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Mechanism of Oxidation of Benzaldehyde by Polypyridyl Oxo Complexes of Ru(IV)

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The oxidation of benzaldehyde and several of its derivatives to their carboxylic acids by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ ($Ru^{IV}{=}O^{2+}$; bpy is 2,2′-bipyridine, py is pyridine), *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ ($Ru^{III}–OH^{2+}$), and $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ (tpy is 2,2′:6′,2′′-terpyridine) in acetonitrile and water has been investigated using a variety of techniques. Several lines of evidence support a one-electron hydrogen-atom transfer (HAT) mechanism for the redox step in the oxidation of benzaldehyde. They include (i) moderate k_{C-H}/k_{C-D} kinetic isotope effects of 8.1 ± 0.3 in CH_3CN, 9.4 ± 0.4 in H_2O, and 7.2 ± 0.8 in D_2O; (ii) a low k_{H_2O/D_2O} kinetic isotope effect of 1.2 ± 0.1; (iii) a decrease in rate constant by a factor of only ∼5 in CH_3CN and ∼8 in H_2O for the oxidation of benzaldehyde by *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ compared to *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$; (iv) the appearance of *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ rather than *cis*-$[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$ as the initial product; and (v) the small ρ value of -0.65 ± 0.03 in a Hammett plot of log k vs σ in the oxidation of a series of aldehydes. A mechanism is proposed for the process occurring in the absence of O_2 involving (i) preassociation of the reactants, (ii) H-atom transfer to $Ru^{IV}{=}O^{2+}$ to give $Ru^{III}–OH^{2+}$ and $Ph\dot{C}O$, (iii) capture of $Ph\dot{C}O$ by $Ru^{III}–OH^{2+}$ to give $Ru^{II}–OC(O)Ph^+$ and H^+, and (iv) solvolysis to give *cis*-$[Ru^{II}(bpy)_2(py)(NCCH_3)]^{2+}$ or the aqua complex and the carboxylic acid as products.

Introduction

The kinetics and mechanisms of oxidation of aliphatic and aromatic aldehydes by oxidants such as chromic acid,[1] permanganate,[2] manganic pyrophosphate,[3] *N*-bromoamide,[4] peroxomonosulfate,[5] bromate,[6] peroxomonophosphoric acid,[7] dichromate,[8] chromyl acetate,[9] aquachromium(IV),[10] V(V),[11] Ce(IV),[12] Co(III),[13] and hexachloroiodate(IV)[14] have been extensively studied. In some cases, the mechanism involves intermediate ester formation between the substrate and the oxidant, followed by redox decomposition of the ester to give the final products.[1−8] In others, initial radical formation is followed by further oxidation to give the final products.[9−14]

Green et al. have reported the use of $[Ru^{VI}O_4]^{2-}$ in the oxidation of aldehydes.[15] They obtained nearly quantitative

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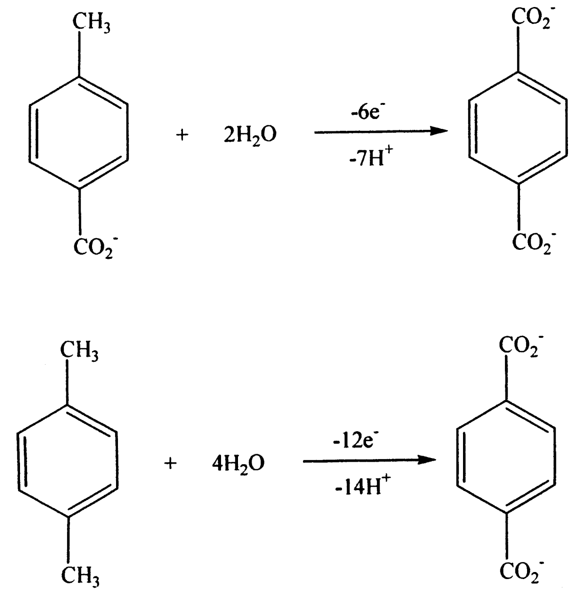
conversion of benzaldehyde to benzoic acid in nonaqueous solution. Although no mechanistic details are available for the series of benzaldehydes investigated, the order of reactivity of substituted benzaldehydes was found to be 4-NO_2 > 4-H > 4-OMe.

A series of polypyridyl oxo complexes of Ru and Os are known that have proven to be versatile stoichiometric and/or catalytic oxidants toward a variety of organic and inorganic substrates.[16] An example is the Ru(IV) complex *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ ($Ru^{IV}{=}O^{2+}$; bpy is 2,2′-bipyridine, py is pyridine). This complex is coordinatively stable, as are the lower-oxidation-state forms *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ ($Ru^{III}{-}OH^{2+}$) and *cis*-$[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$ ($Ru^{II}{-}OH_2{}^{2+}$), and the ^{18}O-labeled oxidant, *cis*-$[Ru^{IV}(bpy)_2(py)(^{18}O)]^{2+}$, is easily accessible. The electrocatalytic oxidation of alcohols, aldehydes, and unsaturated hydrocarbons has been achieved by using the related couple $[Ru^{IV}(tpy)(bpy)(O)]^{2+}/[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ (tpy is 2,2′:6′,2″-terpyridine).[17] In these reactions, it was found that *p*-toluic acid and *p*-xylene undergo six-electron and 12-electron oxidations, respectively, to terephthalic acid and continue through at least 100 catalytic cycles.

Presumably, these reactions proceed via a series of sequential two-electron steps through discrete alcohol and aldehyde intermediates.



An early mechanistic study on the oxidation of aromatic hydrocarbons by $Ru^{IV}{=}O^{2+}$ incorrectly reported a dependence on added water in the rate law in acetonitrile as the solvent.[18a,b] A more recent study by Bryant and Mayer points to H-atom transfer (HAT) as a dominant mechanism.[18c] A large k_H/k_D isotope effect in the oxidation of benzyl alcohol derivatives to aldehydes by $Ru^{IV}{=}O^{2+}$ has been observed that led to the suggestion of a hydride-transfer mechanism.[19] We report here the results of kinetic and mechanistic studies on the final step in the net oxidation of aromatic hydrocarbons to carboxylic acids, the oxidation of aromatic aldehydes to carboxylic acids, by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ in water and acetonitrile.

Experimental Section

Materials. Benzaldehyde from Aldrich Chemical Co. was purified immediately before use by distillation under a nitrogen atmosphere. Benzaldehyde-*d* was either prepared by a reported method[20] or obtained from Aldrich and used as received. The solid aldehydes *p*-bromobenzaldehyde, *m*-chlorobenzaldehyde, *p*-chlorobenzaldehyde, and *p*-nitrobenzaldehyde were purchased from Aldrich; each was recrystallized from ethanol−water mixtures and then sublimed under vacuum at a temperature slightly above its melting point. The liquid aldehydes *m*-anisaldehyde, *p*-anisaldehyde, and *p*-tolualdehyde were obtained from Aldrich and distilled under reduced pressure shortly before use. Deuterium oxide (99.8 atom % D) and ampoule-sealed CD_3CN (99 atom %D) were used as received from Aldrich. Deionized water was obtained using a Barnstead D0809 demineralization apparatus. Acetonitrile from Burdick & Jackson Laboratories was distilled over P_2O_5 under argon by means of a Vigreux column prior to use. HPLC-grade dichloromethane was used as obtained from Burdick & Jackson Laboratories. Oxygen-18-labeled water (isotopic purity > 97.1%) was purchased from Isotec, Inc. and used as received. All other reagents were ACS grade and were used without further purification.

