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Oxygen Transfer in the Oxidation of Triphenylphosphine by $(bpy)_2pyRuO^{2+}$

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The oxidation of PPh_3 by $(bpy)_2pyRuO^{2+}$ (bpy is 2,2′-bipyridine) has been studied in acetonitrile solution. The observation of $(bpy)_2pyRu^{II}O{=}PPh_3^{2+}$ as an intermediate demonstrates that the reaction proceeds via an initial redox step $(bpy)_2pyRuO^{2+} + PPh_3 \rightarrow (bpy)_2pyRu^{II}O{=}PPh_3^{2+}$ which is followed by relatively slow (k(25 °C) = 1.15 (±0.10) × 10^{-4} s^{-1}) solvolysis: $CH_3CN + (bpy)_2pyRu^{II}O{=}PPh_3^{2+} \rightarrow (bpy)_2pyRuCH_3CN^{2+} + O{=}PPh_3$. From the results of an ^{18}O-labeling experiment, oxygen transfer from $Ru^{IV}{=}O$ to PPh_3 is quantitative within experimental error. The kinetics of the redox step were studied by stopped-flow spectrometry. The reaction is first order in both reactants with k(26.6 °C) = 1.75 ± 0.10 × 10^5 M^{-1} s^{-1}. Activation parameters were calculated from the temperature dependence of the rate constant, an analysis of which gave $\Delta H^{*} = 4.7 \pm 0.5$ kcal/mol and $\Delta S^{*} = -19 \pm 3$ eu. The probable microscopic details of the reaction are discussed in terms of a 2-equiv step with strong electronic-vibrational coupling between the electron-donor (P) and -acceptor (Ru) sites through Ru–O and O–P stretching vibrations. The possible role of the spin change which occurs in the net reaction is discussed.

Introduction

Oxo complexes of transition metals such as MnO_4^-, RuO_4, and CrO_3 are strongly oxidizing and are often used in synthetic organic chemistry as general purpose, stoichiometric oxidizing agents.[1,2] Much attention has been given to the mechanistic aspects of the reactions involved, and a wide variety of oxidative reaction pathways are known including both electron transfer and atom transfer. Such systems tend to be rather complex chemically due, in part, to the great diversity of mechanistic possibilities and to the presence of several oxidation states of the metal, more than one of which may be chemically active in the overall reaction. Hence, the details of the reaction mechanisms can be easily obscured, leaving open important questions concerning (1) the site of the initial attack of the reductant (i.e., metal vs. ligand), (2) nucleophilic vs. electrophilic behavior of the oxo ligand, (3) oxygen vs. hydrogen or hydride transfer, and (4) inner-sphere vs. outer-sphere electron transfer.[3] Owing to the importance of oxo complexes as redox agents in chemical synthesis[1,2] and in biological systems,[4,5] there is a clear need to establish the factors that govern the nature of reactivity in particular cases. There is also the possibility that the knowledge gained may be useful in the "rational design" approach to the development of redox catalysts.

The oxo cation $(bpy)_2pyRuO^{2+}$ (bpy is 2,2′-bipyridine)[6] provides an interesting opportunity for study in this regard for several reasons. The complex contains one isolated, reactive oxo site, and the five remaining coordination sites are occupied by relatively nonlabile, aromatic nitrogen heterocycles. The oxo–aquo chemistry at the sixth coordination site enables the metal to span three oxidation states reversibly in aqueous solution accompanied by the gain or loss of protons (see Scheme I) (pH 7; potentials vs. the saturated calomel electrode, SCE). Initial experiments suggest that a range of 1- and 2-equiv redox mechanistic pathways are available to the system. Further, recent work has shown that a series of redox processes can be carried out electrocatalytically with use of the $(bpy)_2pyRu(OH_2)^{2+}/(bpy)_2pyRuO^{2+}$ couple or the more stable $(trpy)(bpy)Ru(OH_2)^{2+}/(trpy)(bpy)RuO^{2+}$ (trpy is 2,2′,2″-terpyridine) couple as redox carriers in electrochemical shuttle mechanisms. The catalyzed reactions observed include oxidation of selected organic compounds including alcohols, olefins, and aromatic hydrocarbons[7] and reduction of the NO_3^- ion.[8] The potential of such systems as specific catalysts can be appreciated when the background synthetic chemistry which allows the systems to be modified almost at will is taken into account.[9,10]

In overall 2-equiv oxidations by terminal oxo complexes where the thermodynamics of sequential 1-equiv steps is unfavorable, oxygen-transfer processes are known to provide an efficient pathway for the incorporation of an oxygen atom into a substrate molecule.[2,11] In microscopic reverse, oxygen transfer may explain the remarkable reactivity of certain aquo complexes of ruthenium, including $(bpy)_2pyRu(OH_2)^{2+}$, toward oxidizing but normally unreactive oxyanions such as NO_3^- or ClO_4^-.[8,12]

In this paper we present the results of a study on the oxidation of triphenylphosphine (PPh_3) by $(bpy)_2pyRuO^{2+}$ in acetonitrile solution. In itself, the oxidation of PPh_3 is not a particularly interesting or useful reaction, but it poses few problems for analysis, it provides a possibly clear-cut example of an oxygen transfer reaction involving the $(bpy)_2pyRuO^{2+}$ system, and it is a reaction which can be made catalytic by electrochemical regeneration of $(bpy)_2pyRuO^{2+}$.[7] The results obtained may also be useful in defining a reaction pathway whose essential details may be a common feature in a series of related reactions.

