)_2(OH)$ was estimated as 0.28 ± 0.03 $M^{-1}\ s^{-1}$ (μ = 0.10 M ($NaCF_3COO$), 25 °C). Diethyl phosphite and phosphorous acid react with $[Ru(NH_3)_5(H_2O)]^{2+}$, yielding respectively *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{2+}$ ($E°' = 0.60 \pm 0.02$ V versus NHE, μ = 1.0 M (CF_3COOH), 25 °C, λ_{max} = 316 nm, $\epsilon = (5.1 \pm 0.2) \times 10^2\ M^{-1}\ cm^{-1}$) and *trans*-$[Ru(NH_3)_4P(OH)_3(H_2O)]^{2+}$ ($E°' = 0.65 \pm 0.02$ V versus NHE, μ = 1.0 M (CF_3COOH), 25 °C, λ_{max} = 316 nm, $\epsilon = (5.3 \pm 0.2) \times 10^2\ M^{-1}\ cm^{-1}$). The pK_a's for these mono(phosphite) complexes with the metal center in the II and III oxidation states have been estimated on the basis of cyclic voltammetric data. The pK_a values are 1.5 ± 0.2 (III) and 3.6 ± 0.2 (II) and 1.0 ± 0.02 (III) and 4.7 ± 0.2 (II) for the $P(OH)(OEt)_2$ and $P(OH)_3$ complexes, respectively. The $E°'$ for Ru(III)/Ru(II) couple in the species *trans*-$[Ru(NH_3)_4P(OEt)_2(O)]^{2+/+}$ and *trans*-$[Ru(NH_3)_4P(OH)_2(O)]^{2+/+}$ are respectively 0.44 ± 0.02 and 0.32 ± 0.02 V versus NHE (μ = 0.10 M ($NaCF_3COO$), 25 °C). The formation constants for the pyrazine (pz) derivatives *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(pz)]^{2+}$, *trans*-$[Ru(NH_3)_4P(OEt)_2(O)(pz)]^+$, *trans*-$[Ru(NH_3)_4P(OH)_3(pz)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OH)_2(O)(pz)]^+$ have been estimated as 15, 45, 16 and 44 M^{-1} (μ = 0.10 M ($NaCF_3COO$), t = 25 °C), respectively. Comparing the $E°'$ data for the Ru(III)/Ru(II) couple in mono(phosphite) complexes and the respective affinities of such compounds for pz, the series of decreasing Ru(II)-P(III) back-bonding for the phosphorus ligands already studied are as follows: $P(OH)_3 \sim P(OEt)_2(OH) > P(OMe)_3 > P(OEt)_3 > P(OBut)_3 > P(O^iPr)_3 >> P(OEt)_2O^- \cong P(OH)_2O^-$. The fact that Ru(II) is able to shift the tautomeric equilibrium phosphite $\rightleftarrows$ phosphonate to the phosphite form suggests that Ru(II) → P(III) back-bonding is stronger than the O(II) → P(III) back-bonding.

Introduction

Despite the intrinsic and practical relevance of phosphorus esters, little information is available in the literature concerning the chemistry of phosphite molecules as ligands. Most of the scarce publications refer to labile complexes or to complexes where the metal ion is not in a well-defined environment and so does not permit a proper evaluation of the effect of the metal center on the properties of the phosphite ligand.[1-3]

Because of their chemical properties,[4] the ruthenium(II)/ruthenium(III) ammines were chosen as models for a systematic study of the mutual influences of the metal center and phosphite ligand upon their respective chemical reactivities. Previous papers[5-9] have reported the synthesis, aquation, "trans influence", and "trans effect" of trialkyl phosphites. The purpose of this work is to describe the interactions between Ru(II) and diethyl phosphite or phosphorous acid, respectively, and to compare the relative strengths of the P=Ru and P=O bonds. On this basis, we attempt to understand the chemical reactivities of coordinated and free phosphite molecules.

Experimental Section

Chemicals and Reagents. Doubly distilled water was used throughout. Acetone, ethanol, and ether were distilled before use. Pyrazine (pz) (Aldrich Puriss grade), $Na_2HPO_3{\cdot}5H_2O$ (BDH Reagent), and $[Ru(NH_3)_6Cl_3]$ (Matthey Bishop, Inc.) were used as supplied. Triethyl and diethyl phosphite were purified as described in the literature.[5] The complexes $[Ru(NH_3)_5Cl]Cl_2$, $[Ru(NH_3)_5(H_2O)](CF_3SO_3)_3$ and $[Ru(NH_3)_5(H_2O)](PF_6)_2$ were prepared by using the procedures described in the literature.[9-12] The purity of the complexes was checked in each case by cyclic voltammetry and spectrophotometric measurements.

Apparatus and Techniques. Ultraviolet and visible spectra were recorded on a Varian Techtron Model 635 spectrophotometer. The temperature of the cell comparment was maintained constant within ±0.1 °C with a Superhom thermostat.

pH values were recorded by using a Corning-30 pH-meter equipped with a Metrohm Model EA-120 electrode.