Preparations. The cis-complex-containing salts $[Ru(bpy)_2(py)(OH_2)](ClO_4)_2$, $[Ru(bpy)_2(py)(^{18}OH_2)](ClO_4)_2$, $[Ru(bpy)_2(py)(OH)](ClO_4)_2$, $[Ru(bpy)_2(py)(O)](ClO_4)_2$, $[Ru(bpy)_2(py)(^{18}O)](ClO_4)_2$, and $[Ru(bpy)_2($*p-tert*-bupy$)_2](PF_6)_2$, $[Ru(tpy)(bpy)(OH_2)](ClO_4)_2$, and $[Ru(tpy)(bpy)(O)](ClO_4)_2$ were prepared according to reported procedures.[17,18]

Benzaldehyde-*d*. To a stirred solution of 13.9 g of benzil (66.1 mmol) in 30 mL of *p*-dioxane was added 144 g of deuterium oxide (0.719 mol) followed by 4.68 g of potassium

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cyanide (71.9 mmol) in five portions over 30 min. The reaction mixture was stirred for an additional 30 min and then diluted with 120 mL of water. The mixture was extracted with anhydrous ethyl ether (3 × 50 mL). The ether solution was washed with saturated sodium bicarbonate (2 × 50 mL), dried with $MgSO_4$, and evaporated. Fractional distillation gave the product (4.32 g, 61%) as an oil. IR (NaCl): ν_{max} at 2100 and 2050 cm^{-1}, C−D stretch of the CDO group. ^1H NMR ($CDCl_3$): δ 7.2−7.9 ppm (m, 5H), aromatic protons. No signal was observed in the aldehydic proton region (8−12 ppm).[21]

***cis*-[Ru(bpy)$_2$(*p-tert*-bupy)(OCOPh)](PF$_6$).** The complex as the PF_6^- salt was prepared in the same manner as described for [Ru(bpy)$_2$(*p-tert*-bupy)(CF$_3$CO$_2$)](PF$_6$) (*p-tert*-bupy is *para-tert*-butylpyridine),[22] except that benzoic acid was used as the source of the benzoate anion. *cis*-[Ru(bpy)$_2$(*p-tert*-bupy)$_2$](PF$_6$)$_2$ (200 mg) was dissolved in 200 mL of CH_2Cl_2, then 1 molar equiv of benzoic acid was added. The solution was photolyzed for 3 h under reflux. The solution volume was reduced by rotary evaporation, and diethyl ether was added. The resulting precipitate was collected by filtration. The precipitate was placed on a column of neutral alumina (Fisher A-540) in a minimum amount of CH_2Cl_2 and eluted with CH_3CN. The salt was efficiently recovered by reducing the volume by rotary evaporation and precipitating with diethyl ether. The precipitate was collected by filtration, washed with diethyl ether (3 × 10 mL), and then dried in air. Anal. Calcd for $C_{36}H_{34}N_5O_2F_{12}P_2Ru$: C, 53.07; H, 4.21; N, 8.60. Found: C, 53.02; H, 4.31; N, 8.52.

***cis*-[Ru(bpy)$_2$(CH$_3$CN)$_2$](CF$_3$SO$_3$)$_2$.** To a suspension of 50 mg of [(bpy)$_2$Ru(O$_2$CO)]·2H$_2$O in 10 mL of acetonitrile was added two drops of 1 M CF_3SO_3H. The suspension immediately dissolved to form a bright orange solution of [Ru(bpy)$_2$(CH$_3$CN)$_2$](CF$_3$SO$_3$)$_2$. This solution was added dropwise into stirred anhydrous diethyl ether (150 mL). The orange precipitate was filtered and collected on a medium glass frit and stored in the dark. Yield: 72 mg, 92%. UV−visible (CH_3CN): λ_{max} at 426 nm. ^1H NMR (CD_3CN, ppm from TMS): δ 9.29 (2H, d), 8.50 (2H, d), 8.36 (2H, d), 8.26 (2H, t), 7.92 (t, 2H), 7.82 (t, 2H), 7.56 (d, 2H), 7.23 (t, 2H). Anal. Calcd for $C_{26}H_{22}N_6O_6F_6S_2Ru$: C, 39.35; H, 2.79; N, 10.59. Found: C, 39.22; H, 2.91; N, 10.44.

Photochemical Procedures. Preparative photolysis experiments were carried out using Pyrex glassware and a GE 275-W sunlamp at a distance of approximately 10 in. The glassware consisted of a round-bottom flask fitted with a condenser. The solutions were magnetically stirred.

Instrumentation. Routine UV−vis spectra were recorded and kinetics studies were performed on a Hewlett-Packard 8450A diode array spectrophotometer. FT IR spectra were obtained on a Nicolet model 20DX FT IR spectrophotometer either as Nujol mulls or in CH_3CN solution using NaCl plates. Proton NMR spectra were recorded on either an IBM AC 200 spectrophotometer or a Varian Gemini 200 FT NMR spectrometer in CD_3CN as the solvent with tetramethylsilane (TMS) as the reference. Stopped-flow measurements were carried out on a Hi-Tech SF-51 stopped-flow apparatus interfaced with a Zenith 158 computer by use of an On Line Instrument Systems (OLIS) stopped-flow program or a Photal RA-451 stopped-flow spectrophotometer. Fits of data to kinetic equations were performed on a Zenith 158 microcomputer using OLIS software. Temperature was controlled within ±0.2 °C by a Brinkman Lauda K-2/RD water bath circulator. Using a PAR model 173 potentiostat/galvanostat equipped with a PAR model 175 universal programmer, cyclic voltammetry and controlled potential electrolyses were performed. All potential values reported are referenced to the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2 °C and are uncorrected for junction potential effects. Cyclic voltammetry measurements were carried out in a 10-mL beaker with a 2-cm^3 glassy-carbon-disk electrode (Tokai Carbon, Inc.) as the working electrode and a platinum wire as the auxiliary electrode. The sweep rate was 100 mV/s, and the peak amplitude was 2−5 μA/cm. All $E_{1/2}$ values reported were estimated from cyclic voltammograms as the average of the peak potentials for the oxidative and reductive waves, $(E_{pa} + E_{pc})/2$.

Infrared Measurements. Quantitative infrared analysis was carried out by dissolving the benzoic acid completely in exactly 1 mL of CH_3CN and measuring the peak height of the 1726 cm^{-1} carbonyl stretching band by the baseline method. Experiments were conducted under air and with argon purging.[23] The calibration curve for benzoic acid in CH_3CN was linear over the concentration range 2−100 mM. Blank experiments showed that little or no air oxidation of benzaldehyde to benzoic acid occurred in the CH_3CN solutions over the course of the experiment. Overall, the accuracy of the infrared results is estimated to be ±10%.

Kinetics Measurements. Rate data for oxidations involving *cis*-[Ru^{IV}(bpy)$_2$(py)(O)]$^{2+}$ in argon-purged CH_3CN were collected by following the absorbance increase at 391 nm. This wavelength is an isosbestic point between *cis*-[Ru^{II}(bpy)$_2$(py)(OH$_2$)]$^{2+}$ and *cis*-[Ru^{II}(bpy)$_2$(py)(NCCH$_3$)]$^{2+}$, as shown in Figure 1A. The disappearance of Ru(IV) can therefore be followed with no interference from solvolysis of the aqua complex by CH_3CN. The reactions were carried out in the presence of pseudo-first-order excess concentrations of the aldehydes. Pseudo-first-order rate constants were calculated from the slopes of plots of $\ln(A_\infty - A_t)$ vs t according to the equation

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

where A_∞ is the final absorbance, A_0 is the initial absorbance, A_t is the absorbance measured at time t, and k is the pseudo-first-order rate constant. The plots were linear for at least four half-lives.