By way of background chemistry, a number of catalytic schemes for the oxidation of phosphines are known, based on O_2 or nitro complexes of transition metals.[13] In general, oxo

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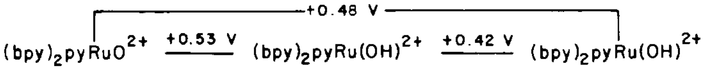
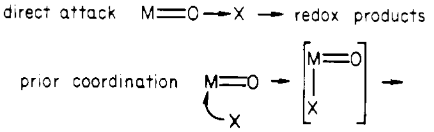
Scheme I



Scheme II



complexes are also effective oxidants for phosphines[14] as seen, for example, in the catalytic oxidation of PPh_3 by O_2 using bis(dithiocarbamato) complexes of Mo(VI).[15] $Co(acac)_2$ has been found to be an efficient catalyst for the O_2 oxidation of phosphines, but unlike several related complexes, the reaction appears to involve an oxo–Co(IV) intermediate, $(Bu_3P)(acac)_2CoO^{2+}$, which forms by cleavage of a binuclear O_2 complex.[16] While it appears that many of the phosphine oxidations by oxo and dioxygen complexes involve oxygen transfer of some kind, important mechanistic ambiguities still often exist concerning questions such as whether the phosphine must first coordinate to the metal or can undergo a more direct attack on the oxo ligand; e.g., Scheme II, and whether, in an initial step, one-electron transfer occurs to give PPh_3^+, e.g., $M{=}O + PPh_3 \rightarrow M{=}O^- + PPh_3^+$.

Experimental Section

Materials. Triphenylphosphine was recrystallized twice from ethanol and checked periodically by IR to confirm the absence of triphenylphosphine oxide ($\nu_{P=O}$ = 1190 cm^{-1}; mull[17]). Triphenylphosphine oxide was obtained as an undergraduate preparation. Acetonitrile (MCB Spectrograde or Matheson Spectra AR) was purified by fractional distillation over CaH_2 and passage through a column of alumina activated at 350 °C for 24 h. For removal of nonvolatile impurities, Spectrograde or reagent grade toluene was distilled once. Deionized water was distilled once over alkaline $KMnO_4$ to remove organic contaminants, and N_2 was deoxygenated by passing through an alkaline dithionite solution[18] followed by KOH pellets and P_2O_5 as drying agents.

Preparations. $[(bpy)_2pyRuO](ClO_4)_2$, $[(bpy)_2pyRu(OH_2)](PF_6)_2{\cdot}H_2O$,[6,19] and $[(bpy)_2pyRu(NO)](PF_6)_3$[20] were prepared as described previously.

$[(bpy)_2pyRu(CH_3CN)](PF_6)_2$. A total of 79 mg of $[(bpy)_2pyRu(OH_2)](PF_6)_2{\cdot}H_2O$ was dissolved in approximately 5 mL of CH_3CN and allowed to stand for 2 h protected from light. The solution was then added dropwise to 200 mL of anhydrous ether while being stirred and the precipitate collected by filtration and dried in vacuo to give a yellow powder. The yield was 60 mg (75% theoretical). Anal. Calcd for $[(bpy)_2pyRu(CH_3CN)](PF_6)_2$: C, 39.38; N, 10.20; H, 2.94. Found: C, 39.12; N, 10.19; H, 2.74. The complex was also prepared by another route described by Brown.[20]

Measurements. Routine UV/vis spectral measurements were carried out with 1-cm cells on Cary 14 or Bausch and Lomb Spectronic 210UV spectrophotometers. IR spectra were obtained with use of a Beckman 4250IR spectrophotometer. Elemental analyses were performed by Integral Microanalytical Labs, Raleigh, N.C.

UV/Vis Measurements. The rapid formation of $(bpy)_2pyRu(CH_3CN)^{2+}$ upon dissolving $[(bpy)_2pyRu(OH_2)](PF_6)_2{\cdot}H_2O$ in CH_3CN was shown spectrophotometrically, and extinction coefficients were calculated as the average of three dilutions of a stock solution. Spectral observations with time show that solvation occurs on a time scale of minutes. Stoichiometric relationships in the reaction between $(bpy)_2pyRuO^{2+}$ and PPh_3 in CH_3CN were in part determined in a spectrophotometric titration where the PPh_3:Ru(IV) mole ratio was varied between 0 and 2 by adding different volumes of a stock solution of PPh_3 to equal volumes of a Ru(IV) stock solution and diluting each to 10 mL. No precautions were taken to exclude air. Spectra taken at different times after mixing indicated that the reaction took place in two stages with the buildup of an intermediate at 479 nm. A blank solution of Ru(IV) without added PPh_3 showed only minor spectral changes over a time span of several hours for which data are reported, but after 16 h, $(bpy)_2pyRu(CH_3CN)^{2+}$ had formed appreciably, accounting for approximately 20% of the initial Ru(IV) complex added.