Cyclic voltammograms were recorded on the following PARC system: Model 173 potentiostatt/galvanostatt, a Model 176 current-to-voltage converter, a Model 175 universal programmer, and a Model R.E. 0074 X-Y recorder. The cell employed carbon paste, vitreous carbon, or platinum as working electrodes and SCE as reference electrodes. The reversibility of the systems was verified by comparing the ratio of the peak current for the cathodic process relative to that of the anodic process and the peak-to-peak separation with that of the $[Ru(NH_3)_6]^{3+/2+}$ system, known to be reversesible.[4] The formal potential $E°' = E_{1/2}$ for the Ru(III)/Ru(II) couple in the phosphite complexes was calculated as the arithmetic average of the peak potentials. The formal potentials were converted to the NHE reference by adding 242 mV.

All experiments and manipulations were carried out under purified Ar or N_2 atmosphere. All-glass connections were used, and routine techniques for transferring air-sensitive materials were utilized.[13] The ionic strength in all experiments was maintained with sodium trifluoracetate unless otherwise indicated.

Kinetic Measurements. The reactions were studied under pseudo-first-order conditions. The aqueous ethanol and aqueous solutions with the pH and ionic strength previously adjusted were degassed in a Zwickel[14] flask immersed in a constant-temperature bath. After deaeration of the solutions, a weighed sample of the $[Ru(NH_3)_5(H_2O)](PF_6)_2$ salt was dissolved. The reaction was initiated by adding, with a syringe, an aliquot of diethyl phosphite, previously deaerated, into the Zwickel flask. The solution was transferred by gas pressure into the connected spectrophotometric cell and the reaction followed by measuring the change in absorbance at 316 or 268 nm for about 6 half-lives.

The pseudo-first-order rate constants were determined graphically from a log $(A_\infty - A_t)$ versus time plot (where A_∞ and A_t are the final absorbance and that at time t, respectively). The plots of log $(A_\infty - A_t)$ versus time were linear over a range of more than 3 half-lives. The kinetic data obtained by using diethyl phosphite purchased from Aldrich and diethyl phosphite generated from hydrolysis of triethyl phosphite, just before use, agree fairly well.

The activation parameters, ΔH_1^* and ΔS_1^* were evaluated from log k_1/T versus $1/T$ data by using the Eyring equation.[15] The data were analyzed with a conventional least-squares program employing a HP-97 calculator.

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Table I. Kinetic Data for the $P(OEt)_2(OH)-[Ru(NH_3)_5(H_2O)]^{2+}$ Reaction

$C_{P(OEt)_2}$, M	T, °C	C_{H^+}, M	10^3k_{obs},[a] s^{-1}	$10k$, M^{-1} s^{-1}
0.112	25.0	1.0×10^{-2}	1.33	1.19
0.151	25.0	1.0×10^{-2}	1.77	1.17
0.150	25.0	1.0×10^{-2}	2.10	1.40[b]
0.224	25.0	1.0×10^{-2}	2.64	1.18
0.250	25.0	1.0×10^{-2}	3.37	1.35[b]
0.295	25.0	1.0×10^{-2}	3.55	1.20
0.224	25.0	1.0×10^{-3}	2.69	1.20
0.224	25.0	1.0×10^{-1}	2.66	1.20
0.224	25.0	1.0×10^{-3}	2.66	1.20
0.224	34.0	1.0×10^{-2}	5.10	2.27
0.295	15.5	1.0×10^{-2}	1.94	0.658

[a] $\mu = 0.10$ M, ($NaCF_3COO$, CF_3COOH), water–ethanol 5:1, diethyl phosphite generated in solution, $C_{Ru(II)} = 1.0 \times 10^{-3}$ M. [b] $\mu = 0.10$ M, ($NaCF_3COO$, CF_3COOH), water medium, $C_{Ru(II)} = 1.0 \times 10^{-3}$ M.

Table II. Equilibrium Data[a] for the Reaction

$$trans\text{-}[Ru(NH_3)_4P(OR)_2(OH)(H_2O)]^{2+} + pz \rightleftharpoons trans\text{-}[Ru(NH_3)_4P(OR)_2(OH)(pz)]^{2+} + H_2O$$

R	pH	K,[b] M^{-1}	λ_{max}, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}
Et	2.7	15 ± 1	375	2.4 ± 0.3
	3.1	10 ± 1	378	3.3 ± 0.3
	4.5	37 ± 3	400	3.1 ± 0.3
	5.4	45 ± 5	413	3.4 ± 0.3
	6.8	45 ± 5	415	3.3 ± 0.3
	5.9[c]	46 ± 5		
H	2.6	16 ± 1	365	3.6 ± 0.3
	6.9	44 ± 3	415	3.0 ± 0.3

[a] $\mu = 0.10$ M ($NaCF_3COO$), 25 °C. [b] Mean of at least five independent determinations. [c] Reference 29.