Rate data for the disappearance of Ru(IV) in argon-purged water were collected by monitoring the absorbance at

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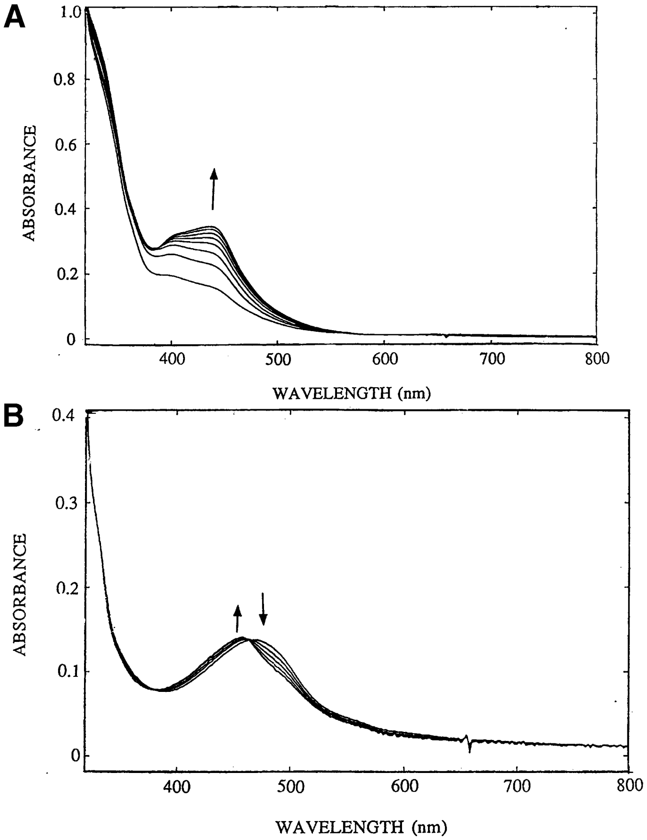

Figure 1. (A) Repetitive UV−visible scans taken at 1 min intervals after the mixing of *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and benzaldehyde in CH_3CN. The initial concentrations after mixing were 5.3×10^{-5} and 5.7×10^{-3} M, respectively. (B) Successive spectral changes recorded at 40-s intervals after the mixing of benzaldehyde and $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ in CH_3CN. The initial concentrations after mixing were 4.7×10^{-3} and 4.2×10^{-5} M, respectively.

397 nm, which is an isosbestic point for *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ and *cis*-$[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$. At this wavelength, it is possible to follow the reduction of Ru(IV) to Ru(III) free of complications from the further reduction of Ru(III) to Ru(II), which is slower. For the runs containing $Ru^{IV}{=}O^{2+}$ and benzaldehyde in aqueous solutions, there were occasional problems in the absorbance−time plots in buffered solutions at pH 7. In these runs, the absorbance traces were noisy, and there were drifts in A_∞. These complications did not occur in distilled water at constant ionic strength of 0.1 M with added $MgSO_4$. The kinetics data in water were analyzed as described above for the data in acetonitrile.

For the oxidation of benzaldehyde by $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ in argon-purged CH_3CN, rate data were obtained by monitoring the absorbance increase at 387 nm, which is an isosbestic point for $[Ru^{III}(tpy)(bpy)(OH)]^{2+}$ and $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$. The kinetic analyses were the same as described previously for *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ as the oxidant.

Results

Spectral Changes. Shown in Figure 1A are the spectral changes that accompany the oxidation of benzaldehyde by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ in argon-purged CH_3CN. Upon addition of benzaldehyde, the initially featureless spectrum of $Ru^{IV}{=}O^{2+}$ quickly changes to that of *cis*-$[Ru^{II}(bpy)_2(py)(NCCH_3)]^{2+}$ with no evidence for the formation of an intermediate. Such spectral changes are similar to those observed for the oxidations of olefins or nitrosobenzene by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$, which have been demonstrated to occur by O-atom transfer.[23] The spectral changes observed for the reactions between the various benzaldehyde derivatives and *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ are virtually identical. However Figure 1A reveals a hint of isosbestic behavior in the final spectral scans.

For $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ as the oxidant in the presence of a sufficient excess of benzaldehyde, the initial redox step is completed nearly in the time of mixing. As shown in Figure 1B, repetitive scans at 40-s intervals clearly show the presence of a Ru(II) intermediate. This intermediate undergoes solvolysis to give the nitrile complex $[Ru^{II}(tpy)(bpy)(NCCH_3)]^{2+}$ with which it has an isosbestic point at 465 nm. Spectral changes show that the reaction between $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ and benzaldehyde in CH_3CN occurs in two stages. In the initial stage, Ru(IV) is reduced to a Ru(II) intermediate with $\lambda_{max} = 480$ nm. In the second stage, the intermediate is solvolyzed to give $[Ru^{II}(tpy)(bpy)(NCCH_3)]^{2+}$ with $\lambda_{max} = 455$ nm. The fact that the intermediate is not simply the aqua complex $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ is shown by the relatively rapid rate of solvolysis of the intermediate ($t_{1/2} = 40$ s) compared to that of solvolysis of $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ to give $[Ru^{II}(tpy)(bpy)(NCCH_3)]^{2+}$, which occurs with $t_{1/2} = 9$ min at 25 °C in CH_3CN.

Stoichiometry and Product Analysis. Organic product analyses for the reaction between *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and benzaldehyde were carried out by a combination of FT IR and ^1H NMR measurements. In an experiment in CH_3CN solution containing equimolar $Ru^{IV}{=}O^{2+}$ and benzaldehyde (22.6 mM) under air, FT IR measurements in the $\nu_{C=O}$ region showed that benzoic acid was the sole oxidized organic product and appeared in 50 (±10)% yield. Also recovered was 15 (±10)% yield of unreacted benzaldehyde based on $Ru^{IV}{=}O^{2+}$ consumed. When the reaction was repeated with a benzaldehyde concentration of 90.4 mM, the organic product was benzoic acid in 99 (±10)% yield based on $Ru^{IV}{=}O^{2+}$ consumed. The stoichiometry of the benzaldehyde oxidation was also investigated with excess $Ru^{IV}{=}O^{2+}$. In an aerated CH_3CN solution initially 45.2 mM in $Ru^{IV}{=}O^{2+}$ and 22.6 mM in benzaldehyde, quantitative band intensity measurement indicated that benzoic acid was formed in 30 (±10)% yield based on $Ru^{IV}{=}O^{2+}$ consumed. None of the initial benzaldehyde remained. The rest of the oxidative equivalents were tied up as μ-oxo-bridged dimers. In argon-purged acetonitrile in a drybox, a solution initially 11.3 mM in $Ru^{IV}{=}O^{2+}$ and 22.6 mM in benzaldehyde gave benzoic acid in 90 (±10)% yield. The products of reactions between $Ru^{IV}{=}O^{2+}$ and the other benzaldehyde derivatives at the same $Ru^{IV}{=}O^{2+}$/ArCHO ratio under argon were also determined with the aid of ^1H NMR and FT IR spectroscopies and were substantially the same as for benzaldehyde oxidation. When equimolar benzaldehyde and $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ in CH_3CN were allowed to react, the products were benzoic acid and $[Ru^{II}(tpy)(bpy)(NCCH_3)]^{2+}$, quantitatively to within experimental error.

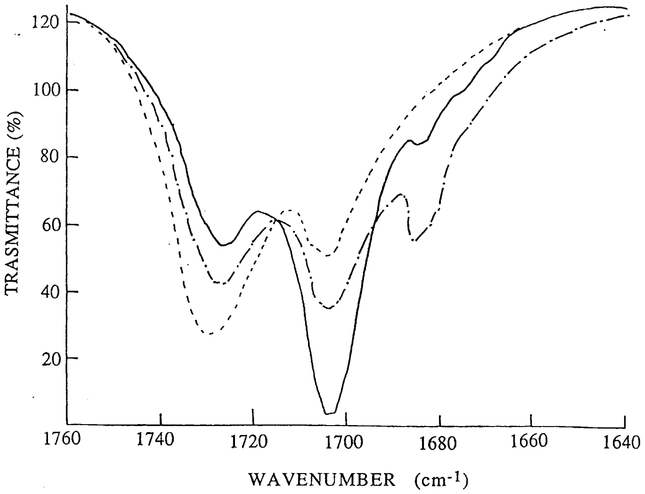

Figure 2. FT IR spectra of the solutions that result from the reactions between benzaldehyde (22.6 mM) and *cis*-$[Ru^{IV}(bpy)_2(py)(^{16}O)]^{2+}$ (- - -, 22.6 mM) and *cis*-$[Ru^{IV}(bpy)_2(py)(^{18}O)]^{2+}$ (—, 10.7 mM) in aerated CD_3CN and between benzaldehyde (22.6 mM) and *cis*-$[Ru^{IV}(bpy)_2(py)(^{18}O)]^{2+}$ (— • — • —, 7.2 mM) in CD_3CN under argon. The bands at 1726 and 1702 cm^{-1} are the ν(CO) stretching modes of $PhC^{16}O_2H$. The bands at 1702 and 1686 cm^{-1} are the ν(CO) modes of $PhC^{18}O^{16}OH$.