Infrared Measurements. For observation of the infrared spectral changes that occur in the course of the reaction between PPh_3 and $(bpy)_2pyRuO^{2+}$ in CH_3CN, 1 mL of a solution of 13.5 mg of freshly recrystallized PPh_3 in 10 mL of CH_3CN (to give 5.2 μmol) was added to 3.6 mg (5.2 μmol) of solid $[(bpy)_2pyRuO](ClO_4)_2$, and the reaction was monitored at different times in an approximately 1-mm NaCl cell (vs. CH_3CN in the reference cell) in the region 1250–1100 cm^{-1}. Due to the proximity of strong ClO_4^- absorptions, no attempt was made to make the observations quantitative, but instead, a procedure was devised to separate the final ruthenium complex product from the phosphine oxide product. Completely reacted (1 day old) solutions of approximately the same initial concentrations as above were added dropwise to 40–50 mL of previously distilled toluene while being stirred to precipitate the complex. After filtering, the solution was carefully evaporated to dryness on a rotary evaporator in a small (~10 mL) round-bottom flask. Comparison of the infrared spectrum of the residue of one such reaction (evaporated to a thin film from CH_3CN onto NaCl plates) with an infrared spectrum of $OPPh_3$ confirmed the identity of the residue as $OPPh_3$ without any other detectable products. Quantitative infrared analysis for $OPPh_3$ was carried out by taking up the residue completely in exactly 1 mL of CH_3CN and measuring the peak height of the 1195-cm^{-1} phosphine oxide stretch[21] by the base-line method.[22a] The calibration curve for $OPPh_3$ in CH_3CN was linear over the concentration range (4–8) × 10^{-3} M, yielding the expression $C = (A - 0.017)/44.3b$, where C is the molar concentration of $OPPh_3$, b is the path length in millimeters (determined by counting the number of interference fringes between two wavelengths),[22b] and A is the absorbance of the phosphine oxide stretch. Blanks showed that little or no air oxidation of PPh_3 to $OPPh_3$ occurred in the CH_3CN solutions over the course of the experiment or as a result of the following workup procedure. Overall, the accuracy of the infrared results is estimated to be ±10%.

Kinetics. The reaction between PPh_3 and Ru(IV) produces as an intermediate $(bpy)_2pyRu(OPPh_3)^{2+}$. Initial attempts to measure the decay of the intermediate in CH_3CN produced erratic results apparently due to the high sensitivity of the intermediate to light. In the presence of light the reaction is markedly accelerated, but the overall stoichiometry appears to be unaffected since the final products appear in the expected yield whether or not precautions are taken to exclude light. The photolysis reaction is expected given the photochemical properties of $(bpy)_2Ru(py)_2^{2+}$ which is known to lose pyridyl groups with a relatively high quantum efficiency.[10] Reproducible rate measurements were obtained by employing low slit widths and higher concentrations of complex and by exposing the solutions to the sample beam only long enough to make the absorbance measurement. Data were taken on a thermostated Gilford Model 240 spectrophotometer. Conventional mixing techniques were used to introduce the solutions

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into the 1-cm cells for measurement in subdued light. First-order rate constants were calculated on the basis of a least-squares fit (uniform weighting) to the relation[23a]

$$\ln |A_\infty - A| = -kt + \ln |A_\infty - A_0|$$

where A_∞ is the final absorbance at completion of the reaction, a_0 is the initial absorbance, A is the absorbance (corrected for drift and solvent) measured at time t, and k is the first-order rate constant. Reactions were monitored for approximately $2^1/_2$–3 half-lives after which the scatter became appreciable. Reported extinction coefficients for the intermediate were calculated from the initial absorbances extrapolated from the kinetic plots.

Stopped-flow measurements of the rate of formation of the intermediate in the reaction between Ru(IV) and PPh_3 were carried out on an Aminco-Morrow stopped-flow apparatus attached to a Beckman DU monochromator, details of which are given elsewhere.[24] Pseudo-first-order conditions were maintained throughout the experiments with either PPh_3 or Ru(IV) in excess. Reported values of the rate constants are the average of four or more experiments in which the same solutions were reacted under the conditions employed. All solutions were protected from the atmosphere with use of serum caps and immediately purged with N_2 for 15 min after mixing. Hamilton gas-tight syringes, three-way Kel-F stopcocks, and Teflon tubing permitted delivery of the reactant solutions to the stopped-flow apparatus without exposure to the atmosphere. Due to the time-consuming nature of maintaining anaerobic conditions, activation parameters were determined with use of only one solution each of PPh_3 and Ru(IV).

Some difficulty was encountered in that the initial stopped-flow transient accounted for less than the total expected change in absorbance on the basis of the calculated extinction coefficients of the intermediate ($\epsilon = 9000$ at 479 nm). Deliberate addition of water to or aging of the Ru(IV) solutions tended to decrease further the total absorbance change, and since over more prolonged periods (6–12 h) the buildup of $(bpy)_2pyRu(CH_3CN)^{2+}$ could be observed spectrophotometrically (and visually) in CH_3CN solutions of Ru(IV), the problem was attributed to the instability of $(bpy)_2pyRuO^{2+}$ at the low concentrations employed ($\leq 5 \times 10^{-5}$ M). In addition, at wavelengths greater than 404 nm, a second much slower increase in absorbance (15–30-min duration) was detected which could not be explained by the occurrence of the solvolysis of the intermediate, $(bpy)_2pyRu(OPPh_3)^{2+}$, which is a slower reaction. Complications from the latter reaction, which is a minor pathway, were avoided by monitoring at 404 nm which gave stable rather than drifting base lines apparently because of the existence of an isosbestic point for the interfering process.