Equilibrium Constant Determinations. Standard 2×10^{-3} M solutions of *trans*-$[Ru(NH_3)_4P(OH)(OR)_2(H_2O)]^{2+}$ ions were prepared by reacting $[Ru(NH_3)_5(H_2O)]^{2+}$ and the desired phosphorus ligand under an argon atmosphere. Standard solutions of pyrazine were separately degassed in a flask tightly covered with a serum cap. In a Zwickel flask immersed in a constant-temperature bath, 10-mL solutions with the pH and ionic strength previously adjusted were prepared and deaerated.

With syringes, aliquots of the pyrazine and the desired aquo complex solutions were transferred to the Zwickel flask. The resulting solutions were transferred by gas pressure into the connected spectrophotometric cell. The concentration of the pyrazine derivative generated in solution was measured spectrophotometrically.

Since only one species is formed at pH 2.7 and 6.8, the equilibrium constants for the species *trans*-$[Ru(NH_3)_4P(OH)(OEt)_2(pz)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OEt)_2(O)(pz)]^{2+}$ were accessible by measuring the solutions containing the same concentration of the monophosphite complex, C_x, and variable concentrations of ligand from C_L' to C_L''. The concentration of complexes with be C_z' and C_z'' and the absorbance values A_1 and A_2, respectively, at one fixed wavelength. The equilibrium constants were calculated from the equation[16]

$$K = \frac{pC_z'}{(C_x - pC_z')C_z''}$$

where

$$C_z' = \frac{C_z(C_L'' - pC_L')}{p(C_L'' - C_L')}$$

and

$$C_z'':C_z' = A_2:A_1 = p$$

For solutions with pH in the range 3.1–4.5, the constants shown in Table II are mixed constants since they are related to the formation of both *trans*-$[Ru(NH_3)_4P(OR)_2(OH)(pz)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OR)_2(O)(pz)]^{+}$ complexes (R = H or Et), in equilibrium in such solutions. The equilibrium constant data for the *trans*-$[Ru(NH_3)_4P(OH)_3(pz)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OH)_2(O)(pz)]^{+}$ complexes have been estimated at pH 2.7 and 5.5, respectively.

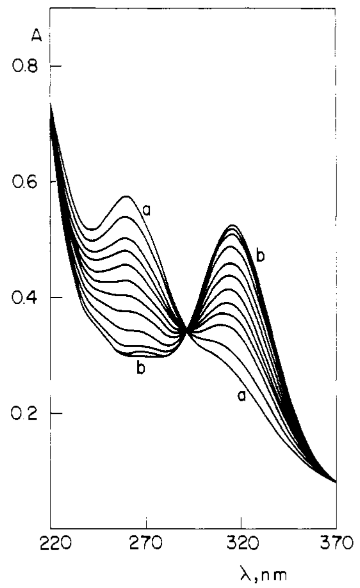

Figure 1. Absorption spectra changes during the $[Ru(NH_3)_5(H_2O)]^{2+}-P(OEt)_2(OH)$ reaction: (a) t = 0 min; (b) t = 15 min. $C_{Ru(II)} = 1.0 \times 10^{-3}$ M, $\mu = 0.10$ M (Na CF_3COO), $C_{H^+} = 10^{-3}$ M, 25 °C.

pK_a Determinations. Cyclic voltammetry was used[17] to estimate acid dissociation constants of the *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{2+}$ *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{3+}$, *trans*-$[Ru(NH_3)_4P(OH)_3(H_2O)]^{2+}$, and *trans*-$[Ru(NH_3)_4P(OH)_3(H_2O)]^{3+}$ species. Plots of $E_{1/2}$ versus pH were constructed from CV data. The plots yield straight lines with slope values close to 0.059 V. As the Ru(III) species is more acidic than the corresponding Ru(II) complex, the pH value corresponding to the first break on the plot of $E_{1/2}$ versus pH has been assigned to the Ru(III) species and the second to the Ru(II) acid.

CV data at pH higher than 5 are not computed since the cyclic voltammogram shows departure from reversible behavior.

Results

When diethyl phosphite is added to aqueous aquopentaammineruthenium(II), the solution changes color and a decrease in the hydrogen ion concentration of the resulting solution is detected. The peak at 268 nm, characteristic of the $[Ru(NH_3)_5(H_2O)]^{2+}$ ion, decreases and simultaneously a new absorbance maximum is developed at 316 nm ($\epsilon = (5.2 \pm 0.2) \times 10^2$ M^{-1} cm^{-1}). An isosbestic point is detected at 292 nm and remains constant for at least 4 half-lives (see Figure 1). The electronic spectrum of the reaction product is qualitatively the same as that exhibited by all mono(phosphite) complexes so far studied.[5-9] Thus the diethyl phosphite aquopentaammineruthenium(II) reaction can be expressed by the scheme

$$[Ru(NH_3)_5(H_2O)]^{2+} + P(OEt)_2(OH) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(NH_3)_5P(OEt)_2(OH)]^{2+} + H_2O$$

$$[Ru(NH_3)_5P(OEt)_2(OH)]^{2+} + H_2O \xrightarrow{k_2} [Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{2+} + NH_3$$

The substitution reaction of $P(OEt)_2(OH)$ in $[Ru(NH_3)_5(H_2O)]^{2+}$ is first order in the phosphite concentration and independent of hydrogen ion concentration in the 10^{-1}–10^{-3} M range. The second-order specific rate constant k_1 has been calculated as 1.2×10^{-2} M^{-1} s^{-1}.