To determine the origin of the added oxygen atom in the benzoic acid product, the labeled complex *cis*-$[Ru^{IV}(bpy)_2(py)(^{18}O)]^{2+}$ (10.7 mM, 70% ^{18}O) was allowed to react with benzadehyde (21.4 mM) in an aerated CH_3CN solution. The benzoic acid product was analyzed for ^{18}O content by FT IR by integration of the peak area for the $C{=}^{18}O$ stretching band at 1686 cm^{-1} as shown in Figure 2. From this result, there was only 10 (±10)% ^{18}O transfer. In an experiment carried out under argon in a drybox in CD_3CN with *cis*-$[Ru^{IV}(bpy)_2(py)(^{18}O)]^{2+}$ (7.2 mM, 45% ^{18}O) and benzaldehyde (14.4 mM) added, the benzoic acid product contained 40 (±10)% ^{18}O as determined by FT IR spectrometry (Figure 2), showing that O-atom transfer from $Ru^{IV}{=}O^{2+}$ is nearly quantitative under these conditions. In an additional experiment, $H_2{}^{18}O$ (100 mM) was added to a CD_3CN solution 10.7 mM in *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and 21.4 mM in benzaldehyde. Within experimental error, there was no incorporation of ^{18}O in the benzoic acid product.

Mixing Studies. The course of the reaction between *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and benzaldehyde-*d* was also followed by ^1H NMR measurements. Spectra of a reaction mixture initially 14.9 mM in *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and 39.3 mM in benzaldehyde-*d* in 1 mL of aerated CD_3CN are shown as a function of time in Figure 3. Previously, we showed that the chemical shift of the 6′ proton of the bipyridine ligand in *cis*-$[Ru^{II}(bpy)_2(py)(L)]^{n+}$ (L = Cl, OH_2, NO_2, DMSO, etc.) lying nearest to L (labeled $6_1'$) is sensitive to the nature of L and usually falls in the range 9−11 ppm.[24a] Variations in chemical shift for the $6_1'$ proton are characteristic for L and provide a useful means of detecting intermediates.[24b]

As can be seen in Figure 3, 5 min after the solution was mixed in aerated CD_3CN at 25 °C, a broad peak appeared at 9.74 ppm. Between 10 and 25 min, a doublet at 9.42 ppm for *cis*-$[Ru^{II}(bpy)_2(py)(NCCD_3)]^{2+}$ appeared, along with the peak at 9.74 ppm. At longer times, the intensity at 9.74 ppm diminished concomitant with the growth of a new doublet at 9.32 ppm. After 1 h, the peaks at 9.32 and 9.42 ppm had increased at the expense of the peak at 9.74 ppm. The spectrum taken at 5 h shows that *cis*-$[Ru^{II}(bpy)_2(py)(NCCD_3)]^{2+}$ at 9.42 ppm and a second product with a resonance at 9.32 ppm were formed in equal amounts. After 1 day, the peak at 9.32 ppm grew at the expense of the peak at 9.42 ppm. The broad peak at 9.74 ppm is assumed to be from the benzoate intermediate. The new resonance at 9.52 ppm seems to arise from a diamagnetic intermediate.

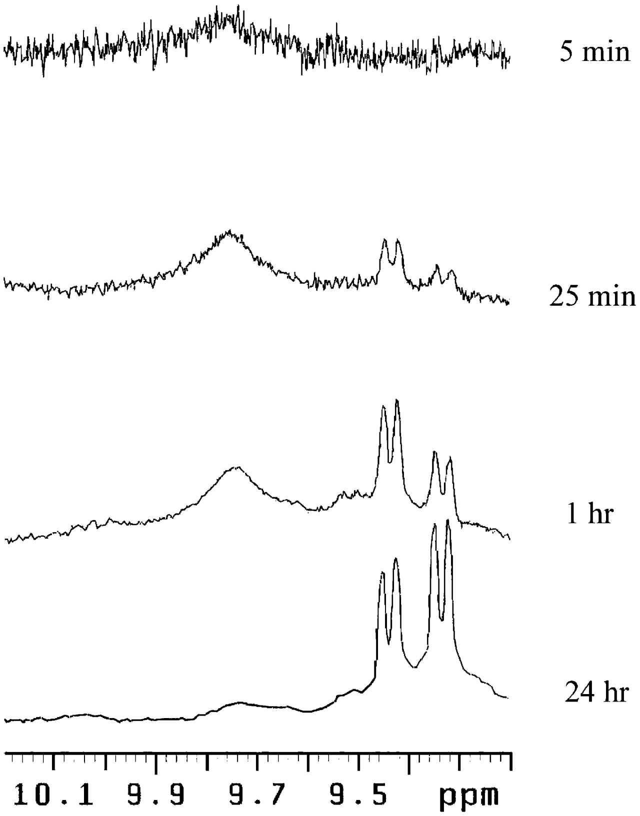

Figure 3. ^1H NMR specra in the $6_1'$ bpy proton region for a reaction mixture initially containing benzaldehyde (39.3 mM) and *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ (14.9 mM) in CD_3CN at 5 min, 25 min, 1 h, and 24 h.

The stepwise nature of the reaction was also investigated in argon-purged solutions. The resonance at 9.74 ppm does not appear in the absence of O_2. After 30 min, which is near the end of the oxidation reaction, *cis*-$[Ru^{II}(bpy)_2(py)(NCCD_3)]^{2+}$ (9.42 ppm) is the sole product in the solution. Over a longer period of time, loss of pyridine occurs to give *cis*-$[Ru^{II}(bpy)_2(NCCD_3)_2]^{2+}$ as the final product.

Cyclic voltammograms of a reaction mixture that initially contained *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ (1.6 mM) and benzaldehyde (3.2 mM) in argon-purged 0.1 M TBAH−CH_3CN in a drybox were obtained as a function of time. Voltammograms obtained after 18 min and 2 h at a relatively low concentration of benzadehyde are shown in Figure 4. Small waves appear at E_p = 1.22 and 1.34 V and a large wave at $E_{1/2}$ = 0.74 V (vs SSCE in CH_3CN). After 2 h, the waves at

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(24) (a) Hammett, L. P. In *Physical Organic Chemistry*; McGraw-Hill Book Co., Inc.: New York, 1970; p 221. (b) Ramakrishnan, P. S.; Chockalingam, P. *J. Indian Chem. Soc.* **1993**, *70*, 581−582.

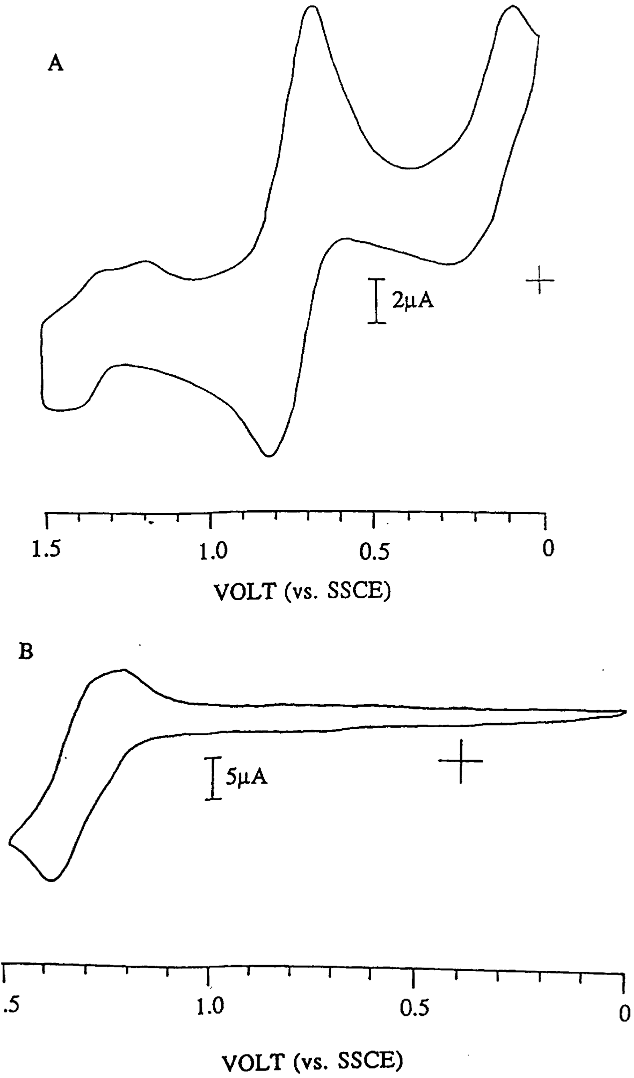

Figure 4. Cyclic voltammograms of the products resulting from the addition of *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ (1.6 mM) to benzaldehyde (3.2 mM) solution in 0.1 M TBAH/CH_3CN after (A) 18 and (B) 120 min (scan rate = 100 mV/s).

