conclude that an organic molecule that contains a (C–)H atom adjacent to a nitrogen atom is especially likely to form C—H···X hydrogen bonds. This is of interest because two classes of biologically important molecules fall into this category: the amino acids,[41] and the nucleosides and nucleotides. The importance of C—H···O and C—H···Cl hydrogen bonds in the crystal structures of these compounds has been recognized in the literature.[12,13]

The above observations suggest that (C–)H atoms that are not adjacent to electron-withdrawing groups are unlikely to form C—H···X hydrogen bonds and may even be incapable of doing so. Thus, some of the short contacts listed in Tables V and VII may actually be repulsive interactions, which occur only because of crystal packing forces. However, the results outlined in the preceding sections indicate that the majority of the contacts are likely to be attractive.

(2) Proton Acceptor. The (C–)H···O contacts listed in Table V involve a wide variety of acceptor groups—sulfonate, carboxylate, nitro, carbonyl, ether, etc. Apparently, almost any type of oxygen atom is inherently capable of participating in a C—H···O hydrogen bond. We therefore conclude that the energy of the C—H···O hydrogen bond is very sensitive to the nature of the (C–)H atom, but insensitive to the nature of the oxygen atom. This may be rationalized as follows. The electrostatic energy, *E*, due to the Coulombic interaction between (C–)H and O can be approximated by

$$E = (q_H q_O)/r \qquad (5)$$

where q_H is the partial charge on the (C–)H atom, q_O is the partial charge on the O atom, and r is the interatomic distance.[42] The absolute value of q_H will invariably be smaller than that of q_O. Consequently, a change in q_H will have a greater effect on E than an equal change in q_O.

(3) Stoichiometry of the Crystal Structure. Nine of the 59 short (C–)H···O contacts listed in Table V occur in crystal structures that contain oxygen atoms but no O–H or N–H groups. This is a surprisingly large number, because there are only eight such structures in our sample. Furthermore, the α_i values (see eq 3) of seven of these structures fall in the range 0.0–0.075; the eighth is 0.250. These are somewhat lower than would be expected by comparison with the α_i values of the remaining structures. It seems that short (C–)H···O contacts are particularly likely to occur in crystal structures that contain a large number of oxygen atoms, but relatively few proton donor groups (i.e., O–H or N–H). One possible explanation is that oxygen atoms which are not involved in O—H···O or N—H···O hydrogen bonds are more accessible to (C–)H atoms than they would otherwise be.

Summary

We conclude that the majority of short C—H···O, C—H···N, and C—H···Cl contacts are attractive interactions, which can reasonably be described as hydrogen bonds. Our conclusion is based on a survey of 113 published crystal structures, which have been determined very precisely by neutron diffraction. It is consistent with the results of spectroscopic and theoretical studies. The C—H···X hydrogen bond may be a significant factor in determining the minimum energy packing arrangements of small organic molecules that contain nitrogen, e.g., the amino acids and nucleosides.

Acknowledgment. We thank Dr. P. M. E. Altham of the Cambridge University Statistical Laboratory for advice on the statistical methods used. Financial support was provided by the Medical Research Council.

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(41) A total of 37 of the 47 amino acid (C_α–)H atoms in our sample form at least one contact to a hydrogen bond acceptor atom with $d > 0.0$ Å and C—H···X > 90°.

(42) Dauber, P.; Hagler, A. T. *Acc. Chem. Res.* **1980**, *13*, 105–112.

Kinetics and Mechanism of Oxidation of Aromatic Hydrocarbons by Ru(trpy)(bpy)O^{2+}

Mark S. Thompson and Thomas J. Meyer*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received November 30, 1981