Labeling Studies. $[(bpy)_2pyRu^{18}O](ClO_4)_2$, containing an estimated 56% ^{18}O, was available from previous experiments described in earlier papers.[6] It was allowed to react with PPh_3 essentially as before. A total of 4.2 mg (5.9 μmol) of complex was dissolved in approximately $^1/_2$ mL of CH_3CN, and exactly 1 mL (5.7 μmol) of a PPh_3 solution containing 37.5 mg of PPh_3 in 25 mL of CH_3CN was added. Stoppered and protected from light, the solution was allowed to stand for approximately 16 h at which time it was added to 50 mL of toluene, filtered, and evaporated to dryness. The residue was taken up in exactly 1 mL of CH_3CN and analyzed in the region 1250–1100 cm^{-1} as described previously for $^{16}OPPh_3$. As expected,[17] the $^{18}OPPh_3$ absorption was shifted approximately 30 cm^{-1} to lower energy, and it was assumed for quantitative purposes that the relative oscillator strengths of the $\nu_{P={}^{16}O}$ and $\nu_{P={}^{18}O}$ bands are solvent independent. (In CCl_4 or CS_2 as solvent, the intensity of the $\nu_{P={}^{18}O}$ peak is 15% lower than the intensity of the $\nu_{P={}^{16}O}$ peak.[17]) No change in the relative intensities of the $\nu_{P={}^{18}O}$ and $\nu_{P={}^{16}O}$ peaks was observed over a 24-h period following the initial analysis, consistent with the known resistance of $^{18}OPPh_3$ to exchange even in boiling H_2O.[17] The experiment was repeated once in the same way except that all solutions were protected from the atmosphere under a blanket of N_2 with use of syringe/serum cap techniques, but essentially no difference in results was observed.

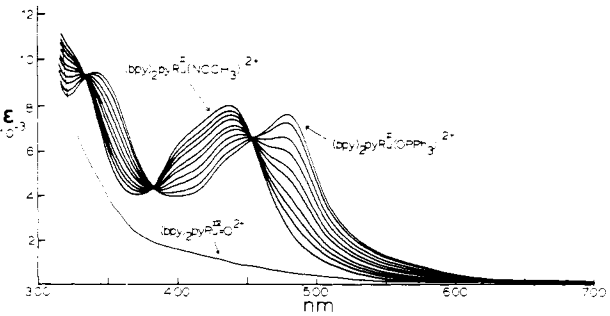

Figure 1. Spectral changes with time in the oxidation of PPh_3 by $(bpy)_2pyRuO^{2+}$. Solid PPh_3 was added to a solution of $[(bpy)_2pyRuO](ClO_4)_2$ in CH_3CN (approximately 5×10^{-4} M, 1-cm cells) at room temperature. The initial spectrum, after mixing, labeled $(bpy)_2pyRu^{II}(OPPh_3)^{2+}$, has a λ_{max} at 479 nm, and the spectrum after 12 h, labeled $(bpy)_2pyRu^{II}(NCCH_3)^{2+}$, has λ_{max} at 441 nm.

For determination of possible exchange with trace water in CH_3CN, 11.2 mg of unlabeled $[(bpy)_2pyRuO](ClO_4)_2$ was stirred for 10 min in 1 mL CH_3CN to which approximately 35 mg of 95.0% $H_2{}^{18}O$ (BioRad Laboratories) had been added to give 1.8 M $H_2{}^{18}O$. The solution was then evaporated to dryness in vacuo at room temperature (20–30 min), and the residue was analyzed in the infrared (800–600 cm^{-1}) as a mull on KBr plates. A similar experiment was subsequently run in which 3.7 mg (5.2 μmol) of unlabeled $[(bpy)_2pyRuO](ClO_4)_2$ in $^1/_2$ mL of CH_3CN was allowed to react with 1 mL (5.3 μmol) of a PPh_3 solution containing 6.9 mg of PPh_3 in 5 mL of CH_3CN. The CH_3CN used in this run contained 38.1 mg of 95.0% $H_2{}^{18}O$ in 10 mL of CH_3CN so that the resulting solution was 0.18 M in $H_2{}^{18}O$. The analysis of the $^{18}OPPh_3$ to $^{16}OPPh_3$ ratio was carried out as before.

Results

Stoichiometry. Figure 1 shows the changes that occur in the visible spectrum during the reaction of $(bpy)_2pyRuO^{2+}$ with PPh_3 at room temperature in acetonitrile. Initially, with no added PPh_3, the visible spectrum of Ru(IV) has no noticeable absorption bands, but upon addition of PPh_3, charge-transfer bands at 338 ($\epsilon = 10\,300$) and 479 nm ($\epsilon = 9000$) appear rapidly. Over the course of several hours, both the 338- and 479-nm bands disappear, giving rise to a new absorption at 440 nm ($\epsilon = 8400$) and a shoulder at 325 nm adjacent to more intense π(bpy) $\rightarrow$ π^*(bpy) transitions in the UV.[25] By comparison with previously recorded spectral values ($\lambda_{max} = 437$ nm, $\epsilon = 7730$)[20] and results obtained here ($\lambda_{max} = 441$ nm, $\epsilon = 8000$),[26] the final ruthenium product is $(bpy)_2pyRu(CH_3CN)^{2+}$, formed in quantitative yield from $(bpy)_2pyRuO^{2+}$ in the overall reaction.

