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Stepwise Oxidation of Anilines by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$

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The net six-electron oxidation of aniline to nitrobenzene or azoxybenzene by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ (bpy is 2,2′-bipyridine; py is pyridine) occurs in a series of discrete stages. In the first, initial two-electron oxidation is followed by competition between oxidative coupling with aniline to give 1,2-diphenylhydrazine and capture by H_2O to give *N*-phenylhydroxylamine. The kinetics are first order in aniline and first order in Ru(IV) with $k(25.1\ °C, CH_3CN) = (2.05 \pm 0.18) \times 10^2\ M^{-1}\ s^{-1}$ ($\Delta H^{\ddagger} = 5.0 \pm 0.7$ kcal/mol; $\Delta S^{\ddagger} = -31 \pm 2$ eu). On the basis of competition experiments, k_{H_2O}/k_{D_2O} kinetic isotope effects, and the results of an ^{18}O labeling study, it is concluded that the initial redox step probably involves *proton-coupled two-electron transfer* from aniline to *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ ($Ru^{IV}{=}O^{2+}$). The product is an intermediate nitrene (PhN) or a protonated nitrene ($PhNH^+$) which is captured by water to give PhNHOH or aniline to give PhNHNHPh. In the following stages, PhNHOH, once formed, is rapidly oxidized by $Ru^{IV}{=}O^{2+}$ to PhNO and PhNHNHPh to PhN═NPh. The rate laws for these reactions are first order in $Ru^{IV}{=}O^{2+}$ and first order in reductant with $k(14.4\ °C, H_2O/(CH_3)_2CO) = (4.35 \pm 0.24) \times 10^6\ M^{-1}\ s^{-1}$ for PhNHOH and $k(25.1\ °C, CH_3CN) = (1.79 \pm 0.14) \times 10^4\ M^{-1}\ s^{-1}$ for PhNHNHPh. In the final stages of the six-electron reactions, PhNO is oxidized to $PhNO_2$ and PhN═NPh to PhN(O)═NPh. The oxidation of PhNO is first order in PhNO and in $Ru^{IV}{=}O^{2+}$ with $k(25.1\ °C, CH_3CN) = 6.32 \pm 0.33\ M^{-1}\ s^{-1}$ ($\Delta H^{\ddagger} = 4.6 \pm 0.8$ kcal/mol; $\Delta S^{\ddagger} = -39 \pm 3$ eu). The reaction occurs by O-atom transfer, as shown by an ^{18}O labeling study and by the appearance of a nitrobenzene-bound intermediate at low temperature.

Introduction

There is a well documented oxidation chemistry of the anilines.[1] The products that appear depend on the reaction conditions and the nature of the oxidant. Reactions have been found in which (1) oxidation leads to nitroso (ArNO)[2] or nitro compounds ($ArNO_2$),[3,4] (2) oxidative coupling occurs to give hydrazine (ArNHNHAr),[5] azo (ArN═NAr),[4,6] or azoxy compounds (ArN(O)═NAr),[7] (3) attack occurs at the N-atom to give *N*-oxide products ($Ar(Me)_2N{\rightarrow}O$),[8] or attack occurs at an alkyl group adjacent to the N-atom to give dealkylated compounds (ArNHMe),[9] and (4) oligomerization occurs to give emeralidine, or polymerization occurs to give polyaniline.[1]

Of the chemical oxidants based on the higher oxidation states of Ru or Os,[10,11] mono-oxo, polypyridyl complexes such as *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ (bpy is 2,2′-bipyridine and py is pyridine) have proven to be especially valuable in

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mechanistic studies.[12,13] For this oxidant, there are coordinatively stable Ru(III) and Ru(II) forms such as *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ and *cis*-$[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$. Because of the color changes that occur between oxidation states, straightforward spectral measurements can be used for product analysis and kinetic studies. The ^{18}O labeled oxidant $[Ru^{IV}(bpy)_2(py)(^{18}O)]^{2+}$ is available and provides isotope labeling information.

We report here product and mechanistic studies on the oxidation of anilines by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$. Our initial goal was to apply the well defined redox properties of *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ to elucidate the reaction mechanisms involved. Another was to develop the insight required to explain product distributions with an eye toward possible applications in chemical synthesis.

Experimental Section

Materials. Aniline from the Aldrich Chemical Co. was dried by stirring with CaH_2 followed by fractional distillation at reduced pressure. *p*-Toluidine (Aldrich Gold Label) was recrystallized from petroleum ether and dried in a vacuum desiccator. The other anilines such as *p*-anisidine, *p*-bromobenzene, *p*-chloroaniline, *p*-fluoroaniline, and *p*-phenetidine were obtained from Aldrich and purified by using standard techniques.[14] Nitrosobenzene from Aldrich was recrystallized from ethanol twice. 1,2-Diphenylhydrazine obtained from Aldrich was used after recrystallization from hot ethanol. Deuterium oxide purchased from Aldrich (99.8 atom % D) was used as received. Sealed ampule acetonitrile-d_3 (99 atom % D) was obtained from Aldrich and used as received. ^{18}O labeled water (isotope purity >97.1%) was purchased from Isotec Inc. and used as received. A Millipore water system was used to purify house-distilled water. High-purity acetonitrile obtained from Burdick & Jackson (the water content was ~0.002−0.008 wt %) was purified by distillation from P_2O_5 under argon atmosphere. $HClO_4$ (70%) was obtained from G. Frederick Smith and used without further purification. Ionic strength was maintained with the use of sodium sulfate, which was recrystallized once from distilled water. All other common reagents were ACS grade and were used without additional purification. *N*-Phenylhydroxylamine was synthesized by reducing nitrosobenzene with zinc dust followed by recrystallization from benzene.[15] 1,2-Diphenylhydrazine-d_2 was prepared by heating at reflux a solution of *N*,*N*-bis(trimethylsilyl)-1,2-diphenylhydrazine in CH_3OD.[16]

Preparation. Salts of *cis*-$[Ru(bpy)_2(py)(OH_2)]^{2+}$, *cis*-$[Ru(bpy)_2(py)(^{18}OH_2)]^{2+}$, *cis*-$[Ru(bpy)_2(py)(O)]^{2+}$, and *cis*-$[Ru(bpy)_2(py)(^{18}O)]^{2+}$ were prepared by previously reported procedures.[13b]

cis-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ was prepared by dissolving *cis*-$[Ru(bpy)_2(py)(OH_2)]^{2+}$ (13 mg) in a minimum of water (~3 mL) initially. The perchlorate salt of *cis*-$[Ru(bpy)_2(py)(O)]^{2+}$ (8.7 mg) was added to the resulting solution, which immediately turned golden brown. One drop of saturated sodium perchlorate solution was added, and the resulting solid was collected by filtration, washed with cold water, and vacuum-dried.

Instrumentation. Routine UV−visible spectra and slow kinetic studies were followed on a Hewlett-Packard 8450A diode array spectrophotometer. IR spectra were obtained on a Nicolet model 20DX FT-IR spectrophotometer in solutions by using NaCl plates. ^1H NMR spectra were recorded on an IBM AC 200 spectrometer by using CD_3CN as deuterated solvent and are referenced versus tetramethylsilane (TMS). Temperatures were controlled by using a Varian variable temperature accessory calibrated with methanol by the Van Geet method.[17] Stopped-flow measurements were carried out on two separate systems. Early measurements were performed on an Aminco-Morrow stopped-flow apparatus attached to a Beckman DU monochromator, details of which are given elsewhere.[18] The absorbance−time traces were analyzed by the use of a Commodore PET computer, model 4032, which utilized locally written programs. Later experiments were carried out on a Hi-Tech SF-51 stopped-flow apparatus interfaced to a Zenith 158 microcomputer by using software from On Line Instrument Systems (OLIS). Temperature was maintained to ±0.1 °C by a Brinkman Lauda K-2/RD water bath. GC analyses were performed on a Hewlett-Packard model 5890A gas chromatograph fitted with a 6 ft × $^1/_8$ in. column of Carbowax 20M on Chromosorb W-HP (80−100 mesh). We also used a Hewlett-Packard 5750 instrument containing a 10 ft × 0.125 in. stainless steel column packed with 20% SF-96 on 60−80 mesh Chromosorb W. The temperature gradient ranged from 50 to 250 °C.