1.22 and 1.34 V were considerably increased at the expense of the wave at 0.74 V.

Kinetics. The kinetics of oxidation of benzaldehyde by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ or by $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ were studied in argon-purged H_2O or CH_3CN with benzaldehyde in excess. Plots of the observed rate constant, k_{obs}, vs the aldehyde concentration in the range 11.1 to 49.2 mM were linear consistent with the rate law

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

Kinetics for the substituted aldehydes were studied under the same conditions. Second-order rate constants (k) were calculated by a linear least-squares procedure utilizing data taken over at least a 10-fold range in aldehyde concentration with the aldehyde in pseudo-first-order excess. In some instances, fewer data were collected, and k was determined by dividing k_{obs} by [PhCHO]. The results are summarized in Table 1.

The Hammett plot in Figure 5 shows that a correlation exists between log k and σ with a slope of $\rho = -0.65$ (± 0.03).[25] The correlation demonstrates that the rate constant for oxidation of the benzaldehydes by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ is sensitive to changes in the electronic properties of the aldehyde, with electron-donating substituents increasing reactivity and electron-attracting groups decreasing it.

Activation parameters for the oxidations of benzaldehyde, its derivatives, and benzaldehyde-*d* by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ were obtained from plots of ln(k/T) vs $1/T$ in CH_3CN, H_2O, and D_2O over the temperature range 14.5−40.4 °C. Solvent and substrate kinetic isotope effects were also investigated. k_{H_2O/D_2O} for the oxidation of benzaldehyde or benzaldehyde-*d* by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ is insignificant. Moderate C−H/C−D kinetic isotope effects are observed for the oxidation of benzaldehyde by both *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ in CH_3CN. C−H/C−D kinetic isotope effects for the oxidation of benzaldehyde by *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ in H_2O and CH_3CN are larger by a factor of 2−3. These data are presented in Table 1.

Discussion

Under argon in CH_3CN, the oxidation of benzaldehyde by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ yields benzoic acid and *cis*-$[Ru^{II}(bpy)_2(py)(NCCH_3)]^{2+}$ as final products, as shown by the reaction in eq 1.

$$cis\text{-}[Ru^{IV}(bpy)_2(py)(O)]^{2+} + PhCHO + CH_3CN \rightarrow cis\text{-}[Ru^{II}(bpy)_2(py)(NCCH_3)]^{2+} + PhCO_2H + H_2O \quad (1)$$

The spectral changes in Figure 1A show that the initial ruthenium product is the nitrile complex *cis*-$[Ru^{II}(bpy)_2(py)(NCCH_3)]^{2+}$ ($\lambda_{max} = 440$ nm, $\epsilon_{max} = 8000\ M^{-1}\ cm^{-1}$) rather than *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ or *cis*-$[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$. Successive UV−visible spectral scans are reminiscent of those previously observed in the oxidations of styrene, *cis*- and *trans*-stilbene, DMSO, and PhNO in that there is no direct evidence for the formation of an intermediate.[23]

To establish the source of the added oxygen atom in the benzoic acid product, an ^{18}O-labeling study was performed. With *cis*-$[Ru^{IV}(bpy)_2(py)(^{18}O)]^{2+}$ (7.2 mM, 45% ^{18}O) and benzaldehyde (14.4 mM) in argon-purged CH_3CN, O-atom transfer is quantitative to within ±10% (Figure 2) based on IR measurements ($\nu_{C={}^{18}O}$ at 1686 cm^{-1}).

Reaction between *cis*-$[Ru^{IV}(bpy)_2(py)(^{18}O)]^{2+}$ (10.7 mM, 70% ^{18}O) and benzaldehyde (21.4 mM) in CH_3CN under air gave only 10% labeled benzoic acid product determined by FT IR spectroscopy. ^{18}O added as $H_2{}^{18}O$ did not appear in the benzoic acid product. When taken together, these two observations point to oxygen as the primary source of the added O atom in the carboxylic acid product

The kinetics of the reaction between *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and benzaldehyde under argon is first-order in each. There is a rate enhancement in H_2O compared to CH_3CN

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(25) Kuhn, R.; Meyer, K. *Naturwissenschaften* **1928**, *16*, 1028−1030.

Table 1. Kinetic Parameters for the Oxidations of Benzldehyde and Several of Its Derivatives by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$, *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$, and $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ in Argon-Purged CH_3CN, H_2O, and D_2O^{a-c}

medium	substrate	k^c, $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, e.u.	$k_{C-H/C-D}{}^d$
		$[Ru(bpy)_2(py)(O)]^{2+}$			
CH_3CN	benzaldehyde	1.05	10.7 ± 0.9	−23 ± 2	
CH_3CN	benzaldehyde-*d*	0.13	10.8 ± 1.2	−26 ± 3	8.1 ± 0.3
CH_3CN	*p*-anisaldehyde	1.52	10.3 ± 1.3	−23 ± 3	
CH_3CN	*p*-chlorobenzaldehyde	0.68	11.9 ± 2.4	−20 ± 4	
CH_3CN	*p*-tolualdehyde	1.31			
CH_3CN	*m*-anisaldehyde	0.89			
CH_3CN	*p*-bromobenzaldehyde	0.63			
CH_3CN	*m*-chlorobenzaldehyde	0.60			
CH_3CN	*p*-nitrobenzaldehyde	0.32			
H_2O	benzaldehyde	1.92	6.8 ± 1.0	−34 ± 5	
H_2O	benzaldehyde-*d*	0.21	8.9 ± 1.4	−32 ± 5	9.4 ± 0.4
D_2O	benzaldehyde	1.44	7.1 ± 0.8	−34 ± 4	(1.3 ± 0.1)^e
D_2O	benzaldehyde-*d*	0.20	9.9 ± 2.0	−29 ± 6	7.2 ± 0.8 (1.1 ± 0.1)^e
		$[Ru(bpy)_2(py)(OH)]^{2+}$			
CH_3CN	benzaldehyde	0.22			
CH_3CN	benzaldehyde-*d*	0.15×10^{-1}			14.7 ± 1.7
H_2O	benzaldehyde	2.48			
H_2O	benzaldehyde-*d*	0.12×10^{-1}			23.3 ± 2.5
		$[Ru(tpy)(bpy)(O)]^{2+}$			
CH_3CN	benzaldehyde	3.67	4.7 ± 0.6	−40 ± 5	
CH_3CN	benzaldehyde-*d*	0.64	5.1 ± 0.7	−42 ± 6	5.7 ± 0.4

[a] $\mu = 0.1$ M in added $MgSO_4$. [b] ±0.1 C. [c] Average of three or more separate kinetic runs at four different concentrations of the substrate in pseudo-first-order excess. [d] Temperature = 23.8−25.0 °C.

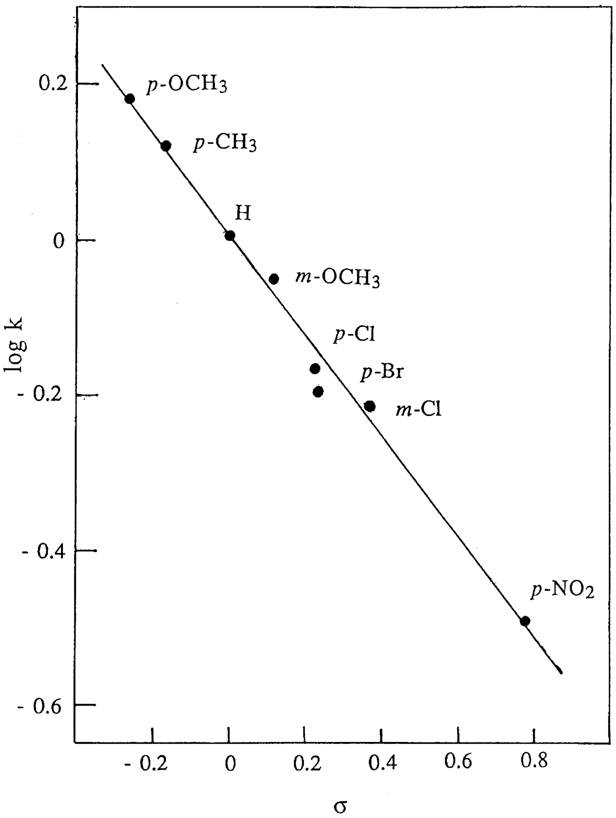


Figure 5. Hammett plot of log k vs σ for the oxidations of substituted benzaldehydes by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ in CH_3CN at 25 °C.

by a factor of ∼2 (Table 1). For the substituted benzaldehydes, the rate constant increases for electron-donating groups and decreases for electron-withdrawing groups added to the aromatic ring.