A mole ratio plot of the spectrophotometric titration data taken near the end of the reaction shown in Figure 1 indicated a 1:1 mole relationship between $(bpy)_2pyRuO^{2+}$ and added PPh_3, and under more concentrated conditions, free $OPPh_3$ was detected by infrared spectroscopy ($\nu_{P=O} = 1195$ cm^{-1}) in the completely reacted solutions. Quantitative analysis for $OPPh_3$ was carried out as described in the Experimental Section. The results obtained show that $OPPh_3$ is formed quantitatively (97 ± 5%; average of two experiments) and that the overall reaction is

$$(bpy)_2pyRu^{IV}O^{2+} + PPh_3 \xrightarrow{CH_3CN} (bpy)_2pyRu^{II}(CH_3CN)^{2+} + OPPh_3 \quad (1)$$

Infrared spectral changes occur which parallel the changes in the UV–visible spectra shown in Figure 1. Shortly after $[(bpy)_2pyRuO](ClO_4)_2$ and PPh_3 are mixed in acetonitrile,

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(26) The small discrepancy in λ_{max} is probably due to the use of different spectrophotometers.

Table I. Kinetic Data for the Solvolysis of the $(bpy)_2pyRu(OPPh_3)^{2+}$ Intermediate in CH_3CN at 25.0 ± 0.2 °C

$10^5 \times [Ru(IV)]_0$,[a] M	$[PPh_3]_0$,[b] M	$10^3 \times [OPPh_3]$, M	$10^2 \times$ [TEAP],[c] M	$10^{-4} \times k$,[d] s^{-1}
6.26	9.84×10^{-5}			1.15[e]
9.64	1.45×10^{-4}			1.15[e]
9.40	4.42×10^{-4}			1.19
9.40	1.47×10^{-4}	4.77		1.21
9.40	1.47×10^{-4}		5.02	1.23

[a] Initial molar concentration of $[(bpy)_2pyRuO](ClO_4)_2$. [b] Initial molar concentration of PPh_3. [c] [TEAP] is the molar concentration of $[(C_2H_5)_4N]ClO_4$. [d] First-order rate constants obtained from a least-squares fit to eq 1 of the data taken at 485 nm for at least 2½ half-lives. [e] Average of three runs.

Table II. Kinetic Data for the Initial Fast Step of the Reaction between $(bpy)_2pyRuO^{2+}$ and PPh_3 in CH_3CN

$10^5[Ru(IV)]_0$,[a] M	$10^4[PPh_3]_0$,[b] M	$10^{-5}k$,[c] M^{-1} s^{-1}	T, °C
3.96	7.90	1.72 ± 0.08	26.5
3.96	5.54	1.72 ± 0.07	26.6
3.53	3.53	1.80 ± 0.06	26.5
2.88	2.50	1.76 ± 0.05	26.7
3.43	2.19	0.91 ± 0.01	5.6
3.43	2.19	0.99 ± 0.04	9.7
3.43	2.19	1.22 ± 0.03	14.1
3.43	2.19	1.33 ± 0.10	19.0
3.43	2.19	1.60 ± 0.02	25.8
3.43	2.19	1.92 ± 0.10	30.2
3.43	2.19	2.33 ± 0.08	36.2

[a] Initial molar concentration of $[(bpy)_2pyRuO](ClO_4)_2$. [b] Initial molar concentration of PPh_3. [c] Second-order rate constant as determined under pseudo-first-order conditions in dry CH_3CN solvent under N_2. Each rate constant is the average of four or more experimental determinations under the conditions employed.

an intense peak is observable at 1150 cm^{-1} which is within the range 1125–1175 cm^{-1}, usually associated with the P=O stretching frequency of coordinated $OPPh_3$.[21,27] Over the duration of the slow reaction shown in Figure 1, the 1150-cm^{-1} peak disappears as the 1195-cm^{-1} peak of free $OPPh_3$ grows in. The electronic spectral characteristics of the intermediate (λ_{max} = 338, 479 nm) are typical of a great many bipyridine complexes of Ru(II),[9,25] especially those with oxygen-bound ligands, L, in complexes of the type $(bpy)_2pyRu^{II}L^{n+}$ (e.g.: L = H_2O[6], λ_{max} = 470 nm, ϵ = 8400; L = OH^-,[6] λ_{max} = 488 nm, ϵ = 8100; L = ClO_4^-, λ_{max} = 474 nm, ϵ = 8600). It seems clear that the intermediate is the Ru(II) complex, $(bpy)_2pyRu(OPPh_3)^{2+}$, and that the overall reaction observed (eq 2) involves a rapid 2-equiv oxidation of PPh_3 to give the

$$(bpy)_2pyRu^{IV}O^{2+} + PPh_3 \xrightarrow{\text{fast}} (bpy)_2pyRu^{II}(OPPh_3)^{2+} \xrightarrow{CH_3CN} (bpy)_2pyRu^{II}(CH_3CN)^{2+} + OPPh_3 \quad (2)$$

bound $OPPh_3$ product followed by a far slower solvolysis of $OPPh_3$. Attempts to isolate $(bpy)_2pyRu(OPPh_3)^{2+}$ in pure form from the reaction or from alternate routes[9] did not yield acceptable analytical results probably due to the labile nature of the $OPPh_3$ ligand bound to Ru(II), but the solids isolated did have spectral characteristics (IR, UV–visible) consistent with those expected for the phosphine oxide complex.

Kinetics. The kinetics of the solvolysis of the $(bpy)_2pyRu(OPPh_3)^{2+}$ intermediate in CH_3CN at 25 °C were monitored spectrophotometrically at 485 nm. Over a period of 3 half-lives, the reaction obeyed precise first-order kinetics as determined by a least-squares fit of the data to eq 1. As given by Table I, the first-order rate constant averaged over six runs is 1.15 (±0.10) × 10^{-4} s^{-1} ($t_{1/2}$ = 100 min) at 25 °C. Only a minor variation in rate was observed upon addition of $OPPh_3$, $[(C_2H_5)_4N]ClO_4$, or excess PPh_3, consistent with the proposed irreversible dissociation of $OPPh_3$ from $(bpy)_2pyRu(OPPh_3)^{2+}$.