Kinetic Measurements. Rate data for the disappearance of Ru(IV) in the oxidation of anilines by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ were obtained by following the absorbance increase at 391 nm. This wavelength is an isosbestic point for *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ and *cis*-$[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$ in CH_3CN. At this wavelength, the disappearance of Ru(IV) can be followed without a contribution from the subsequent conversion of Ru(III) to Ru(II), which is slower. The reactions were carried out under pseudo-first-order conditions in aniline. Pseudo-first-order rate constants were calculated from the slopes of plots of $\ln(A_\infty - A_t)$ versus t according to the relation

$$\ln(A_\infty - A_t) = -kt + \ln(A_\infty - A_0)$$

In this equation, A_∞ is the final absorbance, A_0 is the initial absorbance, and A_t is the absorbance measured at time t. The constant k is the pseudo-first-order rate constant. The plots were linear for at least 4 half-lives. In experiments where *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ was the oxidant, the complex was either generated in situ by mixing *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ with an excess of *cis*-$[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$ or prepared as described in the Experimental Section. The same results were obtained within experimental error by either method of preparation. Rate data for the disappear-

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ance of Ru(II) at 470 nm, which is a λ_{max} for *cis*-[Ru^{II}(bpy)$_2$(py)(OH$_2$)]$^{2+}$, gave the same results. Plots of ln($A_\infty - A_t$) versus *t* for oxidations by Ru(III) were nonlinear in H_2O. The nonlinearity arises because of a significant contribution from initial disproportionation, 2Ru(III) → Ru(IV) + Ru(II),[13f,19] followed by oxidation of aniline by Ru(IV) and by O_2 in the solutions. The linearity of the plots could be significantly improved by deaerating the solutions by N_2 bubbling and, in water, by adding *cis*-[Ru^{II}(bpy)$_2$(py)(OH$_2$)]$^{2+}$ to suppress the disproportionation reaction.

Rate constants for the oxidation of *N*-phenylhydroxylamine or 1,2-diphenylhydrazine by *cis*-[Ru^{IV}(bpy)$_2$(py)(O)]$^{2+}$ were obtained by following the absorbance increase at the λ_{max} for Ru(II) at 470 nm in $H_2O/(CH_3)_2CO$ or at 450 nm in CH_3CN. The latter wavelength is an isosbestic point between *cis*-[Ru^{II}(bpy)$_2$(py)(OH$_2$)]$^{2+}$ and *cis*-[Ru^{II}(bpy)$_2$(py)(CH$_3$CN)]$^{2+}$ in CH_3CN. In the oxidation of PhNDNDPh, the ^{1}H NMR spectrum in CD_3CN showed that H/D exchange with trace added H_2O in the solvent was slow on the time scale of the kinetics experiments.

Rate data for the oxidation of nitrosobenzene by *cis*-[Ru^{IV}(bpy)$_2$(py)(O)]$^{2+}$ in CH_3CN were collected by following the absorbance increase at 440 nm, which is a λ_{max} for *cis*-[Ru^{II}(bpy)$_2$(py)(CH$_3$CN)]$^{2+}$, or at 391 nm with identical results.

Infrared Measurements. Quantitative infrared analyses of nitrosobenzene and nitrobenzene, which are products of the oxidation of aniline by *cis*-[Ru^{IV}(bpy)$_2$(py)(O)]$^{2+}$, were carried out by infrared measurements. In the measurements, the peak heights of the ν(NO) stretching frequencies for PhNO at 1507 cm^{-1} and the asymmetric and symmetric ν(NO$_2$) stretching frequencies at 1530 and 1352 cm^{-1} for $PhNO_2$ were determined by using the baseline method.[20] For nitrosobenzene, the calibration curve in CD_3CN was linear over the concentration range 1.87−19.6 mM, and for nitrobenzene in CD_3CN, over the concentration range 5.50−38.9 mM. Blank experiments showed that little or no air oxidation of aniline to nitrosobenzene or nitrobenzene occurred in the CD_3CN solutions used for the calibration experiments or after the workup procedures, which were used for the product analyses. The accuracy of the infrared procedure is estimated to be ±10%.

Results

Stoichiometry and Product Analysis. The oxidation of aniline by *cis*-[Ru^{IV}(bpy)$_2$(py)(O)]$^{2+}$ (Ru^{IV}=O^{2+}) in CH_3CN occurs via a series of sequential, stepwise reactions. We investigated the product distribution at each stage.

Stage 1. The UV−visible spectral changes that occur at 20 s intervals after mixing Ru^{IV}=O^{2+} and aniline in excess (8.6×10^{-2} M) are shown in Figure 1A. The spectral changes show that the aqua complex, *cis*-[Ru^{II}(bpy)$_2$(py)(OH$_2$)]$^{2+}$ (Ru^{II}−OH$_2$$^{2+}$), is an initial product of a rapid redox step. The redox step is complete by the first spectral scan taken 20 s after mixing. The slower spectral changes that follow arise from subsequent solvolysis of the aqua complex ($t_{1/2}$ ∼ 8 min at 23 °C).[12]

$$cis\text{-}[\mathrm{Ru^{II}(bpy)_2(py)(OH_2)}]^{2+} + \mathrm{CH_3CN} \rightarrow cis\text{-}[\mathrm{Ru^{II}(bpy)_2(py)(CH_3CN)}]^{2+} + \mathrm{H_2O} \quad (1)$$

The acetonitrilo complex is formed quantitatively (ϵ_{max} = 8000 M^{-1} cm^{-1} at λ_{max} = 440 nm) for either aniline or *p*-toluidine as the reductant.

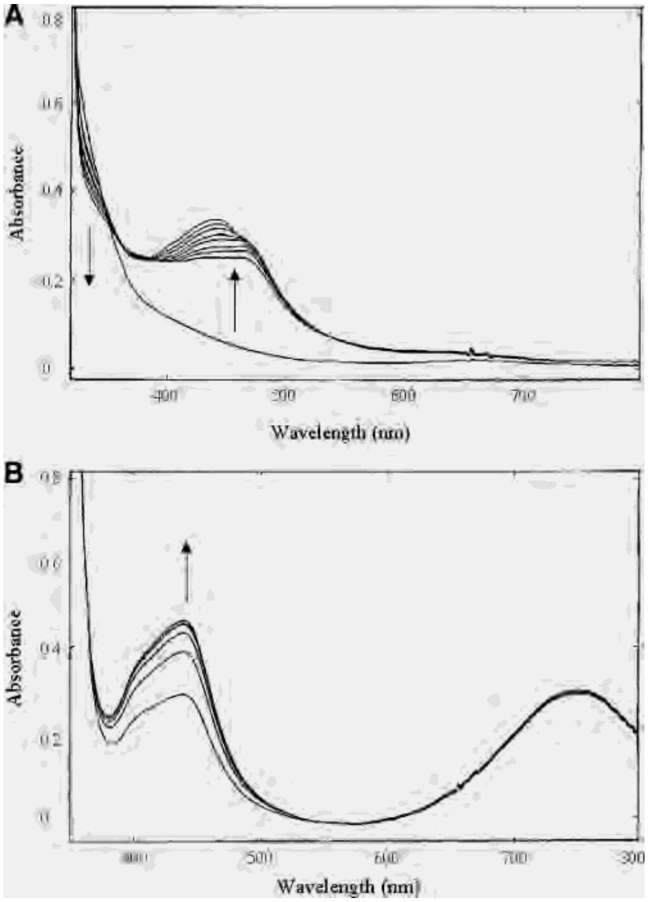

Figure 1. (A) Repetitive UV−visible scans in a 1 cm cell at 20 s intervals for the reaction between [Ru(bpy)$_2$(py)(O)]$^{2+}$ (8.6×10^{-5} M) and aniline (8.6×10^{-2} M) in CH_3CN. The spectra illustrate that [Ru(bpy)$_2$(py)(OH$_2$)]$^{2+}$ (λ_{max} = 470 nm) is present during the first scan. It then solvolyzes to give [Ru(bpy)$_2$(py)(NCCH$_3$)]$^{2+}$ (λ_{max} = 440 nm). (B) Successive spectral scans in a 1 cm cell at 1 min intervals during the oxidation of PhNO (3.5×10^{-3} M) by [Ru(bpy)$_2$(py)(O)]$^{2+}$ (2.5×10^{-5} M) in CH_3CN. The absorption at λ_{max} = 750 nm arises from PhNO.

Organic product analyses for the oxidations of aniline or *p*-toluidine by Ru^{IV}=O^{2+} in CH_3CN were carried out by a combination of quantitative FT-IR, GC, and ^{1}H NMR measurements. In a typical experiment with Ru(IV) at 21.9 mM and *p*-toluidine at 21.9 mM, analysis of the product solution revealed only the nitroso compound *p*-CH$_3$C$_6$H$_4$-NO and unreacted *p*-toluidine as products. The stoichiometry of the reaction with regard to the nitroso compound (±5%) is shown in eq 2.

$$2cis\text{-}[\mathrm{Ru^{IV}(bpy)_2(py)(O)}]^{2+} + p\text{-}\mathrm{CH_3C_6H_4NH_2} + \mathrm{H_2O} \rightarrow 2cis\text{-}[\mathrm{Ru^{II}(bpy)_2(py)(OH_2)}]^{2+} + p\text{-}\mathrm{CH_3C_6H_4NO} \quad (2)$$

The products depend on the Ru^{IV}=O^{2+}/*p*-toluidine ratio. With Ru^{IV}=O^{2+} in ×2 excess, a metal-complex-based product or products appear with low energy absorption features in the region λ_{max} = 550−650 nm. This is a spectral region in which an intermediate arising from ring attack of Ru^{IV}=O^{2+} on phenol to give [Ru^{II}(bpy)$_2$(py)(*p*-benzoquinone)]$^{2+}$ absorbs,[21a] as do μ-oxo bridged complexes of Ru(III).[21b]

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With *p*-toluidine in large excess over $Ru^{IV}{=}O^{2+}$, only the nitroso and hydrazine compounds appear as products. The nitroso product decreases and the hydrazine product increases as the toluidine concentration is increased (see below).