From the kinetic data in Table I, ΔH_1^* has been calculated as 11 ± 2 kcal/mol. The ΔS_1^* value was estimated assuming[18] that the $P(OEt)_2(OH)$ concentration is only 5% of the total $P(OEt)_2(O)(H)$. Under these conditions, k_1 assumes the value of 0.24 ± 0.02 M^{-1} s^{-1} and ΔS_1^* has an upper limit value of −24.6 cal K^{-1} M^{-1}.

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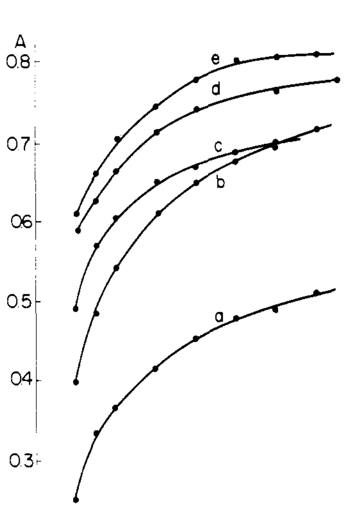

Figure 2. Plot of A versus C_{pz} for the system *trans*-$[Ru(NH_3)_4P(OH)(OEt)_2(pz)]^{2+}$: (a) pH 2.7; (b) pH 3.1; (c) pH 4.5; (d) pH 5.4; (e) pH 6.8. $C_{Ru(II)} = 2.5 \times 10^{-4}$ M, $\mu = 0.10$ M ($NaCF_3COO/CF_3COOH$), 25.0 ± 0.1 °C.

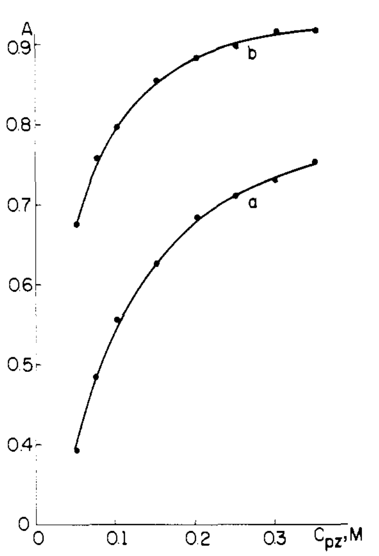

Figure 3. Plot of A versus C_{pz} for the system *trans*-$[Ru(NH_3)_4P(OH)_3(pz)]^{2+}$: (a) pH 2.6; (b) pH 7.0. $C_{Ru(II)} = 2.5 \times 10^{-4}$ M; $\mu = 0.10$ M ($NaCF_3COO/CF_3COOH$), 25.0 ± 0.1 °C.

As inferred from the electronic spectra, phosphorous acid behaves similarly to the diethyl phosphite molecule relative to the Ru(II) center. The compound *trans*-$[Ru(NH_3)_4P(OH)_3(H_2O)]^{2+}$ absorbs at 316 nm ($\epsilon = (5.3 \pm 0.2) \times 10^2\ M^{-1}\ cm^{-1}$) and is the product of the reaction between H_3PO_3 and the $[Ru(NH_3)_5(H_2O)]^{2+}$ ion.

The characteristic colors of the $4d_\pi \rightarrow \pi^*$ MLCT bands are developed immediately upon mixing pyrazine with the solution containing the phosphite complexes. These observations are strongly indicative[5-9] of the presence of *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(pz)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OH)_3(pz)]^{2+}$ ions in solution.

The λ_{max} values for the charge-transfer bands of the *trans*-$[Ru(NH_3)_4P(OH)(OR)_2(pz)]^{2+}$ complexes exhibit bathochromic shifts as the hydrogen ion concentration of the medium decreases. The formation constants for the pyrazine derivatives of the ions *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OH)_3(H_2O)]^{2+}$ were measured at several hydrogen ion concentrations. Their formation constants are calculated from the values in Figures 2 and 3, respectively, as described in the Experimental Section, and are shown in Table II.

When the hydrogen ion concentration in solution is lower than 6.3×10^{-6} M, no changes are observed in the apparent stability constant data for the pyrazine derivative of the *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{2+}$ system.

Table III. pK_a Values for Some Acids

compd	pK_1
H_3PO_4[a]	2.1
H_3PO_3[a]	1.3
$P(OEt)_2(OH)$[b]	6.1
$P(OH)_3$[b]	7.4
$[Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{2+}$	3.7
$[Ru(NH_3)_4P(OEt)_2(OH)(pz)]^{2+}$	3.7
$[Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{3+}$	1.5
$[Ru(NH_3)_4P(OH)_2(H_2O)]^{2+}$	4.7
$[Ru(NH_3)_4P(OH)_2(H_2O)]^{3+}$	1.0

[a] Reference 2. [b] Reference 25.