The formation of the intermediate was studied by stopped-flow spectrophotometry. Under pseudo-first-order conditions with either PPh_3 or $[(bpy)_2pyRuO](ClO_4)_2$ in excess, the reaction is first order in both PPh_3 and $(bpy)_2pyRuO^{2+}$ consistent with the fast bimolecular step in eq 2. With use of the results from a series of wavelengths, the visible spectrum of the product formed in the reaction agreed reasonably well with the spectrum of the intermediate obtained in the conventional mixing experiments. Table II lists the final results of the stopped-flow analysis for the formation of the $(bpy)_2pyRu(OPPh_3)^{2+}$ intermediate. At 26.5 ± 0.2 °C the second-order rate constant for the reaction was found to be 1.75 (±0.10) × 10^5 M^{-1} s^{-1} averaged over four concentrations of PPh_3 in pseudo-first-order excess. An experiment with Ru(IV) in excess produced a slightly lower value for the second-order rate constant probably because of partial reduction of $(bpy)_2pyRuO^{2+}$ in the stock solution prior to the reaction. As would be expected for a kinetic step involving an ion and a neutral molecule,[23b] addition of either $LiClO_4$ or $[(C_4H_9)_4N]PF_6$ as electrolytes had only a minor effect on the rate constant. Activation parameters as defined in eq 3

$$\ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} + \ln \frac{k_B}{h} \quad (3)$$

from transition-state theory[23c] were obtained from a plot of ln (k/T) vs. $1/T$, yielding the values $\Delta H^\ddagger$ = 4.7 ± 0.5 kcal/mol and $\Delta S^\ddagger$ = −19 ± 3 eu where the error limits were calculated with use of standard methods of error analysis.

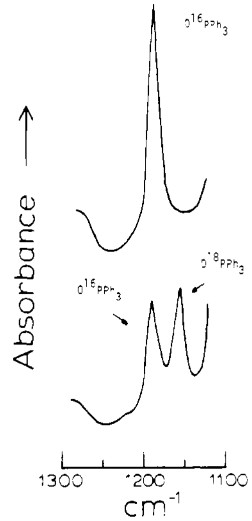

Figure 2. Infrared tracer study of oxygen transfer in the oxidation of PPh_3 by $(bpy)_2pyRuO^{2+}$. The spectra are of the product $OPPh_3$ in acetonitrile. The top spectrum is a "dry run" with unlabeled complex, and the bottom spectrum is the result obtained by using approximately 56% ^{18}O-labeled $(bpy)_2pyRuO^{2+}$. The analysis for $OPPh_3$ which gave 53% $^{18}OPPh_3$ and 46% $^{16}OPPh_3$ was run after the $[(bpy)_2pyRu(CH_3CN)](ClO_4)_2$ product had been removed from the solution.

Labeling Studies. A tracer study using ^{18}O-labeled $(bpy)_2pyRuO^{2+}$ was conducted to rule out ClO_4^-, O_2, and trace H_2O as possible sources of the oxygen that appears in the $OPPh_3$ product. Figure 2 shows the result of an experiment in which $[(bpy)_2pyRuO](ClO_4)_2$ containing approximately 56 atom % $(bpy)_2pyRu^{18}O^{2+}$ was allowed to react with PPh_3 in CH_3CN and analyzed in the manner previously described. A quantitative analysis (±10%) for $^{18}OPPh_3$ (1158 cm^{-1}) and

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$^{16}OPPh_3$ (1195 cm^{-1}) using data from two separate experiments showed essentially complete oxygen transfer from $(bpy)_2pyRuO^{2+}$ to PPh_3 (56% ^{18}O product expected vs. 56% and 47% observed) whether or not precautions were taken to exclude air. A test for trace water as the oxygen source was made by allowing unlabeled Ru(IV) and PPh_3 to react in CH_3CN which was 0.18 M in $H_2{}^{18}O$ (90% ^{18}O). The results showed that only 4% of the $OPPh_3$ formed had incorporated the label, suggesting that, at best, only a minor portion of the oxygen transferred to the product can have its origin in added water. The origin of the small amount of ^{18}O incorporation could lie in an initial exchange reaction between $(bpy)_2pyRuO^{2+}$ and H_2O. However, unlabeled $[(bpy)_2pyRuO](ClO_4)_2$ in CH_3CN containing 1.8 M $H_2{}^{18}O$ (90% ^{18}O) does not undergo a detectable exchange within 30 min as shown by the absence of the $\nu_{Ru=^{18}O}$ stretch in the infrared spectrum (mull) of the complex after evaporation of the solution at room temperature. It should be noted that for detectability, probably more than 15–20% exchange would have had to have taken place since the $\nu_{Ru=O}$ infrared stretch occurs amidst aromatic C–H deformation modes.

Discussion

The oxidation of PPh_3 by $(bpy)_2pyRuO^{2+}$ in acetonitrile occurs by a net oxygen transfer. The final products, $OPPh_3$ and $(bpy)_2pyRuCH_3CN^{2+}$, are formed quantitatively by the sequence of reactions shown in eq 2. In an initial rapid step, the phosphine oxide complex, $(bpy)_2pyRuOPPh_3{}^{2+}$, is formed as an identifiable intermediate which subsequently undergoes a far slower solvolysis reaction to give the final products. The observation of the bound phosphine oxide and the ^{18}O-labeling experiment show clearly that the origin of the transferred oxygen is the oxyl group of the Ru(IV) oxidant.