In an experiment in CH_3CN with $Ru^{IV}{=}O^{2+}$ at 21.9 mM and aniline at 21.9 mM, the product solution contained unreacted aniline, nitrosobenzene (80 ± 10% of the organic product formed based on the initial amount of $Ru^{IV}{=}O^{2+}$, assuming a four-electron oxidation from the FT-IR and GC measurements), and 1,2-diphenylhydrazine (20 ± 10% of the organic product formed based on the stoichiometry in eq 3 from GC measurements). The total yield of organic products was 70−75% based on $Ru^{IV}{=}O^{2+}$ consumed.

The ratio of PhNO to PhNHNHPh as products depended on water content and the initial concentration of aniline. The background concentration of water in "dry" acetonitrile in our experiments was ≥12 mM based upon near-infrared measurements in the ν_{OH} first overtone region.[22] When the oxidation of aniline was repeated with water added at 111 mM, the products were PhNO in 99 ± 10% yield and PhNHNHPh in ~1% yield based on $Ru^{IV}{=}O^{2+}$ as the limiting reagent. With aniline at 80 mM, the product distribution was 95 ± 10% PhNHNHPh and ~5% PhNO. By inference, with a large excess of aniline, the oxidation stoichiometry is

$$\textit{cis}\text{-}[Ru^{IV}(bpy)_2(py)(O)]^{2+} + 2C_6H_5NH_2 \rightarrow \textit{cis}\text{-}[Ru^{II}(bpy)_2(py)(OH_2)]^{2+} + C_6H_5NHNHC_6H_5 \quad (3)$$

Under these conditions, the aqua complex is the initial Ru product. It undergoes solvolysis according to eq 1.

To determine the origin of the O-atom in the PhNO product, a reaction was carried out between *cis*-$[Ru^{IV}(bpy)_2(py)(^{18}O)]^{2+}$ (14 mM, ~85% ^{18}O) and aniline (14 mM). The nonexistence of O-atom transfer (±10%) was confirmed by the absence of any shift in the ν_{NO} stretching frequency in the PhNO product. In a blank experiment in CD_3CN containing PhNO (8.7 mM) and $H_2{}^{18}O$ (0.56 M), no $^{18}O/^{16}O$ exchange occurred between PhNO and H_2O over a period of 2 h at room temperature, as shown by FT-IR measurements.

Attempts were made to observe possible intermediates in the oxidation of aniline by low temperature ^1H NMR measurements. For *cis*-$[Ru^{II}(bpy)_2(py)(L)]^{2+}$ (L = H_2O, DMSO, CH_3CN, etc.), the ^1H NMR chemical shift of the 6′ proton on the bipyridine ring lying nearest to ligand L is sensitive to the nature of L. Chemical shifts for protons in this position vary from 9 to 11 ppm.[23a] When *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and aniline in CD_3CN were mixed in equimolar amounts in an NMR tube at −20 °C, the initial product was *cis*-$[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$ ($\delta(6') = 9.2$ ppm). In the initial spectrum, the 6′ resonance was somewhat broadened, apparently by the presence of still unreacted, paramagnetic *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$.[23b] When the sample was warmed to room temperature, the 6′ resonance of the final product *cis*-$[Ru^{II}(bpy)_2(py)(CD_3CN)]^{2+}$ appeared at 9.42 ppm at the expense of *cis*-$[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$. No evidence was found for additional intermediates.

Although not studied in detail, the product distribution in the oxidation of aniline by $[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ in CH_3CN is quite different from that by $Ru^{IV}{=}O^{2+}$. A significant product is polyaniline, as evidenced by the appearance of a visible absorption band at 580 nm.[1] PhNHNHPh also appeared as a product but in small amount (<10% by GC). There was no sign of PhNO as a product within experimental error (±5%).

Stage 2. The oxidation of aniline to nitrosobenzene is a four-electron change. A reasonable two-electron intermediate is PhNHOH. The oxidation of PhNHOH by $Ru^{IV}{=}O^{2+}$ was studied by quantitative UV−visible spectral measurements. Under the conditions described in the caption to Figure 1A, the redox step is rapid and the only spectral change observed was the solvolysis of the aqua complex. Quantitative FT-IR measurements based on $\nu_{N=O} = 1507\ cm^{-1}$ were used to establish the stoichiometry with regard to PhNO (±10%) shown in eq 4.

$$\textit{cis}\text{-}[Ru^{IV}(bpy)_2(py)(O)]^{2+} + C_6H_5NHOH \rightarrow \textit{cis}\text{-}[Ru^{II}(bpy)_2(py)(OH_2)]^{2+} + C_6H_5NO \quad (4)$$

The oxidative pathway that leads to N−N coupling and 1,2-diphenylhydrazine as product, eq 3, is also a two-electron pathway. Once formed, 1,2-diphenylhydrazine undergoes further oxidation by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$. The stoichiometry of the reaction in eq 5 was established by quantitative UV−visible measurements for the aqua complex and by ^1H NMR spectroscopy (±10%) for PhN=NPh (δ(phenyl) = 7.46−7.94 ppm). The aqua complex subsequently undergoes the solvolysis reaction in eq 1.

$$\textit{cis}\text{-}[Ru^{IV}(bpy)_2(py)(O)]^{2+} + C_6H_5NHNHC_6H_5 \rightarrow \textit{cis}\text{-}[Ru^{II}(bpy)_2(py)(OH_2)]^{2+} + C_6H_5N{=}NC_6H_5 \quad (5)$$

Stage 3. The stoichiometry of the oxidation of PhNO by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ is shown in eq 6.

$$\textit{cis}\text{-}[Ru^{IV}(bpy)_2(py)(O)]^{2+} + C_6H_5NO + CH_3CN \rightarrow \textit{cis}\text{-}[Ru^{II}(bpy)_2(py)(NCCH_3)]^{2+} + C_6H_5NO_2 \quad (6)$$

It was established by UV−visible measurements for the acetonitrilo complex and by quantitative IR measurements for $C_6H_5NO_2$ (±10%). The latter analysis utilized the intensities of the $\nu(NO_2)$ bands at 1530 and 1352 cm^{-1}.

The spectral changes in Figure 1B show that, in contrast to the two-electron and four-electron stages, the initial Ru(II) product at room temperature is the acetonitrilo complex. Under the conditions of the experiment, the redox step is

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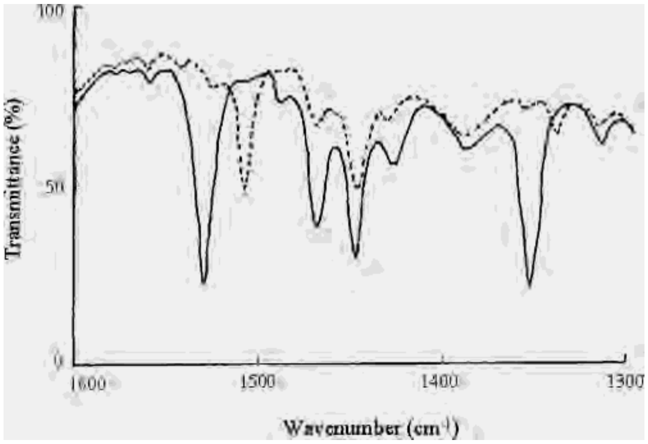


Figure 2. FT-IR spectra in CD$_3$CN following oxidation of PhNO (20.5 mM) by [Ru(bpy)$_2$(py)(^{16}O)]$^{2+}$ (—, 20.5 mM) and by [Ru(bpy)$_2$(py)(^{18}O)]$^{2+}$ (85% ^{18}O; - - -, 14.2 mM).

more rapid than the rate of solvolysis of the aqua complex, eq 1, and it can be ruled out as an intermediate.

The appearance of the acetonitrilo complex as the initial product leads to the inference that O-atom transfer occurs between Ru^{IV}=O^{2+} and C$_6$H$_5$NO to give C$_6$H$_5$NO$_2$. This implication was verified by the results of an ^{18}O labeling experiment in which *cis*-[Ru^{IV}(bpy)$_2$(py)(^{18}O)]$^{2+}$ (~85% ^{18}O) was used as the oxidant. In the experiment, Ru^{IV}=^{18}O^{2+} (14.2 mM) and C$_6$H$_5$NO (20.5 mM) were allowed to react in CH$_3$CN. The relative peak heights of the ν(NO$_2$) bands at 1530 and 1352 cm^{-1} and the ν(N^{18}O$_2$) bands at 1506 and 1336 cm^{-1} indicated that O-atom transfer was quantitative within experimental error (±10%) (Figure 2).