Assuming that under these conditions, 1% or less of the complex is in the protonated form, it is possible to estimate from

$$pK_a = 5.2 + \log (1/100)$$

the pK_a for the acid *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{2+}$ as being 3.2.

The voltammetric spectrum of the solution containing the product of the reaction between $[Ru(NH_3)_5(H_2O)]^{2+}$ and $P(OEt)_2(OH)$ and $[Ru(NH_3)_5(H_2O)]^{2+}$ and $P(OH)_3$, respectively, shows only one component. The $E_{1/2}$ values for the Ru(III)/Ru(II) couple obtained from CV measurements are +0.60 ± 0.02 V ($\mu = 0.10$ M (CF_3COOH), 25 °C), and +0.65 ± 0.02 V ($\mu = 1.0$ M (CF_3COOH), 25 °C) for *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OH)_3(H_2O)]^{2+}$ respectively. The $E_{1/2}$ value for the Ru(III)/Ru(II) couple in such mono(phosphite) complexes varies with the hydrogen ion concentration of the medium. The dissociation constants for the acids *trans*-$[Ru(NH_3)_4P(OH)_3(H_2O)]^{2+}$, *trans*-$[Ru(NH_3)_4P(OH)_3(H_2O)]^{3+}$, *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{2+}$, and *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{3+}$ have been measured by following the pH dependence of $E_{1/2}$ with cyclic voltammetry and using $E_{1/2}$ versus pH plots as usual.[16] The results obtained are reported in Table III.

The pK_a value of 3.7 for the *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{2+}$ ion, measured through cyclic voltammetric data, is not far from the value of 3.2 estimated from the changes in the stability constant values of the complex ion *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(pz)]^{2+}$ as a function of pH.

The complexes *trans*-$[Ru(NH_3)_4P(OEt)(OH)(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OH)_3(H_2O)]^{2+}$ are not fully protonated at 1.0 M CF_3COOH. Thus the $E^{\circ\prime}$ data for the Ru(III)/Ru(II) couples in such complexes were estimated from

$$E_{pK_{III}} = E^{\circ\prime}{}_{Ru(III)/Ru(II)} - 0.0179$$

where $E_{pK_{III}}$ is the $E_{1/2}$ value at the pK_a of the Ru(III) species obtained from $E_{1/2}$ versus pH plots.

A similar procedure was followed to estimate $E^{\circ\prime}$ for the Ru(III)/Ru(II) couple for fully deprotonated phosphite complexes. For such systems cyclic voltammograms at hydrogen ion concentrations higher than 5.0 exhibit a departure from reversibility. The $E^{\circ\prime}$ values are estimated from

$$E_{pK_{II}} = E^{\circ\prime}{}_{Ru(III)/Ru(II)} + 0.0179$$

where $E_{pK_{II}}$ is the $E_{1/2}$ value corresponding to the pK_a of the Ru(II) species obtained from $E_{1/2}$ versus pH plots.

Phosphoric acid and sodium phosphite do not react with $[Ru(NH_3)_5(H_2O)]^{2+}$ as far as the voltammetric and electronic spectra are concerned. Furthermore, no experimental evidence for aquation of the deprotonated phosphorus ligand has been observed during the experiments.

Discussion

For the case of the *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ complex ions, the X-ray crystallographic data[19] indicate that the phosphite molecule is

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(19) Francisco, R. H. P.; Franco, D. W. Manuscript in preparation.

attached to the ruthenium center through the phosphorus atom. Taking into account the similarity between the chemical properties and the voltammetric and the electronic spectra of monophosphite complexes of ruthenium and those described in this paper, it is reasonable to assume that for the $P(OH)(OEt)_2$ and $P(OH)_3$ molecules phosphorus is also the donor atom.

Diethyl phosphite and the phosphorous acid molecule exhibit the tautomeric equilibria[18-20] $P(III) \rightleftarrows P(IV)$:

$$P(OR)_2(O)(H) \rightleftharpoons P(OR_2)(OH)$$

Only the phosphite form, formally P(III), has empty $3d_\pi$ orbitals available to interact with the t_{2g} orbitals of the Ru(II) center. Therefore, for the calculation of the second-order specific rate for diethyl phosphite substitution on $[Ru(NH_3)_5(H_2O)]^{2+}$ the actual concentration of $P(OEt)_2(OH)$ must be taken into account. From NMR data,[18] it was possible to evaluate the upper limit for the concentration of diethyl phosphite in equilibrium with the phosphanate form, as 5% of the total ligand concentration. Therefore, the rate constants of Table I should be multiplied by a factor of 20 to obtain the lower limit for k_1. The value of 0.24 $M^{-1}\ s^{-1}$ is in the range expected[4] for the substitution reactions of $[Ru(NH_3)_5(H_2O)]^{2+}$ with neutral molecules.