There are a number of mechanistic possibilities for the redox step. Despite the intuitive and justifiable appeal of a single, two-electron oxygen transfer, a more complicated mechanism involving sequential one-electron steps could be obscured from direct experimental observation. However, given the chemical nature of the reactants, one-electron steps are unlikely. In aqueous solution, one-electron reduction of $(bpy)_2pyRuO^{2+}$ occurs with the addition of one proton ($2 < pH < 8$) to give $(bpy)_2pyRu(OH)^{2+}$. Since the Ru(III)–OH complex is a weak acid, $pK_a > 9$ and, probably, $pK_a \gg 9$, in aprotic solvents where the redox couple would be $(bpy)_2pyRuO^{2+/+}$, $(bpy)_2pyRuO^{2+}$ is a much weaker oxidant. The point is shown by a cyclic voltammetry experiment where, although reduction of $(bpy)_2pyRuO^{2+}$ is chemically irreversible, it can be estimated that $E_{1/2} < 0.1$ V vs. the saturated sodium chloride calomel electrode (SSCE).[19] Under the same conditions, oxidation of PPh_3 is also chemically irreversible with $E_{1/2} > 1.32$ V vs. SSCE for the $PPh_3{}^{+/0}$ couple. By combination of the two electrochemical estimates, a simple outer-sphere electron transfer can be ruled out for the initial step, since for reaction 4, $\Delta G > 20$ kcal/mol and experimentally $\Delta G^\ddagger(25\ °C) = 10.4$ kcal/mol. It is also unlikely that the reaction occurs by a discrete one-electron "oxidative addition" or "inner-sphere" step (eq 5) given the extreme reducing properties of $Ph_3PO^-\cdot$.[28]

$$(bpy)_2pyRuO^{2+} + PPh_3 \rightarrow (bpy)_2pyRuO^+ + PPh_3{}^+ \qquad (4)$$

$$(bpy)_2pyRu^{IV}O^{2+} + PPh_3 \rightarrow [(bpy)_2pyRu^{III}OPh_3P^-\cdot]^{2+} \qquad (5)$$

Even if the redox chemistry involves a single, 2-equiv oxygen transfer, that step could be preceded by coordination of the phosphine at ruthenium (eq 6). Both six-[29] and seven-coordinate complexes of Ru(IV) are known.[30] However, the formation of the seven-coordinate intermediate demanded by eq 6 is unlikely on steric grounds as predicted both by molecular models and experience with related complexes.[31]

$$(bpy)_2pyRuO^{2+} + PPh_3 \rightarrow (bpy)_2pyRu({=}O)PPh_3{}^{2+} \qquad (6)$$

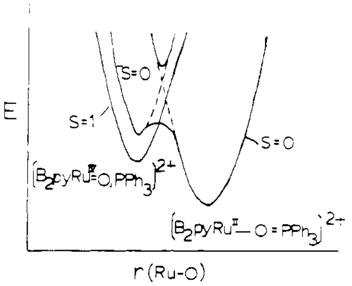

Figure 3. Reaction coordinate diagram for the redox step $[B_2pyRu^{IV}{=}O,PPh_3]^{2+} \rightarrow [B_2pyRu^{II}OPPh_3]^{2+}$ (B is 2,2′-bipyridine). Spin multiplicities for the reactant and product states are indicated on the diagram.

The picture that emerges for the oxidation of PPh_3 by $(bpy)_2pyRuO^{2+}$ is a synchronous 2-equiv step in which oxygen atom transfer occurs from Ru to P. In the net reaction, the redox step is preceded by a preequilibrium association of the reactants (eq 7), and the observed kinetic parameters (eq 9–11)

$$(bpy)_2pyRuO^{2+} + PPh_3 \overset{K_A}{\rightleftharpoons} (bpy)_2pyRuO^{2+},PPh_3 \qquad (7)$$

$$(bpy)_2pyRuO^{2+},PPh_3 \xrightarrow{k_R} (bpy)_2pyRuOPPh_3{}^{2+} \qquad (8)$$

$$k = k_R K_A \qquad (9)$$

$$\Delta H^\ddagger = \Delta H_A + \Delta H_R{}^\ddagger \qquad (10)$$

$$\Delta S^\ddagger = \Delta S_A + \Delta S_R{}^\ddagger \qquad (11)$$

reflect the equilibrium properties of eq 7 as well as the microscopic details of the redox step. In eq 9–11 the subscripts A and R refer to the association and redox steps, respectively. The contributions to k, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ from the preequilibrium can be estimated from a statistical thermodynamic treatment.[32] Using the results of that treatment and assuming that the average separation between reactants in the association complex is ~12 Å gives $K_A \approx 0.1$, $\Delta H_A \approx -0.3$ kcal/mol, and $\Delta S_A \approx -4$ eu. It follows from eq 10 and 11 that for the redox step $\Delta H_R{}^\ddagger \approx 5$ kcal/mol and $\Delta S_R{}^\ddagger \approx -15$ eu.