Attempts were made to detect the possible PhNO$_2$-bound intermediate [Ru^{IV}(bpy)$_2$(py)(ON(O)Ph)]$^{2+}$ by low temperature ^{1}H NMR measurements.[23] In ^{1}H NMR spectra in CD$_3$CN, the appearance of a 6′-proton resonance at 9.28 ppm at −10 and −20 °C (Supporting Information Figure 1) provides evidence for an intermediate. It disappears with the concomitant appearance of *cis*-[Ru^{II}(bpy)$_2$(py)(NCCD$_3$)]$^{2+}$ (δ(6′) = 9.42 ppm) as the final product.

The oxidation of nitrosobenzene at the third two-electron stage also has its analogue in the N−N coupling chemistry. In CH$_3$CN, azobenzene undergoes further oxidation by *cis*-[Ru^{IV}(bpy)$_2$(py)(O)]$^{2+}$ to give azoxybenzene via eq 7.

$$cis\text{-}[\mathrm{Ru^{IV}(bpy)_2(py)(O)}]^{2+} + \mathrm{PhN{=}NPh} + \mathrm{CH_3CN} \rightarrow cis\text{-}[\mathrm{Ru^{II}(bpy)_2(py)(NCCH_3)}]^{2+} + \mathrm{PhN{=}N(O)Ph} \quad (7)$$

The Ru(II) product was identified by the characteristic UV−visible spectrum and azoxybenzene by TLC and its ^{1}H NMR spectrum (δ(phenyl) = 7.45 ppm).

Kinetics. The oxidation of aniline by *cis*-[Ru^{IV}(bpy)$_2$(py)(O)]$^{2+}$ in CH$_3$CN occurs via a series of stepwise reactions, and we investigated the kinetics at each stage.

Stage 1. Kinetics were followed by stopped-flow monitoring in CH$_3$CN and H$_2$O with aniline in excess. Good pseudo-first-order kinetic plots were obtained over 4 half-lives. The reactions are first order in [Ru^{IV}=O^{2+}] (0.005−0.01 mM) and first order in aniline over the concentration range 1.59−22.3 mM, consistent with the rate law shown below. In CH$_3$CN, k_{obs} was independent of added H$_2$O at least up to 0.1 M.

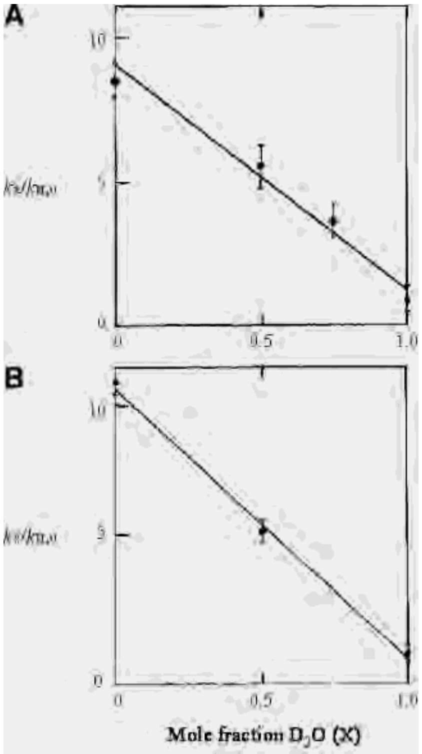


Figure 3. Plots of k_x/k_{H_2O} vs mole fraction of D$_2$O (x) in H$_2$O−D$_2$O mixtures for the oxidation of (A) aniline (2.9 × 10^{-3} M) at 24.9 °C and (B) *p*-toluidine (2.9 × 10^{-3} M) at 25.4 °C by [Ru(bpy)$_2$(py)(O)]$^{2+}$ (5.0 × 10^{-3} M).

$$\frac{-\mathrm{d}[\mathrm{Ru^{IV}{=}O^{2+}}]}{\mathrm{d}t} = k_{obs}[\mathrm{Ru^{IV}{=}O^{2+}}][\mathrm{PhNH_2}]$$

The oxidation kinetics were also studied in D$_2$O and mixed H$_2$O−D$_2$O solutions for both aniline and *p*-toluidine. Plots of k_x/k_{H_2O} versus mole fraction D (X_D) are shown in Figure 3, and k_{H_2O/D_2O} kinetic isotope effects are listed in Table 1.

The same kinetic characteristics were observed for the series of substituted anilines for which data are presented in Table 1 (Supporting Information Table 1). In all cases, the reactions were carried out with the aniline present in pseudo-first-order excess. The products are expected to be the corresponding 1,2-diarylhydrazines as in eq 3, given the large excess of anilines used in the kinetic runs. With this stoichiometry, $k_{obs} = k$ for the redox step. Presumably, with a large excess of anilines, complications arising from competitive four-electron oxidation to the corresponding nitrosoarenes are not important. If subsequent oxidation of the hydrazine to the corresponding azo compound (ArN=NAr) is important (see below), k_{obs} could be as large as 2k, in accordance with the stoichiometry shown in eq 8.

$$2cis\text{-}[\mathrm{Ru^{IV}(bpy)_2(py)(O)}]^{2+} + 2\mathrm{ArNH_2} \rightarrow 2cis\text{-}[\mathrm{Ru^{II}(bpy)_2(py)(OH_2)}]^{2+} + \mathrm{ArN{=}NAr} \quad (8)$$

The fact that k_{obs} could vary from k to 2k could explain some of the scatter in the plot of log k_{obs} versus the Hammett parameter (σ^+) in Figure 4. For the oxidation of aniline in

Table 1. Summary of Kinetic Parameters for the Oxidation of Aniline and Its Oxidized Forms by $[Ru(bpy)_2(py)(O)]^{2+}$ or $[Ru(bpy)_2(py)(OH)]^{2+}$

reaction		medium	k^a, $M^{-1}\,s^{-1}$	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	k_{H_2O/D_2O} or $k_{H/D}$[f]
$[Ru(bpy)_2(py)(O)]^{2+}$	+ $PhNH_2$	CH_3CN	$(2.05 \pm 0.18) \times 10^2$	5.0 ± 0.7	-31 ± 2	
		H_2O, pH = 7	$(2.75 \pm 0.18) \times 10^2$	5.3 ± 0.8	-28 ± 2	
		D_2O, pD = 7	$(1.77 \pm 0.20) \times 10$			15.5 ± 2.2
		H_2O, pH = 1	$(5.88 \pm 0.26) \times 10^3$			
		H_2O, pH = 4.4	$(8.44 \pm 0.38) \times 10^2$			
	+ *p*-toluidine	CH_3CN	$(1.26 \pm 0.08) \times 10^3$	5.0 ± 1.0	-27 ± 5	
		H_2O, pH = 7	$(1.99 \pm 0.16) \times 10^3$			
		D_2O, pD=7	$(1.90 \pm 0.14) \times 10^2$			10.2 ± 1.4
		H_2O, pH = 1	$(4.16 \pm 0.23) \times 10^3$			
		H_2O, pH = 4.4	$(3.73 \pm 0.34) \times 10^3$			
	+ *p*-anisidine	CH_3CN	$(1.28 \pm 0.04) \times 10^4$			
	+ *p*-phenetidine	CH_3CN	$(7.20 \pm 0.38) \times 10^3$			
	+ *p*-fluoroaniline	CH_3CN	$(2.14 \pm 0.12) \times 10^2$			
	+ *p*-chloroaniline	CH_3CN	$(8.53 \pm 0.30) \times 10$			
	+ *p*-bromoaniline	CH_3CN	$(5.10 \pm 0.23) \times 10$			
	+ PhNHOH	H_2O[b]	$(4.35 \pm 0.24) \times 10^6$ [c]			
	+ PhNDOD	D_2O[d]	$(3.55 \pm 0.21) \times 10^5$ [c]			
	+ PhNHNHPh	CH_3CN	$(1.79 \pm 0.14) \times 10^4$			
	+ PhNDNDPh	CH_3CN	$(3.96 \pm 0.24) \times 10^2$			45.2 ± 1.7
	+ PhNO	CH_3CN	6.32 ± 0.33	4.6 ± 0.8	-39 ± 3	
	+ PhNNPh	CH_3CN	24 ± 5			
$[Ru(bpy)_2(py)(OH)]^{2+}$	+ $PhNH_2$	CH_3CN	1.3 ± 0.2[e]			
		H_2O, pH = 1	$(3.9 \pm 0.5) \times 10^2$ [e]			
		H_2O, pH = 4	$(1.0 \pm 0.2) \times 10^2$ [e]			
		H_2O, pH = 7	$(4.5 \pm 0.23) \times 10$[e]	9.2 ± 1.8	-25 ± 9[e]	

[a] At 25.0 ± 0.1 °C. [b] In $H_2O/(CH_3)_2CO$ 10:1 (vol/vol). [c] At 14.4 ± 0.1 °C. [d] In $D_2O/(CD_3)_2CO$ 10:1 (vol/vol). [e] k_{obs}, the reaction stoichiometry is not known. [f] At 24.3 ± 0.1 °C.