A Hammett plot of log k against σ for the reaction is shown in Figure 5. From the slope of the plot, $\rho = -0.65$ (±0.03).[24] This relatively low sensitivity to substituent changes is consistent with the buildup of a small degree of positive charge at the C atom in the redox step.

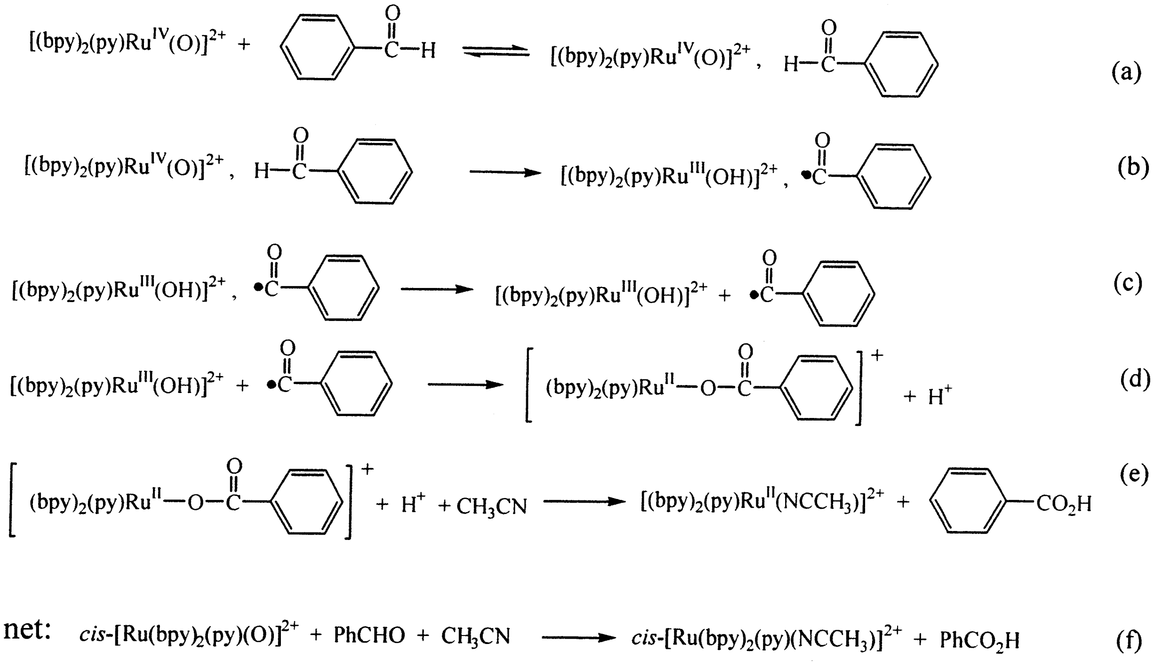
Mechanism. The available results for the oxidation of benzaldehyde by $Ru^{IV}{=}O^{2+}$ point to the mechanism in Scheme 1.

The sequence of steps in the mechanism is (a) preassociation, (b) one-electron oxidation, (c) separation of the benzoyl radical and $Ru^{III}{-}OH^{2+}$, (d) capture of the radical by $Ru^{III}{-}OH^{2+}$ to give the Ru^{II} benzoate complex, and (e) solvolysis to give the acetonitrile complex and benzoic acid.

Initial Redox Step. There are several lines of evidence that support a one-electron hydrogen-atom transfer (HAT) for the redox step in eq b. The one-electron character of the reaction and the appearance of the benzoyl radical in solution are clearly supported by the effect of O_2 on the product distribution as discussed below. The involvement of the aldehydic C−H bond is indicated by the magnitude of the k_{C-H}/k_{C-D} kinetic isotope effects of 8.1 ± 0.3 in CH_3CN and 9.4 ± 0.4 in H_2O. Homolytic bond dissociation energies (BDEs) are known for a variety of substrates of the type H−A.[18c,34] A good linear correlation exists between log k and C−H BDE for several of the aldehydes studied here, as shown in the Supporting Information,.

One-electron transfer can also be inferred by comparing rate constants for the oxidation of benzaldehyde by $Ru^{IV}{=}O^{2+}$ and $Ru^{III}{-}OH^{2+}$ as the oxidation by $Ru^{III}{-}OH^{2+}$ is slower by a factor of 5 in CH_3CN and 8 in H_2O. As an oxidant, $Ru^{III}{-}OH^{2+}$ is only slightly less oxidizing than $Ru^{IV}{=}O^{2+}$, with $E^{0\prime}(Ru^{III/II}) = 0.67$ V and $E^{0\prime}(Ru^{IV/III}) = 0.78$ V (25 °C, $\mu = 0.1$ M at pH = 7 vs NHE). $Ru^{III}{-}OH^{2+}$

Scheme 1



is constrained to be a one-electron oxidant. In other cases involving one-electron transfer, *k* values for $Ru^{III}-OH^{2+}$ and $Ru^{IV}=O^{2+}$ are within a factor of 10 of each other.[16k] In other cases where two-electron mechanisms appear for $Ru^{IV}=O^{2+}$, rate constant enhancements for $Ru^{IV}=O^{2+}$ compared to $Ru^{III}-OH^{2+}$ are in the range of 10^2-10^4.[19]

As an additional observation in support of one-electron transfer, there is no evidence for *cis*-$[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$ as the initial product in the oxidation of benzaldehyde by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$. This is true even at high benzaldehyde concentrations where $Ru^{II}-OH_2^{2+}$ would appear without complication from the subsequent comproportionation reaction, $Ru^{IV}=O^{2+}$ $Ru^{II}-OH_2^{2+} \rightarrow 2Ru^{III}-OH^{2+}$. If the mechanism were initial hydride $(2e^-/1H^+)$ transfer, the aqua complex would have been observed as a product: $Ru^{IV}=O^{2+} + ArCHO + H_2O \rightarrow Ru^{III}-OH_2^{2+} + ArC(O)\text{-}OH$.

As noted above, the ρ value of -0.65 (± 0.03) in the Hammett plot in Figure 5 points to electron-deficient character at the aldehyde in the transition state. This value is considerably less than $\rho = -2.5$ (± 0.2) for the oxidation of a series of anilines by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ in a mechanism that has been described as proton-coupled two-electron transfer.[23c] Given the other evidence, the correlation that is observed and the magnitude of ρ appear to be characteristic for H-atom transfer.