In Figure 3 is shown a reaction coordinate diagram for the redox step. Figure 3 is a schematic attempt to illustrate the variation in potential energy along the Ru–O bond which should respond critically to the redox change. The figure introduces a complicating feature of the reaction which arises from spin considerations. A magnetic study on $[(bpy)_2pyRuO](ClO_4)_2$, shows that at room temperature the d^4 Ru(IV) ion has two unpaired electrons and a "triplet" ($S = 1$) ground state. Since the initial product of the redox step is the d^6 Ru(II) complex $(bpy)_2pyRu^{II}O{=}PPh_3{}^{2+}$, which is no doubt diamagnetic ($S = 0$), a spin change must occur in the reaction which to a first level of approximation is not allowed quantum mechanically.[33]

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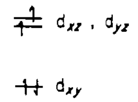
(32) $K_A = d^2(8\pi h^2/\mu k_B T)^{1/2}(N/1000)$, $\Delta H_A = -RT/2$, and $\Delta S_A = R \ln K_A - R/2$, where d is the internuclear separation in cm, h and k_B are Planck's and Boltzmann's constants, μ is the reduced mass of the reactants A and B ($\mu = M_A M_B/(M_A + M_B)$), and N is Avogadro's number: North, A. M. "The Collision Theory of Chemical Reactions in Liquids"; Wiley: New York, 1964.

However, the actual situation is probably more complicated. Neglecting the effects of spin–orbit coupling, the observation of two unpaired electrons is consistent with the orbital splitting scheme



where the Ru═O bond is taken as the z axis and the symmetry of the complex is assumed to be C_{4v}.

Since the actual symmetry of the complex is C_1 rather than C_{4v}, the d_{xz},d_{yz} orbitals are inequivalent and their degeneracy should be lifted. With the lifting of the degeneracy, it is not unreasonable to expect that a relatively low-lying singlet ($S = 0$) state, for example, having the electronic population $(d_{xy})^2(d_{yz})^2$, should exist for $(bpy)_2pyRuO^{2+}$, and such a state is indicated on Figure 3. The effect of spin–orbit coupling will be to mix the three components of the triplet state with the single component of the singlet state to give a new series of states which no longer have pure singlet or triplet character.

As shown in Figure 3, the intersection region between the $S = 0$ reactant and product surfaces is probably a case of a "strongly avoided" surface crossing.[34] Given the apparently 2-equiv nature of the reaction, strong electronic coupling between the Ru ion and P atom through oxygen no doubt exists with strong electronic-vibrational coupling through the Ru–O and P–O stretching vibrations. Because of extensive electronic coupling, the transition between the $S = 0$ reactant and product surfaces is expected to be strongly adiabatic. For such a pathway, the role of solvent vibrational changes should be very small. For redox reactions in which there is extensive charge transfer, changes in solvent polarization lead to an important contribution to the vibrational barrier to the reaction.[35] Because of the synchronous nature of the 2-equiv adiabatic process—electron flow toward the Ru ion, oxide ion stretching toward the P atom—there is little charge-transfer character in the reaction.

To a first approximation, the transition between the $S = 1$ reaction and $S = 0$ product surfaces is forbidden because of the change in spin multiplicity between states. By including spin–orbit coupling, the transition is allowed, but if the triplet ground state character is largely preserved, electronic coupling between reactant and product surfaces would be small. As a consequence, at the intersection region between sufaces, an *abrupt* change in electronic distribution, $Ru^{IV}\doteq O,PPh_3 \rightarrow Ru\doteq O\doteq PPh_3$, would occur.

A spin change must occur somewhere in the reaction. One possible mechanism involves the initial population of the $S = 0$ reactant state (eq 12), followed by the thermally activated,

$$\underset{S\,=\,1}{(bpy)_2pyRuO^{2+},PPh_3} \rightarrow \underset{S\,=\,0}{(bpy)_2pyRuO^{2+},PPh_3} \quad (12)$$

$S = 0 \rightarrow S = 0$, redox step shown in Figure 3. If such a preequilibrium step exists, it must be rapid since, under our conditions, no deviation from second-order kinetics was observed.

It is difficult to know how the spin-state change is manifested in the activation parameters, if at all. If the reaction occurs via eq 12 as a preequilibrium, the observed $\Delta H^{\ddagger}$ value ($\sim$5 kcal/mol) will include the enthalpy difference between the spin-state isomers and $\Delta S^{\ddagger}$ ($\sim$−15 eu) any rate inhibition arising from the spin-state change. The latter contribution should be minor given recent results on $\Delta S = 1$ spin-state changes for first-row transition-metal complexes.[36] On the other hand if the reaction occurs via the $S = 1 \rightarrow S = 0$ surface intersection region through an abrupt change in electronic distribution, there may be a more important contribution from the spin change concealed in $\Delta S^{\ddagger}$. In either case, a negative value for $\Delta S^{\ddagger}$ is expected for a reaction like this where there appear to be specific orientational and vibrational requirements. In order for the reaction to occur, only certain of the thermally accessible reactant orientations in the association complex are available, and the equilibrium Boltzmann distribution throughout the normal modes must be channeled through the critical mode or modes which are essential for the reaction to occur.

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Registry No. $(bpy)_2pyRuO^{2+}$, 76582-01-9; PPh_3, 603-35-0; $(bpy)_2pyRu^{II}O{=}PPh_3^{2+}$, 76514-88-0; $[(bpy)_2pyRu(CH_3CN)](PF_6)_2$, 72525-79-2; $[(bpy)_2pyRu(OH_2)](PF_6)_2$, 72525-78-1; $OPPh_3$, 791-28-6.

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