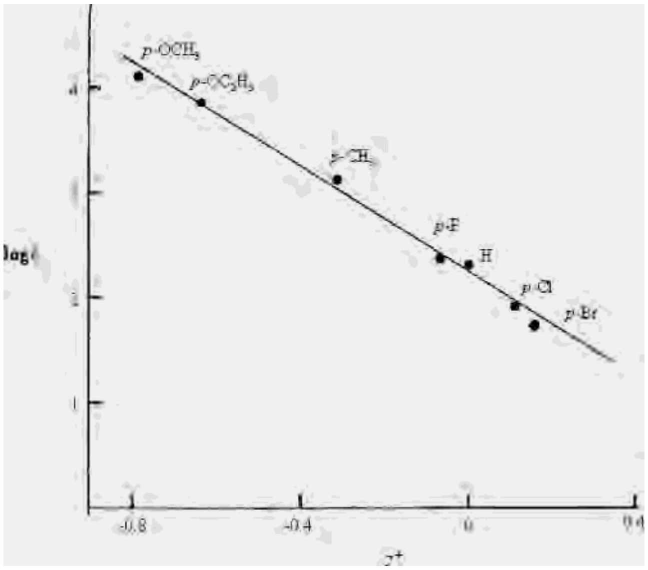


Figure 4. Plot of log *k* vs the Hammett parameter (σ^+) for the oxidation of para-substituted anilines by $[Ru(bpy)_2(py)(O)]^{2+}$ in CH_3CN at 25.1 °C.

water, where the nitrosoarene is expected to be the sole product, $k_{obs} = 2k$.

In either acetonitrile or water, the rate law for the oxidation of aniline by *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ was first order in each, as shown below.

$$\frac{-d[Ru^{III}{-}OH^{2+}]}{dt} = k_{obs}[Ru^{III}{-}OH^{2+}][PhNH_2]$$

Activation parameters for the oxidation of aniline and of *p*-toluidine by $Ru^{IV}{=}O^{2+}$ were obtained from plots of ln(k_{obs}/T) versus $1/T$ both in CH_3CN and in H_2O over the temperature range 14.4−41.9 °C (Supporting Information Table 1). The plots are linear over the temperature range studied in this case. The results are summarized in Table 1.

Stage 2. The kinetics of the oxidation of PhNHOH or PhNHNHPh by $Ru^{IV}{=}O^{2+}$ were investigated in CH_3CN, H_2O, and D_2O. The results are summarized in Table 1 with additional information in Supporting Information Table 2. Both reactions were sufficiently rapid that the stopped-flow technique was required. The reactions were studied under pseudo-first-order conditions with [PhNHOH] or [PhNHNHPh] $\gg$ $[Ru^{IV}{=}O^{2+}]$. In either case, the kinetics data showed that the reactions were first order in $[Ru^{IV}{=}O^{2+}]$ and in [PhNHOH] or [PhNHNHPh], consistent with the rate laws shown below.

$$\frac{-d[Ru^{IV}{=}O^{2+}]}{dt} = k_{obs}[Ru^{IV}{=}O^{2+}][PhNHOH]$$

$$\frac{-d[Ru^{IV}{=}O^{2+}]}{dt} = k_{obs}[Ru^{IV}{=}O^{2+}][PhNHNHPH]$$

Stage 3. The last stage in the six-electron oxidation of aniline, the oxidation of PhNO to $PhNO_2$, was also followed kinetically under pseudo-first-order conditions in PhNO. The variations in k_{obs} with [PhNO] were consistent with the rate law shown below.

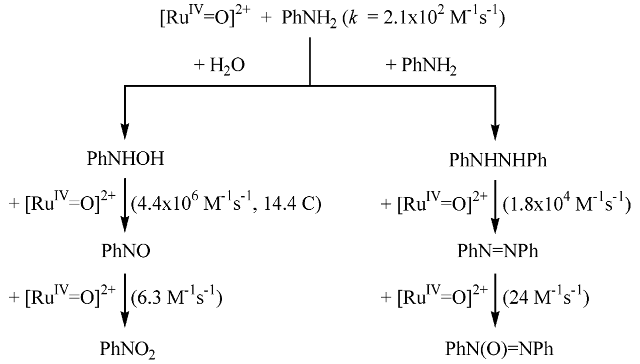
$$\frac{-d[Ru^{IV}{=}O^{2+}]}{dt} = k_{obs}[Ru^{IV}{=}O^{2+}][PhNO]$$

Rate constant data for the oxidation of PhNO are available in Supporting Information Table 2. The temperature dependence of the reaction was studied over the temperature range 14.6−41.8 °C. The activation parameters in Table 1 were obtained from a plot of ln(k_{obs}/T) versus $1/T$.

Discussion

Products of Aniline Oxidation. A summary of the sequence of reactions found in the oxidation of aniline by

Scheme 1



cis-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ is shown in Scheme 1. Second-order rate constants for the individual steps in CH_3CN at 25 °C are shown in parentheses.

The reactions have some important implications for synthesis. In the initial stage, there is no sign of one-electron, ring-coupled products. This is in contrast to *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ which is constrained to be a one-electron oxidant. From the mechanistic discussion below, the ability of $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ to avoid ring-coupled products is apparently tied to its ability to act as a two-electron acceptor. In the individual redox steps, discrete one-electron intermediates are avoided.

Beyond the initial competition between oxidative coupling to give PhNHNHPh and oxidation to give PhNHOH, the individual reactions are quantitative. The individual redox steps are well defined, but the final distribution of products depends on the reaction conditions. In dry acetonitrile, which contains H_2O at ≥ 12 mM, with a 1:1 ratio of $PhNH_2$ to $Ru^{IV}{=}O^{2+}$, both PhNO and PhNHNHPh are observed as products. For *p*-toluidine under the same conditions, *p*-nitrosotoluene is the sole product. For aniline, PhNO also becomes essentially the sole product if excess water is added. In either case, in the presence of excess aniline, the corresponding hydrazine becomes the dominant product.

Because of the relative rate constants and the competition between oxidation and oxidative coupling, the only significant products of the oxidation of aniline by $Ru^{IV}{=}O^{2+}$ with aniline present in stoichiometric or greater amounts are PhNO and PhNHNHPh. The hydrazine dominates with aniline in large excess.

It can be deduced from the rate constant data in Scheme 1 that, except at [aniline]/$[Ru^{IV}{=}O^{2+}]$ ratios which exceed 10^4, the four-electron product PhNO is expected to appear initially rather than PhNHOH. Even with aniline in large excess, PhNHOH, once formed, would be essentially completely oxidized to PhNO.

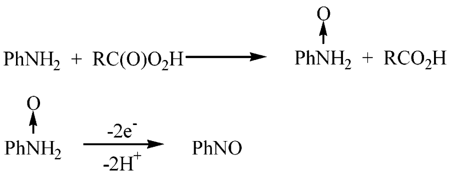
The ratio of second-order rate constants for the oxidations of PhNHNHPh and $PhNH_2$ is lower ($\sim 10^2$). In a dry solvent where oxidative coupling need not compete with the H_2O pathway, azobenzene would be expected to become a significant product at [aniline]/$[Ru^{IV}{=}O^{2+}]$ ratios that exceed 1:1. Azobenzene does not appear as a product if aniline is present in stoichiometric or slightly excess amounts. Azobenzene can also form by the condensation reaction between nitrosobenzene and aniline with aniline in excess but should only become important under our conditions above pH 9−10.[24]

Mechanisms of Aniline Oxidation. Several distinct mechanistic pathways have been proposed for the oxidation of anilines.[1] One feature common to many oxidants is the appearance of oligomeric polyanilines (e.g., emeralidine) or even polymeric polyanilines (e.g., aniline black) as products. The coupling products are thought to arise following initial one-electron oxidation to give anilinium radicals

$$PhNH_2 \xrightarrow{-e^-} PhNH_2^{\bullet+} \rightleftharpoons Ph\dot{N}H + H^+$$

Radical formation is followed by oligomerization via radical chain processes. The one-electron chemistry appears in the electrochemical oxidation of anilines[25] and in oxidations by one-electron outer-sphere oxidants such as $Fe(CN)_6^{3-}$.[26]