Effect of Added Oxygen. The one-electron character of the initial redox step is consistent with the influence of oxygen on the products. In air, the yield of $PhCO_2H$ is dependent on the $Ru^{IV}=O^{2+}/PhCHO$ ratio. The yields are 30% $PhCO_2H$ at 2:1; 50% at 1:2, and 99% at 1:4. Under argon in CH_3CN, the yield is 100% $PhCO_2H$ at a 2:1 ratio

It has been well established that auto-oxidation of aldehydes in the liquid state and in solution proceeds by a radical-chain mechanism.[13] Auto-oxidation of benzaldehyde in acetic acid occurs by the initial formation of perbenzoic acid followed by (1) catalyzed decomposition of perbenzoic acid and (2) reaction of perbenzoic acid with benzaldehyde to give benzoic acid.[13] Kuhn and Meyer have proposed that all aldehydic auto-oxidations are catalyzed by minute traces of heavy metal ions or other impurities.[25]

In the presence of air, capture of $Ph\dot{C}O$ by O_2 to make the perbenzoyl radical probably occurs, followed by competitive oxidation of the radicals $Ph\dot{C}O$ and $PhC(O)O_2^{\bullet}$ by $Ru^{III}-OH^{2+}$ (eqs 3 and 4). The oxidation of $^{\bullet}HO_2$ by $Ru^{III}-OH^{2+}$ to give O_2 and H^+ is known to be rapid.[26]

$$Ru^{IV}{=}O^{2+} + PhCHO \rightarrow Ru^{III}-OH^{2+} + Ph\dot{C}O \quad (2)$$

$$Ph\dot{C}O + O_2 \rightarrow PhC(O)O_2^{\bullet} \quad (3)$$

$$Ru^{III}-OH^{2+} + Ph\dot{C}O \rightarrow Ru^{II}-O_2CPH^{+} + H^{+} \quad (4)$$

$$Ru^{III}-OH^{2+} + PhC(O)O_2^{\bullet} + H_2\,O \rightarrow Ru^{II}-OH_2^{2+} + PhCO_2H + O_2 \quad (5)$$

The radicals can also be captured by $Ru^{IV}=O^{2+}$

$$Ru^{IV}{=}O^{2+} + Ph\dot{C}O \rightarrow Ru^{III}-O_2CPh^{2+} \quad (6)$$

$$Ru^{IV}{=}O^{2+} + PhC(O)O_2^{\bullet} + H_2O \rightarrow Ru^{III}-OH^{2+} + PhCO_2H + O_2 \quad (7)$$

At a 1:2 $Ru^{IV}={}^{18}O^{2+}/PhCHO$ ratio in air, the extent of ^{18}O transfer was only ~10%. This can be explained by considering the relative importance of the reactions between $Ru^{IV}=O^{2+}$ or $Ru^{III}-OH^{2+}$ and $PhC(O)O_2^{\bullet}$ (eqs 5 and 7) over reaction with $Ph\dot{C}O$, which would result in ^{18}O transfer.

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(26) Gilbert, J.; Roecker, L.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1126–1132.

Capture of the peroxo radical by $Ru^{IV}{=}O^{2+}$ and $Ru^{III}{-}OH^{2+}$ is also highly efficient compared to its oxidation of benzaldehyde.

$$PhC(O)O_2^{\bullet} + PhCHO \rightarrow PhC(O)O_2H + Ph\dot{C}O$$

There is no evidence for oxidation past the oxidative content of the initial $Ru^{IV}{=}O^{2+}$.

Remaining Steps in the Mechanism. With $Ru^{IV}{=}O^{2+}$ as the oxidant, the initial redox step occurs by H-atom transfer, with both the proton and electron transferred simultaneously from the aldehydic C−H bond. In the absence of O_2, there must be a subsequent one-electron transfer to $Ru^{III}{-}OH^{2+}$, accompanied by transfer of the $Ru^{III}{-}OH^{2+}$ oxygen atom as demonstrated by the ^{18}O-labeling result (eq (d) in Scheme 1).

Once formed, the benzoate complex undergoes rapid solvolysis in eq 1, probably acid-catalyzed, and is not observed as a detectable intermediate. The evidence for a benzoate intermediate comes from the ^{18}O labeling experiment and the fact that ^{18}O transfer occurs from *cis*-$[Ru^{IV}(bpy)_2(py)(^{18}O)]^{2+}$ to the aldehyde to give the labeled acid $PhC^{18}OOH$.

In a related experiment, the benzoate complex *cis*-$[Ru^{II}(bpy)_2($*p-tert*-bupy$)(OC(O)Ph)](PF_6)$ was prepared and characterized as described in the Experimental Section. This complex was stable in CH_3CN but underwent substitution with added acid consistent with the acid-catalyzed step in eq (e).[27]

Direct evidence was obtained for an intermediate ($\lambda_{max} = 480$ nm), presumably $[Ru^{II}(tpy)(bpy)(OC(O)Ph)]^+$, in the oxidation of PhCHO by $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$. In this case, oxidation is more rapid by a factor of ∼3, and the intermediate builds up to a detectable amount in solution before undergoing solvolysis.

The mechanism in Scheme 1 is sufficient to explain the experimental results with PhCHO in excess in the absence of O_2. With $Ru^{IV}{=}O^{2+}$ and benzaldehyde at a 1:1 initial ratio, the yield of $PhCO_2H$ falls, and there is 15% unreacted aldehyde. The characteristic bridge-based Ru−O−Ru band at 600−700 nm in the UV−visible spectrum, appears in parallel with new chemical shifts in the ^1H NMR spectrum,[29] and $E_{1/2}$ values at 1.22 and 1.34 V in the cyclic voltammogram in Figure 4. All point to an oxo-bridged dimeric complex as the product, most likely *cis,cis*-$[(bpy)_2(py)Ru^{III}ORu^{III}(py)(bpy)_2]^{4+}$. As a reference, there is an extensive chemistry of related μ-oxo-bridged dimeric Ru complexes in the literature.[29−32]

The μ-oxo complex is presumably formed by the reaction

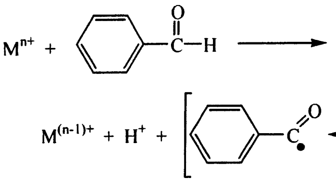
$$\begin{aligned} &cis[Ru^{IV}(bpy)_2(py)(O)]^{2+} + \\ &\quad cis\text{-}[Ru^{II}(bpy)_2(py)(O_2CPh)]^+ \rightarrow \\ &\quad cis,cis\text{-}[(bpy)_2(py)Ru^{III}{-}O{-}Ru^{III}(py)(bpy)_2]^{4+} + \\ &\qquad PhCO_2^- \qquad (8) \end{aligned}$$

The subsequent appearance of *cis*-$[Ru^{II}(bpy)_2(py)(NCCH_3)]^{2+}$ on much longer time scales can be explained by slower oxidation of PhCHO as in eq 9

$$\begin{aligned} &cis,cis\text{-}[(bpy)_2(py)Ru^{III}{-}O{-}Ru^{III}(py)(bpy)_2]^{4+} + \\ &\quad PhCHO + 2CH_3CN \rightarrow \\ &\quad 2\ cis\text{-}[Ru^{II}(bpy)_2(py)(NCCH_3)]^{2+} + PhCO_2H \qquad (9) \end{aligned}$$

followed by loss of the py ligand which is a known reaction.[31]

Related Oxidations. Mechanistic precedence exists for the capture of the intermediate benzoyl radical in the oxidation of aromatic aldehydes to their carboxylic acids by Co(III), V(V), Ce(IV), and Ir(IV).[11−14] With one-electron oxidants, the chemistry of benzaldehyde is dominated by initial one-electron transfer to give the corresponding benzoyl radical, e.g.

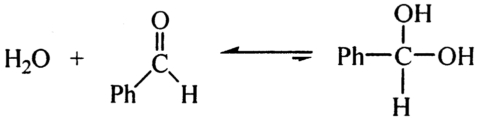


(10)

followed by a fast reaction between the free radical and a second metal ion to give carboxylic products

$$M^{n+} + H_2O + Ph\dot{C}O \rightarrow M^{(n-1)+} + H^+ + PhCO_2H \qquad (11)$$

Additional Mechanistic Details. The hydration equilibrium in eq 12 is catalyzed by both acid and base. The amount of hydrated form of benzaldehyde is negligibly small in CH_3CN solution [$K(H_2O, 25\ °C) = 10^{-4}\ s^{-1}$].[28c]



$$H_2O + PhC(O)H \rightleftharpoons PhC(OH)_2H \qquad (12)$$

There is only a slight rate constant enhancement in H_2O compared to CH_3CN (∼2, Table 1). Small amounts of H_2O added to CH_3CN have no effect on k_{obs}, and there is no evidence in the kinetics data of a significant role for the hydrated form.