At this point, one feature of the $[Ru(NH_3)_5(H_2O)]^{2+}$–P(III) reaction deserves some comment. For a series of trialkyl phosphites, independent of the ratio Ru(II)/P(III), the bis(phosphite) complex[5-7] *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]X_2$ was the only phosphite complex isolated. Conversely, for the ligands $P(OR)_2(OH)$, only the mono(phosphite) species are observed. This behavior can be explained in view of the different π basicity of the $[Ru(NH_3)_5(H_2O)]^{2+}$, *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$, and *trans*-$[Ru(NH_3)_4P(OR)_2(OH)(H_2O)]^{2+}$ complex ions. The coordination of the first phosphite molecule to Ru(II) diminishes markedly the capacity of the metal to back-bond to another ligand in the trans position and therefore to shift the equilibrium phosphonate $\rightleftarrows$ phosphite. The fact that $P(OR)_2(OH)$ (R = H, Et) does not react with *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ while $P(OR)_3$ (R = Me, Et, Pr, ^{i}Pr, But, Ph) does so strongly supports the above considerations.

The shifts of $E^{\circ\prime}_{Ru(III)/Ru(II)}$ for the phosphite complexes as a function of the hydrogen ion concentration offer an interesting possibility to investigate the effect of the deprotonation of the coordinated phosphorous ligands on the $3d_\pi$–$4d_\pi$ bonds. With deprotonation, a competition is established between the Ru(II) center and the O(II) for the back-bonding with P(III). As a consequence of the O(II)–P(III) $3p_\pi$–$3d_\pi$ π-bonding the extension of Ru(II)–P(III) $4d_\pi$–$3d_\pi$ interaction is diminished. This effect is reflected in the shifts of the $E^{\circ\prime}$ for the Ru(III)/Ru(II) couples in such complexes to less positive values. Thus for the complexes *trans*-$[Ru(NH_3)_4P(OR)_2(OH)(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OR)_3(O)(H_2O)]^{+}$, $\Delta E^{\circ\prime}$ changes in $E^{\circ\prime}$ of 0.14 and 0.22 V are observed for R = Et and H, respectively.

A question concerning the nature of the dissociative proton on the acids *trans*-$[Ru(NH_3)_4P(OR)_2(OH)(H_2O)]^{3+/2+}$ could be raised. The pK_a values for the aquopentaammine complexes are 4.5 and 11.5 for the Ru in the III and II oxidation states, respectively.[4] However, plots of $E_{1/2}$ versus pH for *trans*-$[Ru(NH_3)_4P(OEt)_2(H_2O)]^{2+}$ showed no pH dependence in the pH 1–6 range. Furthermore, plots of $E_{1/2}$ versus pH for the *trans*-$[Ru(NH_3)_4P(OR)_2(OH)(H_2O)]^{2+}$ complexes in the presence of pyrazine (1.5 M) in 10^{-2}–10^{-5} M CF_3COOH give the same pK_a value obtained in the absence of pyrazine. Therefore, it may be reasonable to assume that the proton dissociation does occur at the P–O–H and not at the Ru–H_2O bonds, inasmuch as the Ru–H_2O bond must be weakened by the "trans influence" of the phosphanes.[5-9]

A notable feature of the electronic spectra of the pyrazine derivatives of these mono(phosphite) complexes is a strong absorption band attributable to MLCT transition.[5-9] With the substitution of the ammonia molecule trans to pz in the complex $[Ru(NH_3)_5(pz)]^{2+}$ for $P(OEt)_2(OH)$ and $P(OH)_3$, hypsochromic shifts of 97 and 107 nm, respectively, are observed in λ_{max} of the MLCT transition (see Table II).

The $3d_\pi$ orbitals of the phosphorus are close in energy to the $4d_\pi$ orbitals of the metal and stabilize the t_{2g} orbitals through back-bonding, increasing the energy difference ΔE between the metal orbitals and the π^* pyrazine orbitals. With the deprotonation of the phosphorus ligand on the *trans*-$[Ru(NH_3)_4P(OR)_2(O)(pz)]^{+}$ complexes, $\Delta\lambda_{max}$ for the MLCT transition changes by only 57 nm, thus reflecting a decrease in the Ru(II)–P(III) back-bonding. Therefore, a comparison of the $\Delta\lambda_{max}$ for the MLCT transition for these complexes provides an estimate[21,22] of the relative changes in the extension of back-bonding stabilization energy (BBSE). On this basis, the stabilization of these mono(phosphite) complexes due to Ru(II)–P(III) back-bonding, estimated[21,22] as a BBSE, will be on the order of 8–9 kcal mol^{-1} for the neutral ligands $P(OR)_2(OH)$ and 4 kcal mol^{-1} for the deprotonated forms $P(OR)_2O^-$. All these considerations are based on a simplified model, and the values of BBSE calculated are only estimates. Compared with similar data available[21-24] for other ligands with the $[Ru(NH_3)_5]^{2+}$ moiety, the following trend in decreasing back-bonding can be observed: $P(OR)_2(OH) > pz > isn > P(OR)_2O^- > py > SO_3^{2-}$

Another consequence of the modification in the $4d_\pi$ electron distribution on these Ru(II) complexes is the dramatic variation in the affinity of the metal center for pyrazine[4] on the pentaammine and mono(phosphite) complexes[5-7] (see Table II). In terms of free energy the substitution of NH_3 by $P(OEt)_2$, $P(OEt)_2(OH)$, $P(OH)_3$, $P(OEt)_2(O)^-$, and $P(OH)_2(O)^-$ weakens the Ru(II)–pz bonding by 12–13 kcal mol^{-1}.