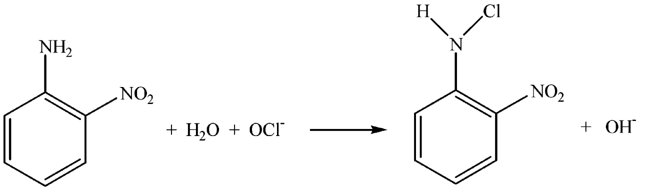
For peroxycarboxylic acids or peroxysulfonic acids used as oxidants,[27,28] it has been suggested that aniline can attack the peroxo link as a nucleophile, for example,

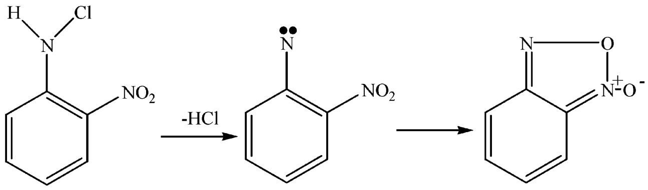


$$PhNH_2 + RC(O)O_2H \longrightarrow Ph\overset{O}{\overset{\uparrow}{N}}H_2 + RCO_2H$$

$$Ph\overset{O}{\overset{\uparrow}{N}}H_2 \xrightarrow[-2H^+]{-2e^-} PhNO$$

With H_2O_2 as oxidant, *N*,*N*-dialkylanilines give the corresponding *N*-oxide, for example, $Ar(Me)_2N{\rightarrow}O$, as a product.[8] Nucleophilic attack by the lone pair on the N-atom has also been invoked in the oxidation of anilines by hypochlorite. On the basis of the appearance of the cyclic nitrite ester shown below as product, it has been suggested that oxidation of 2-nitroaniline by OCl^- occurs through an intermediate nitrene.[29]





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A hydride transfer has been proposed to occur in the oxidation of aniline by MnO_4^-.[5]

$$\mathrm{MnO_4^- + ArNH_2 \rightarrow ArNH^+ + Mn(IV) + H^+}$$

$$\mathrm{ArNH^+ + ArNH_2 \xrightarrow{-H^+} ArNHNHAr \xrightarrow[-2H^+]{-2e^-} ArN{=}NAr}$$

In the oxidation of aniline to azobenzene by V(V), it has been proposed that H-atom transfer is involved in the initial redox step.[30]

In the oxidation of aniline by FeO_4^{2-} in water at pH 9 or 14, the products depend on the reaction conditions.[4] A common first step was invoked involving oxidation to the hydroxylamine

$$\mathrm{FeO_4^{2-} + PhNH_2 \rightarrow PhNHOH + Fe(IV)}$$

followed by rapid oxidation to nitrosobenzene

$$\mathrm{FeO_4^{2-} + PhNHOH \rightarrow PhNO + Fe(IV)}$$

The appearance of azobenzene was explained by rapid coupling of nitrosobenzene and aniline

$$\mathrm{PhNO + PhNH_2 \rightarrow PhN{=}NPh + H_2O}$$

We have attempted to explore the mechanism in the oxidation of aniline by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ in a detailed way. A number of observations give insight into the mechanism: (1) The rate law is first order in aniline and first order in $Ru^{IV}{=}O^{2+}$. H_2O does not appear in the rate law, but the product distribution depends on the H_2O to aniline ratio. These observations point to an intermediate formed in a rate determining redox step, which is subsequently captured by either H_2O or $PhNH_2$. Capture by H_2O gives PhNO as the final product following oxidation of PhNHOH. Capture by $PhNH_2$ gives PhNHNHPh.

(2) There is N−H participation in the initial redox step, given the relatively large $ArNH_2/ArND_2$ kinetic isotope effects of 15.5 ± 2.2 for aniline and 10.2 ± 1.4 for *p*-toluidine in H_2O at 25 °C. The reasonably linear plots of k_x/k_{H_2O} in Figure 3 point to kinetic isotope effects that arise from the transfer of a single N−H hydrogen from the aniline reductant to the $Ru^{IV}{=}O^{2+}$ oxidant.[31]

(3) The O-atom of the initial oxo group is retained as bound H_2O in $Ru^{II}{-}OH_2^{2+}$. This fact and the failure of ^{18}O initially in $Ru^{IV}{=}^{18}O^{2+}$ to appear in the nitrosobenzene product suggest that O-atom transfer is not involved in the redox step. Mechanisms involving $Ru^{III}{-}OH^{2+}$ are constrained to occur by one-electron-transfer steps via the Ru(III/II) couple.[33] As an oxidant, it is slower than $Ru^{IV}{=}O^{2+}$ in the oxidation of aniline by a factor of 110 even though $Ru^{IV}{=}O^{2+}$ and $Ru^{III}{-}OH^{2+}$ differ in oxidizing strength by only 100 mV.[16,33]

(4) The initial redox step appears to involve a net two-electron transfer, since the initial product is $Ru^{II}{-}OH_2^{2+}$ rather than $Ru^{III}{-}OH^{2+}$. This is true unless the initial one-electron-transfer step

$$\mathit{cis}\text{-}\mathrm{[Ru^{IV}(bpy)_2(py)(O)]^{2+} + PhNH_2 \rightarrow}$$
$$\mathit{cis}\text{-}\mathrm{[Ru^{III}(bpy)_2(py)(OH)]^{2+} + Ph\dot{N}H}$$

produces an intermediate which is oxidized far more rapidly by $Ru^{III}{-}OH^{2+}$ than by $Ru^{IV}{=}O^{2+}$. This seems unlikely, since, as noted above, initial oxidation of aniline by $Ru^{IV}{=}O^{2+}$ is 110 times faster than oxidation by $Ru^{III}{-}OH^{2+}$.

(5) The plot in Figure 4 shows that a good correlation exists between log k_{obs} and the Hammett parameter (σ^+). Although a trend exists between log k_{obs} and σ as well, the correlation with σ^+ is far better.[34,35] The σ^+ values are defined on the basis of solvolysis rate constant measurements on para-substituted *tert*-cumyl chlorides in 90% aqueous acid.[34] They include the effects of π electronic delocalization and probably give an indirect, relative measure of the reduction potentials for the series of anilinium and aniline couples. From the slope of the plot, $\rho^+ = -2.5 \pm 0.2$. The large sensitivity toward rate enhancements by electron donating substituents is consistent with a charge transfer reaction and an excess buildup of positive charge in the transition state.[4]

The available experimental evidence points to a mechanism for the initial redox step in which two electrons and one proton are transferred from aniline to the oxidant which points to intermediate nitrene or protonated nitrene formation. The redox reaction follows formation of an association complex, eq 9, in which there may be a H-bond interaction between the oxo group and the aniline. There is no direct experimental evidence for an association complex, for example, by the appearance of saturation kinetics in added $PhNH_2$.

$$\mathrm{[Ru^{IV}(bpy)_2(py)(O)]^{2+} + PhNH_2 \rightleftharpoons [Ru^{IV}(bpy)_2(py)(O)]^{2+}, NH_2Ph} \quad (9)$$

The subsequent redox step could involve the following:

(1) Concerted two-electron/one-proton (hydride) transfer followed by separation and proton equilibration. (A more appropriate mechanistic description may be proton-coupled two-electron transfer, as described below.)

$$\mathrm{[(bpy)_2(py)Ru^{IV}{=}O]^{2+},\ NH_2Ph \longrightarrow [(bpy)_2(py)Ru^{II}\text{-}OH]^+ + {}^+H\ddot{N}Ph} \quad (10a)$$

$$\mathrm{[(bpy)_2(py)Ru^{II}\text{-}OH]^+ + H^+ \longrightarrow [(bpy)_2(py)Ru^{II}\text{-}OH_2]^{2+}} \quad (10b)$$

$$\mathrm{{}^+H\ddot{N}Ph \rightleftharpoons H^+ + {:}\!\ddot{N}Ph} \quad (10c)$$

(2) Sequential one-electron/one-proton transfers within the solvent cage of the association complex

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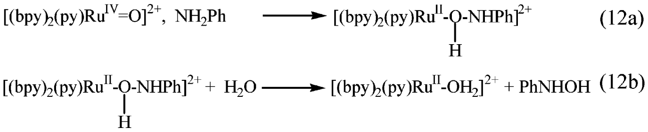
$$[(bpy)_2(py)Ru^{IV}{=}O]^{2+}, NH_2Ph \rightarrow [(bpy)_2(py)Ru^{III}{-}OH]^{2+}, H\underset{..}{\dot{N}}Ph \quad (11a)$$

$$[(bpy)_2(py)Ru^{III}{-}OH]^{2+}, H\underset{..}{\dot{N}}Ph \rightarrow [(bpy)_2(py)Ru^{II}{-}OH]^{+} + {}^{+}H\ddot{N}Ph \quad (11b)$$

before the one-electron intermediates separate in solution.