As noted above, the PhCHO/PhCDO kinetic isotope effects of 9.4 ± 0.4 in H_2O (8.1 ± 0.3 in CH_3CN) and 7.2 ± 0.8 in D_2O clearly point to participation of the C−H bond in the redox step. The slight solvent effect of $k_{H_2O/D_2O} = 1.1{-}1.3$

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(27) A cyclic voltammogram of *cis*-$[Ru^{II}(bpy)_2($*p-tert*-butypy$)(OC(O)Ph)]^+$ in 0.1 M TBAH−CH_3CN includes a reversible wave with $E_{1/2} = 0.68$ V vs SSCE arising from one-electron oxidation. In the ^1H NMR spectrum, the $6_1'$ proton of one of the bpy ligands appeared at 9.62 ppm. Addition of one drop of HPF_6 into a CH_3CN solution containing the complex caused a rapid change in the UV−visible spectrum from $\lambda_{max} = 480$ nm to the characteristic spectrum of the nitrile complex, *cis*-$[Ru^{II}(bpy)_2($*p-tert*-butypy$)(NCCH_3)]^{2+}$, $\lambda_{max} = 440$ nm. A related observation was made by ^1H NMR spectroscopy.

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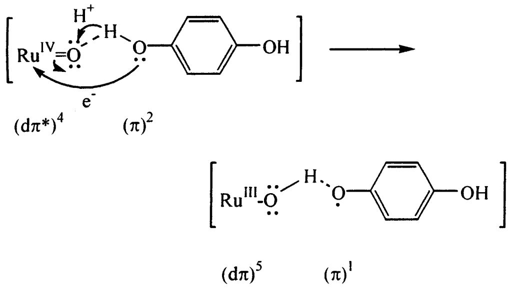
shows that substitution of H for D in the solvent is relatively inconsequential.

This is in contrast to other reactions where very large H_2O/D_2O kinetic isotope effects have been observed, for example, in the oxidation of hydroquinone by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$, where $k_{H_2O/D_2O} = 29 \pm 1$ as shown in eq 13.[33] This reaction occurs by "proton-coupled electron transfer" or electron-proton transfer (EPT) within a H-bonded association complex between hydroquinone (H_2Q) and $Ru^{IV}{=}O^{2+}$ to give semiquinone and $Ru^{III}{-}OH^{2+}$.

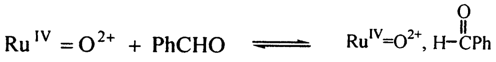


(13)

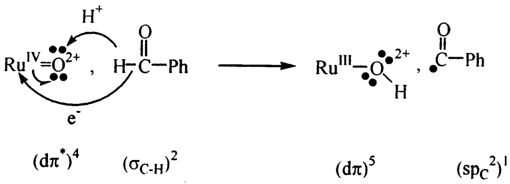
This mechanism differs from the H-atom transfer proposed for benzaldehyde in that the transferring electron and proton come from different sites in the H_2Q electron−proton donor.

In the oxidation of PhCHO by $Ru^{IV}{=}O^{2+}$, there is no acidic proton and no basis for an initial interaction by H-bonding. Rather, reaction occurs from the fraction of preassociation complexes that have an appropriate orientation to maximize electronic mixing between σ_{C-H} of the aldehyde and a $d\pi^*$ acceptor orbital on $Ru^{IV}{=}O^{2+}$ (eq 14). Preassociation is followed by a concerted reaction involving simultaneous donation of both an electron and a proton from the σ_{C-H} aldehydic bond to $Ru^{IV}{=}O^{2+}$ (eq 15). The C−H/C−D kinetic isotope effects of 7−9 provide direct evidence for involvement of the C−H bond and the ν_{C-H} vibrational mode in the activation process. The transfer of the electron occurs to a $d\pi^*$ orbital at Ru(IV), which is largely of antibonding character with regard to the Ru−O interaction. Proton transfer occurs to an oxo lone pair to form σ_{O-H} defining an EPT mechanism at $Ru^{IV}{=}O^{2+}$. At the aldehyde the transfer of proton and electron are simultaneous and occur from the same bond, which defines a net H-atom transfer (HAT) mechanism.

The relatively small H_2O/D_2O solvent kinetic isotope effect shows that quantum modes in the solvent such as ν(O−H) are not strongly coupled to the HAT event. Simultaneous transfer of an electron and a proton from the C−H bond to $Ru^{IV}{=}O^{2+}$ involves local dipole changes but, in contrast to electron transfer, no net charge displacement. A small solvent effect is expected, arising from the local dipole changes and the specific interaction of solvent with the O−H bond formed in the reaction.



$$\mathrm{Ru^{IV}=O^{2+} + PhCHO \rightleftharpoons Ru^{IV}{=}O^{2+},\ H{-}\overset{\overset{\displaystyle O}{\|}}{C}Ph} \qquad (14)$$



(15)

The appearance of an HAT mechanism is understandable based on the anticipated reaction barriers for competing pathways such as initial proton transfer followed by electron transfer

$$\mathrm{PhCHO \rightarrow PhCO^- + H^+}$$

$$\mathrm{Ru^{IV}{=}O^{2+} + PhCO^- \rightarrow Ru^{III}{-}O^+ + Ph\dot{C}O}$$

or the converse, electron transfer followed by proton transfer

$$\mathrm{Ru^{IV}{=}O^{2+} + PhCHO \rightarrow Ru^{III}{-}O^+ + PhCHO^{+\bullet}}$$

$$\mathrm{Ru^{III}{-}O^+ + PhCHO^{+\bullet} \rightarrow Ru^{III}{-}OH^{2+} + Ph\dot{C}O}$$

The other detailed study involving an aldehyde oxidation by $Ru^{IV}{=}O^{2+}$ is of formate anion[19a]

$$\mathrm{H^+ + Ru^{IV}{=}O^{2+} + HCO_2^- \rightarrow Ru^{II}{-}OH_2^{\,2+} + CO_2}$$

There is direct evidence in this reaction for a two-electron transfer with formation of *cis*-$[Ru^{II}(bpy)_2(py)(OH)]^+$ and CO_2 in the rate-limiting step. The reaction occurs with a C−H/C−D kinetic isotope effect of $k_{C-H}/k_{C-D} = 19 \pm 3$ at 25 °C. The rate constant for oxidation of HCO_2^- by the one-electron oxidant *cis*-$[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ is lower by a factor of ∼41 than that for oxidation by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and occurs with $k_{C-H}/k_{C-D} = 3.5 \pm 0.5$. On the basis of these observations, it has been concluded that the oxidation of HCO_2^- by $Ru^{IV}{=}O^{2+}$ occurs by hydride transfer rather than H-atom transfer. In hydride transfer, there is simultaneous transfer of two electrons and one proton from the same C−H bond.

$[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ is more strongly oxidizing than *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ as a two-electron oxidant by 0.08 V.[17] Kinetic studies with stopped-flow monitoring showed that oxidation of benzaldehyde by this oxidant is first-order in both benzaldehyde and $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$. In CH_3CN at 25 °C, the rate constant for oxidation by $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ is greater by a factor of ∼3 than that for oxidation by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$. There is a moderate PhCHO/PhCDO kinetic isotope effect of $k_{C-H}/k_{C-D} = 5.7 \pm 0.4$, and the mechanism of PhCHO oxidation is presumably H-atom transfer as well.

Conclusions

The oxidation of benzaldehyde and a series of ring-substituted aromatic aldehydes by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$

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in CH_3CN and water all occur via H-atom transfer in the key redox step

$$cis\text{-}[Ru^{IV}(bpy)_2(py)(O)]^{2+} + ArCHO \rightarrow cis\text{-}[Ru^{III}(bpy)_2(py)(OH)]^{2+} + ArC\dot{O}$$

In the absence of air, ^{18}O labeling shows that the intermediate radical is captured by *cis*-$[Ru^{III}(bpy)_2(py)(^{18}OH)]^{2+}$ to give a Ru^{II} benzoate intermediate

$$cis\text{-}[Ru^{III}(bpy)_2(py)(^{18}OH)]^{2+} + Ar\dot{C}O \rightarrow cis\text{-}[Ru^{II}(bpy)_2(py)(O^{18}OAr)]^{+} + H^{+}$$

which undergoes rapid solvolysis to give the solvent complex. A benzoate intermediate is observed as an intermediate with $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ as the oxidant.

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Supporting Information Available: Plot showing linear correlation between log *k* and the C−H BDE for several of the aldehydes studied here. This material is available free of charge via the Internet at http://pubs.acs.org.

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