The pK_a's for the free tricoordinated tautomers $P(OEt)_2(OH)$ and $P(OH)_3$ have been estimated theoretically[25] as being 6.1 and 7.4, respectively (see Table III). By comparing the pK_a's values for the free and coordinated $P(OR)_2(OH)$ molecules, we observe an increase in the acidity of the OH bond. This behavior is unexpected since it has been shown[4] that, upon coordination to Ru(II), ligands undergo an increase in their pK_a's values. At first sight, the σ component of the ruthenium–phosphorus bond could be invoked to explain such behavior. Arguments on these lines could account for the changes observed for the pK_a's of the Ru(III) complexes, but certainly will fail when dealing with the corresponding Ru(II) acids. The Ru(II)–P(III) bond is mainly π in character as shown by a large amount of accumulated experimental data[4-9,26] for $[Ru(NH_3)_5(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ systems. As a consequence of the Ru(II)–P(III) back-bonding, the phosphorus atom becomes more basic and the inductive effect is felt at the O–H bond. When the metal ion occurs as Ru(III), not a good π donor but a π acceptor,[27] the effect is reversed. The Ru(III) center, which is a stronger Lewis acid than oxygen, makes the phosphorus less basic and the proton more acidic.

An interesting picture could be drawn comparing the pK_a's values for the phosphite complexes and H_3PO_4. The Ru(II) complexes *trans*-$[Ru(NH_3)_4P(OEt)_2(OH)(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OH)_3(H_2O)]^{2+}$ are less acidic than phosphoric acid by 1.6 and 2.6 pK_a units, respectively, and the corresponding Ru(III) complexes are more acidic by 0.6 and 1.1 pK_a units. Phosphoric acid has a typical tetrahedral configuration exhibited formally by pentavalent phosphorus compounds. In the case of the ruthenium(II) and ruthenium(III) mono(phosphite) complexes, a configuration similar to H_3PO_4 can be adopted with the metal at the corner of the tetrahedron, assuming that phosphorus undergoes an oxidative addition[1,28] upon coordination to ruthenium.

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The relevance of the phosphoryl bond is well-known in phosphorus chemistry. The free phosphite molecules are quite reactive and the formation of a stable P=O bond is assumed to be the driving force for most of the reactions of neutral phosphorus esters.[20,28] The tautomerization equilibrium constants of $10^{7.2}$ and $10^{10.3}$ in favor of the phosphonate tautomer,[25] for R = Et and H, respectively, provides a measure of such preference. However, when coordinated to Ru(II) centers, the phosphites exhibit remarkable resistance to hydrolysis[5-9] (1 M CF_3COOH) and to oxidation[5] (Ce^{4+}, Br_2, H_2O_2).

The great strength of the phosphoryl linkage is indicated by the almost universal preference for the phosphonate form when alternative tautomeric forms are possible. Nevertheless, as pointed out earlier in this section, in accordance with the accumulated experimental data[19] for the complexes dealt with in this study, the metal center is directly bonded to the phosphorus atom. In this aspect, the complexes *trans*-$[Ru(NH_3)_4P(OR)_2(OH)(H_2O)]^{2+,3+}$ and *trans*-$[Ru(NH_3)_4P(OR)_2(O)(H_2O)]^{+,2+}$ (R = H, Et), as far as we know, are the first examples of complexes where diethyl phosphite and phosphorous acid are not bonded to a metal center through oxygen atoms.

The ability of the Ru(II) center to stabilize the phosphite form through $4d_\pi$ (Ru)$\cdots$$3d_\pi$ (P) back-bonding, as the oxygen does in the $2p_\pi$ (O)$\cdots$$3d_\pi$ (P) bond, accounts for the chemical inertness of the coordinated phosphite and strongly suggests that the Ru(II)=P(III) bond is stronger than the O(II)=P(III) bond.