A mechanism involving insertion into an N−H bond to give an O-bound phenylhydroxylamine, eq 12, seems unlikely. There is no sign of a detectable intermediate even on the short time scale of the stopped-flow experiments (10 ms). Also, the absence of ^{18}O labeling in the ultimate PhNO product would require rapid water attack on the N-atom of the bound PhNHOH in the reaction in eq 12b. A blank experiment with $H_2{}^{18}O$ added to an acetonitrile solution containing PhNO showed that O-exchange between H_2O and PhNO is slow.



$$[(bpy)_2(py)Ru^{IV}{=}O]^{2+}, NH_2Ph \longrightarrow [(bpy)_2(py)Ru^{II}\text{-}\underset{\displaystyle H}{\underset{|}{O}}\text{-}NHPh]^{2+} \quad (12a)$$

$$[(bpy)_2(py)Ru^{II}\text{-}\underset{\displaystyle H}{\underset{|}{O}}\text{-}NHPh]^{2+} + H_2O \longrightarrow [(bpy)_2(py)Ru^{II}\text{-}OH_2]^{2+} + PhNHOH \quad (12b)$$

O-atom transfer to give the *N*-oxide as an intermediate

$$[(bpy)_2(py)Ru^{IV}{=}O]^{2+}, NH_2Ph \rightarrow [(bpy)_2(py)Ru^{II}{-}O{=}NH_2Ph]^{2+} \quad (13a)$$

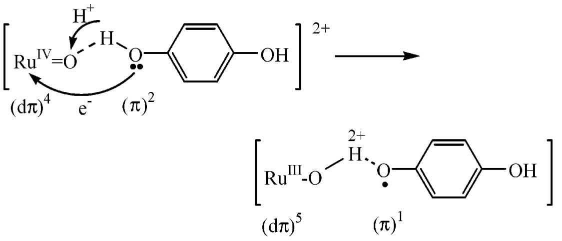
$$[(bpy)_2(pu)Ru^{II}{-}O{=}NH_2Ph]^{2+} + H_2O \rightarrow [(bpy)_2(py)Ru^{II}{-}OH_2]^{2+} + PhN(OH)H \quad (13b)$$

also seems unlikely. It would also require H_2O attack on the N-atom of the bound *N*-oxide in order to explain the absence of ^{18}O transfer. The results of initial experiments with $PhNMe_2$ show that an *N*-oxide product does form in this case, but the reaction is far slower ($\sim 10^{-4}$).[36] The rapid rate constants observed here appear to rely on the presence of a dissociable proton.

The correlation between log k_{obs} and σ^+ points to the buildup of positive charge and supports the two-electron/one-proton mechanism over a one-electron/one-proton mechanism. Simultaneous transfer of a single electron and proton involves no charge transfer.

$Ru^{IV}{=}O^{2+}$ has the electronic configuration $(d\pi_1)^2(d\pi_2)^2(d\pi_3)^0$ and the ability to accept either one or two electrons. Both $d\pi_2$ and $d\pi_3$ are largely 4d(Ru) in character but are strongly mixed with $2p_{\pi,O}$ orbitals on the oxo group and antibonding with regard to the Ru−O interaction. Oxidation of hydroquinone by $Ru^{IV}{=}O^{2+}$ has been shown to occur by one-electron/one-proton transfer through semiquinone as an intermediate.[31] With hydroquinone as the reductant, there is almost no kinetic discrimination between $Ru^{IV}{=}O^{2+}$ and $Ru^{III}{-}OH^{2+}$. With aniline as the reductant, oxidation by Ru(IV) is more facile by 60 at pH = 7 and by 160 in CH_3CN. There is even greater discrimination in favor of Ru(IV) in the oxidation of alcohols.[35]

On the basis of the magnitudes of the k_{H_2O}/k_{D_2O} kinetic isotope effects, the oxidation of aniline shares a mechanistic nuance with the oxidation of hydroquinone or other reductants in which acidic O−H, N−H, S−H, or P−H bonds are coupled to electron transfer.[37,38] For these reactions, the electron and proton donor functions reside at different places in the reductant. In the oxidation of hydroquinone by $Ru^{IV}{=}O^{2+}$ shown in eq 14, hydroquinone acts as an electron/proton donor. Electron transfer occurs from a nonbonding π orbital with some O character and coupled proton transfer occurs from σ_{O-H} (shown in eq 14 H-bonded to the oxo group).

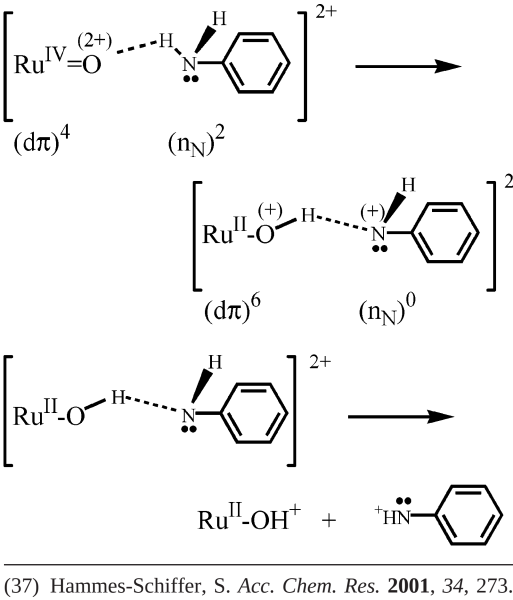


(14)

Electron transfer to Ru(IV) greatly increases the basicity of the O-atom bound to Ru^{III} or Ru^{II}, and a nonbonding lone pair at that site is available for accepting the transferring proton. $Ru^{IV}{=}O^{2+}$ acts as an electron/proton acceptor in the net reaction by adding an electron at $d\pi_3$ and a proton at an oxo lone pair to give the σ_{O-H} bond in $Ru^{III}{-}OH^{2+}$. Hydroquinone acts as an electron/proton donor. Electron transfer occurs by orbital overlap between $d\pi_3(Ru^{IV})$ and π_O through the H-bonded framework illustrated in eq 14.

Because of the orbital difference between the electron and proton transfer sites, such reactions have been described as occurring by proton-coupled electron transfer.[31,37−38] This term has been coined to distinguish this pathway from H-atom transfer where both the electron and proton are transferred from the same bond.

A proposed two-electron/one-proton transfer oxidation for aniline is shown in eq 15. It adds an additional mechanism



(15a)

(15b)

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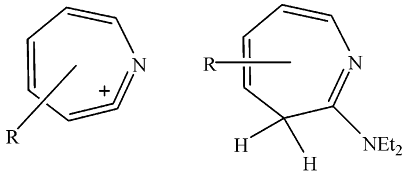
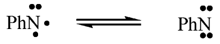
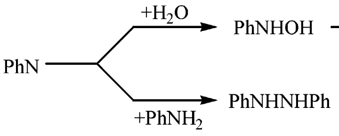
for $Ru^{IV}{=}O^{2+}$ oxidations. This mechanism, *proton-coupled two-electron transfer*, is distinct from hydride transfer where both electrons and the transferring proton are taken from the same bond, as in the oxidation of the formate anion by $Ru^{IV}{=}O^{2+}$.[39]

The experimental evidence points to the net two-electron oxidation of aniline initially to give a nitrene or protonated nitrene intermediate, as in eqs 10, 11, and 15. The chemical properties of the nitrene p-$O_2NC_6H_4\ddot{\underset{\cdot\cdot}{N}}$ have been investigated following its generation by laser flash photolysis of p-$O_2NC_6H_4N_3$ in solution.[40] From these results, it was concluded that: (1) triplet ($^3Ar\underset{\cdot\cdot}{\dot{N}}\cdot$) and singlet ($^1Ar\ddot{\underset{\cdot\cdot}{N}}$) nitrenes are in rapid equilibrium by intersystem crossing; (2) $^3Ar\underset{\cdot\cdot}{\dot{N}}\cdot$ can couple to give ArN═NAr; (3) $^1Ar\ddot{\underset{\cdot\cdot}{N}}$ is in equilibrium with an isomer that has been identified as the dehydroazepine; (4) the dehydroazepine undergoes a reaction with added $HNEt_2$ in cyclohexene solution to give the corresponding azepine.


dehydroazepine azepine

The appearance of a nitrene or protonated nitrene as an intermediate would explain the water and aniline dependent competition between PhNO and PhNHNHPh as products of the oxidation of aniline by $Ru^{IV}{=}O^{2+}$. The first-order dependence on aniline in the rate law and the zero-order dependence on H_2O in CH_3CN show that the two bases compete for an intermediate that appears after the rate determining step. Competition for an intermediate nitrene by H_2O or aniline would account for the product distribution, as shown in eq 16, for the nitrene as the active intermediate.

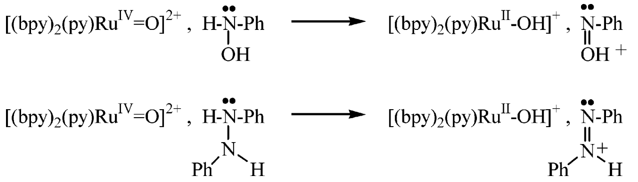

(16a)


(16b)

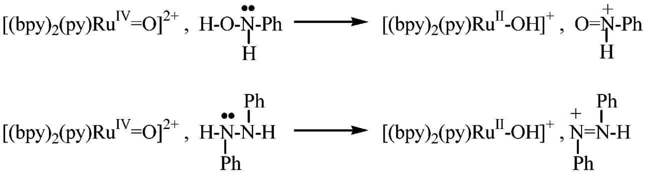
Given the essentially quantitative appearance of six membered ring products: (1) the dehydroazepine isomer is less important for aniline and p-toluidine, (2) the nitrene form dominates the reactivity toward H_2O and aniline, or (3) the protonated nitrene dominates reactivity.

In water, the oxidation of aniline is pH dependent. The pH dependence was not explored in detail, but from data reported in Supporting Information Table 1, k_{obs} increases by 10 as the pH is decreased from pH 7 to pH 1. The pK_a of $PhNH_3^+$ is 4.6 at 25 °C, $\mu = 0.1$ M, and $PhNH_3^+$ is the dominant form of aniline at pH 1. The effect is even more striking for $Ru^{III}{-}OH_2^{2+}$ as oxidant where the rate enhancement is nearly 90 (Table 1). Related observations have been made in the oxidation of p-$XC_6H_4NH_2$ (X = Cl or NO_2) by V(V) where the rate of oxidation also increases with $[H^+]$[29] and in the oxidation of hydroquinone by $[Ru^{III}(bpy)_2(py)(OH)]^{2+}$.[31]

Scheme 2



Scheme 3



For Ru(III) as oxidant at pH 1, both cis-$[Ru^{III}(bpy)_2(py)(OH_2)]^{3+}$ and cis-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ are present in solution, since the pK_a for $Ru^{III}{-}OH_2^{3+}$ is 0.85.[32] The rate enhancement may signal the onset of outer-sphere electron transfer followed by proton loss as the dominant pathway.

$$ArNH_3^+ \rightleftharpoons ArNH_2 + H^+$$

$$cis\text{-}[Ru^{III}(bpy)_2(py)(OH_2)]^{3+} + ArNH_2 \rightarrow cis\text{-}[Ru^{II}(bpy)_2(py)(OH_2)]^{2+} + Ar\dot{N}H_2^+ \quad (17)$$

The $[Ru(bpy)_2(py)(OH_2)]^{3+/2+}$ couple is more strongly oxidizing than the $[Ru(bpy)_2(py)(OH)]^{2+/+}$ couple by 0.56 V.[32,41]

Similarly, preprotonation of $Ru^{IV}{=}O^{2+}$ followed by outer-sphere electron transfer could explain the enhancement for $Ru^{IV}{=}O^{2+}$ as oxidant.[41] It should be noted that a product study was not conducted under these conditions. We cannot rule out a mechanism involving attack on the ring.

Mechanisms of Oxidation of PhNHOH and of PhNHNHPh. The oxidations of PhNHOH to PhNO and of PhNHNHPh to PhN═NPh are well defined kinetically and stoichiometrically. Both reactions are first order in both $Ru^{IV}{=}O^{2+}$ and reductant. The initial Ru product is $Ru^{II}{-}OH_2^{2+}$ rather than $Ru^{III}{-}OH^{2+}$. The PhNHOH/PhNDOD kinetic isotope effect is 12.2 ± 1.2 in 10:1 $D_2O/(CD_3)_2CO$ (vol/vol) at 14.4 °C, and the PhNHNHPh/PhNDNDPh kinetic isotope effect is 45.2 ± 1.7 in CH_3CN at 25.1 °C.

There are several mechanisms by which these reactions might occur, consistent with the appearance of Ru(II) as the initial product. They include (1) hydride transfer from an N─H bond (Scheme 2), (2) proton-coupled two-electron transfer (Scheme 3), (3) the equivalent of (1) or (2) but via sequential one-electron steps (Scheme 4), (4) and oxo transfer (Scheme 5).

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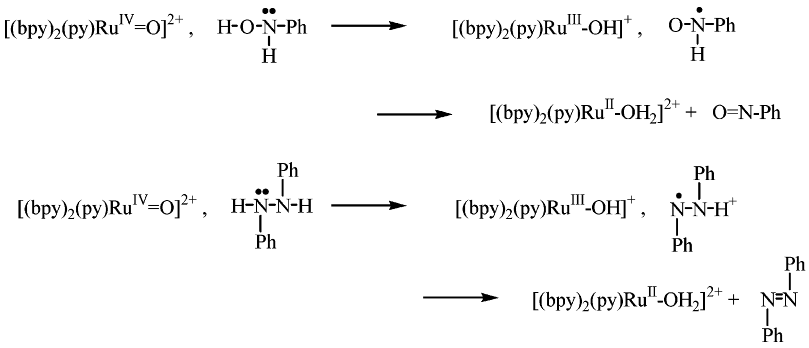
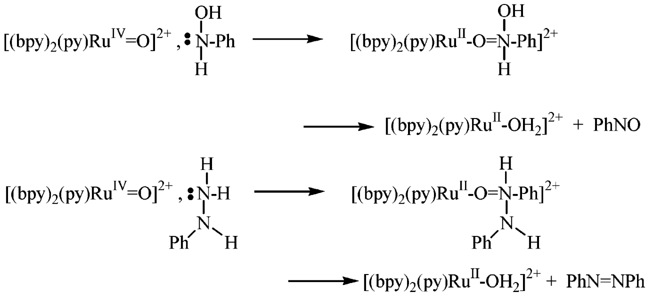
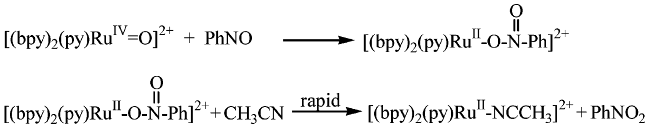
Scheme 4



Scheme 5



Scheme 6



With the absence of additional insight, there is no firm basis for choosing from these mechanistic possibilities. It is clear from the H_2O/D_2O kinetic isotope effects that transfer of a proton from N−H or O−H bonds accompanies electron transfer, which is consistent with the mechanisms in Schemes 2−4.

Mechanisms of Oxidation of ArNO and of PhN═NPh. In the final stage of the oxidation of aniline to nitrobenzene, nitrosobenzene is oxidized to nitrobenzene. The results of the ^{18}O labeling study show conclusively that O-atom transfer occurs in the redox step. That fact and a rate law first order in each of the reactants suggest the mechanism shown in Scheme 6.

The ^{1}H NMR evidence at −10 °C for the appearance of the bound nitrobenzene complex as a discrete intermediate is presented in Supporting Information Figure 1. At temperatures near ambient temperature, solvolysis is rapid and the bound nitrobenzene intermediate was not observed. Net O-atom transfer mechanisms have also been established in the oxidations of R_2S, R_2SO, and PPh_3 by $Ru^{IV}{=}O^{2+}$.[12,23a] The mechanistic information available concerning the oxidation of nitrosoarenes is relatively limited. With peroxyacids in non-hydroxylic acids, rate determining nucleophilic attack of the N-atom on the O−O bond of the peroxide has been suggested to occur.[41] In the disproportionation of PhNO at high temperatures, internal O-atom transfer[42] within a PhNO dimer has been invoked to explain the observed kinetics. On the basis of our observations, the oxidation of PhNO by Ru(IV) appears to proceed via a concerted O-atom transfer mechanism in which net electron transfer occurs from PhNO to Ru(IV).

An analogous mechanism appears to exist for the oxidation of PhN═NPh. In CH_3CN, there is a rapid reaction between $Ru^{IV}{=}O^{2+}$ and PhN═NPh. The products are *cis*-[Ru^{II}(bpy)$_2$(py)(NCCH$_3$)]$^{2+}$ and azoxybenzene, once again indicative of O-atom transfer.

$$\begin{aligned} &cis\text{-}[\mathrm{Ru^{IV}(bpy)_2(py)(O)}]^{2+} + \mathrm{PhN{=}NPh} + \mathrm{CH_3CN} \rightarrow \\ &\qquad cis\text{-}[\mathrm{Ru^{II}(bpy)_2(py)(NCCH_3)}]^{2+} + \mathrm{PhN{=}N(O)Ph} \quad (18) \end{aligned}$$

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Supporting Information Available: Tables showing rate constant data for the oxidation of anilines by [Ru(bpy)$_2$(py)(O)]$^{2+}$ and kinetic data for the oxidation of PhNHOH, PhNHNHPh, and PhNO by [Ru(bpy)$_2$(py)(O)]$^{2+}$ and a figure showing the ^{1}H NMR chemical shift of the 6′ proton of the bipyridine ring for a reaction mixture initially containing PhNO and [Ru(bpy)$_2$(py)(O)]$^{2+}$ in CD_3CN. This material is available free of charge via the Internet at http://pubs.acs.org.

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