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Registry No. $Ru(NH_3)_5(H_2O)^{2+}$, 21393-88-4; $(EtO)_2POH$, 762-04-9; H_3PO_3, 13598-36-2; *trans*-$Ru(NH_3)_4[P(OEt)_2OH](H_2O)^{2+}$, 122093-68-9; *trans*-$Ru(NH_3)_4[P(OH)_3](H_2O)^{2+}$, 122093-69-0; *trans*-$Ru(NH_3)_4[P(OEt)_2(OH)](pz)^{2+}$, 122093-70-3; *trans*-$Ru(NH_3)_4[P(OEt)_2(O)](pz)^+$, 122093-71-4; *trans*-$Ru(NH_3)_4[P(OH)_3](pz)^{2+}$, 122114-36-7; *trans*-$Ru(NH_3)_4[P(OH)_2(O)](pz)^+$, 122093-72-5; Ru, 7440-18-8; P, 7723-14-0; *trans*-$Ru(NH_3)_4[P(OEt)_2(OH)](H_2O)^{3+}$, 122093-73-6; *trans*-$Ru(NH_3)_4[P(OH)_3](H_2O)^{3+}$, 122093-74-7.

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Kinetic Study of the Modes of Decomposition of Pentaaquabenzylchromium(III)

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The preparation of moderately concentrated solutions of $(H_2O)_5CrCH_2C_6H_5^{2+}$ has allowed its visible spectrum to be fully characterized with maxima (nm (molar absorptivities, M^{-1} cm^{-1})) at 533 (31.9) and 358 (2.15×10^3). The kinetics of acidolysis of $(H_2O)_5CrCH_2C_6H_5^{2+}$ have been studied between 56 and 74 °C in 1 M $NaClO_4/HClO_4$ and in the presence of chromium(II) to suppress homolysis. The rate law has terms independent of (k_0) and first order in $[H^+]$ (k_a) with $\Delta H_0{}^*$ and $\Delta H_a{}^*$ values (kcal mol^{-1}) of 21.4 ± 0.4 and 20.3 ± 2.1 and $\Delta S_0{}^*$ and $\Delta S_a{}^*$ values (cal mol^{-1} deg^{-1}) of −11.7 ± 1.9 and −16.5 ± 8.7. Calculated values at 25 °C are $k_0 = 3.8 \times 10^{-6}$ s^{-1} and $k_a = 2.0 \times 10^{-6}$ M^{-1} s^{-1}. The homolysis reaction was studied at 41 °C and found to have apparent half-order kinetics in $[(H_2O)_5CrCH_2C_6H_5^{2+}]$ with an inverse dependence on the hydrogen ion concentration. The products for the heterolysis, homolysis, and decomposition in the presence of ethanol and dioxygen have been characterized by ion-exchange separation and spectrophotometry for the inorganic species and by extraction and proton NMR spectroscopy for the organic products.

Introduction

The decomposition of pentaaqua(organo)chromium(III) complexes in aqueous solution has been observed to occur by homolysis of the Cr–C bond (eq 1) or by acidolysis, which may be viewed as aquation or heterolytic cleavage of the Cr–C bond with assistance from some proton source (eq 2).

$$(H_2O)_5CrR^{2+} \underset{k_{-1}}{\overset{k_1}{\underset{}{\overset{H_2O}{\rightleftarrows}}}} Cr(OH_2)_6{}^{2+} + \{R^\bullet\} \qquad (1)$$

$$(H_2O)_5CrR^{2+} \xrightarrow[H_2O]{k_H} Cr(OH_2)_6{}^{3+} + RH \qquad (2)$$

The homolysis reaction can be studied by adding reagents that will react with either Cr^{2+} or the organic radical to drive the reaction to completion. In favorable cases, the homolysis can be suppressed by adding Cr^{2+} and then the acidolysis reaction can be studied. Work of this type has been summarized in a recent review.[1]

Previous studies on the benzyl complex have produced a somewhat confusing picture of its decomposition mechanism. The early work of Kochi and co-workers[2,3] indicates that this species undergoes relatively rapid acidolysis in ethanol–water mixtures to produce toluene with half-order kinetics in $[(H_2O)_5CrCH_2C_6H_5^{2+}]$. Later, Nohr and Espenson[4] observed a much slower acidolysis in aqueous perchloric acid with an apparent first-order dependence on the chromium complex. Both groups observed that the reaction rate increases with increasing $[H^+]$, with an apparent saturation effect at higher $[H^+]$ in the data of Nohr and Espenson, who also found that the reaction is slowed by the addition of $Cr(ClO_4)_2$ in the 10^{-2}–10^{-3} M range. This could be interpreted to mean that acidolysis really was not being observed exclusively.

Nohr and Espenson also studied the homolysis reaction in the presence of various oxidizing agents, and this aspect seems to have been well characterized with $k_1 = 2.6 \times 10^{-3}$ s^{-1}. More recently Blau et al.[5] have measured the rate constant for the reaction of aqueous Cr^{2+} with the benzyl radical and found $k_{-1} = 8.5 \times 10^7$ M^{-1} s^{-1}. These results were combined to estimate a chromium–carbon bond energy of ~30 kcal mol^{-1} for this system.

In related work, Schmidt and Swaddle[6] studied the decomposition of $(H_2O)_5CrCH_2C_5H_4NH^{3+}$, which gave half-order kinetics in the absence of other reagents and first-order kinetics in the presence of dioxygen, in agreement with the previous work of

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