Abstract: The kinetics of oxidation of p-$^{-}O_2CC_6H_4CH(CH_3)_2$, p-$^{-}O_2CC_6H_4CH_2CH_3$, and p-$^{-}O_2CC_6H_4CH_3$ by Ru(trpy)(bpy)O^{2+} (trpy is 2,2′,2″-terpyridine; bpy is 2,2′-bipyridine) to the corresponding α alcohols in water and of $C_6H_5CH(CH_3)_2$ and $C_6H_5CH_3$ by Ru(bpy)$_2$(py)O^{2+} in acetonitrile have been studied. The following conclusions are drawn from kinetics data obtained spectrophotometrically: (1) Rate constants increase with increasing alkyl substitution; for the carboxylates in water at 24.3 °C, $k = 12.2 \pm 1.2$, 3.4 ± 0.3, and 0.43 ± 0.04 M^{-1} s^{-1} in the order shown above. (2) Rate constants decrease dramatically for the reactions in acetonitrile; k(24.3 °C) = 0.026 ± 0.003 M^{-1} s^{-1} for isopropylbenzene. (3) In water, rate constants are independent of added O_2 or of changes in ionic strength. (4) In acetonitrile the added nucleophiles water, *tert*-butyl alcohol, or bromide ion enter the rate law directly in terms first order in added nucleophile. From the temperature dependence of k for the oxidation of p-$^{-}O_2CC_6H_4CH(CH_3)_2$, $\Delta H^* = 7 \pm 1$ kcal/mol and $\Delta S^* = -32 \pm 4$ eu. It is concluded that the redox step for the reactions involves a two-electron, hydride ion transfer step. The reactions occur by a template mechanism in that oxo group transfer from Ru to the substrate does not occur and the added oxygen atom must come from the solvent, p-$^{-}O_2CC_6H_4CH(CH_3)_2$ (–H:$^-$; +H_2O) → p-$^{-}O_2CC_6H_4C(OH)(CH_3)_2$. The solvent or added nucleophile (in acetonitrile) is directly involved in the redox step, apparently by assisting the loss of the hydride ion by electron pair donation.

Functionalized aromatic hydrocarbons are used as starting materials in a variety of syntheses, and their oxidations have been widely studied[1-3] both synthetically and mechanistically.[2,3] We have reported that the Ru(IV)–oxo complex Ru(trpy)(bpy)O^{2+} (bpy is 2,2′-bipyridine; trpy is 2,2′2″-terpyridine) is capable of

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(1) Ross, S. D.; Finkelstein, M.; Rudd, E. F. "Anodic Oxidation"; Academic Press: New York, 1975.

(2) Benson, D. "Mechanisms of Oxidation by Metal Ions"; Elsevier: New York, 1976.

(3) Wiberg, K. B., Ed. "Oxidation in Organic Chemistry"; Academic Press: New York, 1965.

(4) (a) Thompson, M. S. Ph.D. Dissertation, University of North Carolina, Chapel Hill, NC, 1981. (b) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310.

0002-7863/82/1504-5070\$01.25/0

effecting a variety of organic oxidations,[4] including the aromatic oxidations shown in eq 1–3 in aqueous solution. Especially notable

$$6Ru(trpy)(bpy)O^{2+} + 2H_2O + p\text{-}^{-}O_2CC_6H_4CH_3 \rightarrow 6Ru(trpy)(bpy)OH_1{}^{2+} + p\text{-}^{-}O_2CC_6H_4CO_2{}^{-} + H^+ \quad (1)$$

$$4Ru(trpy)(bpy)O^{2+} + H_2O + p\text{-}^{-}O_2CC_6H_4CH_2CH_3 \rightarrow 4Ru(trpy)(bpy)OH_1{}^{2+} + p\text{-}^{-}O_2CC_6H_4C(O)CH_3 \quad (2)$$

$$2Ru(trpy)(bpy)O^{2+} + H_2O + p\text{-}^{-}O_2CC_6H_4CH(CH_3)_2 \rightarrow 2Ru(trpy)(bpy)OH_1{}^{2+} + p\text{-}^{-}O_2CC_6H_4COH(CH_3)_2 \quad (3)$$

are the facts that the reactions are quantitative as written and can be made catalytic by reoxidizing $Ru(trpy)(bpy)OH^{2+}$ to Ru(IV) electrochemically.

The results of detailed kinetic and mechanistic studies have shown or strongly implicated net oxygen atom[5] or hydride transfer[6] pathways for the oxidation of PPh_3 and 2-propanol, respectively, by $Ru(trpy)(bpy)O^{2+}$ or its analogue $Ru(bpy)_2(py)O^{2+}$ (py is pyridine).

The oxidations of aromatic hydrocarbons by $Ru(trpy)(bpy)O^{2+}$ have several distinguishing features. They include the following: (1) Given the oxidizing strength of the $Ru(trpy)(bpy)O^{2+}/Ru(trpy)(bpy)OH_2{}^{2+}$ couple ($E^{\circ\prime} = 0.81$ V at pH 7 vs. NHE), the reactions are remarkably facile and can be carried out under mild conditions compared to other oxidants. (2) The reactions provide the basis for the chemically catlayzed, not electrochemical oxidation of the hydrocarbons. (3) There is an element of selectivity to the reactions, as shown by the preference of α- vs. β-C–H oxidation in eq 2 and the fact that no evidence for oxidation of the aromatic ring has been found. We report here the results of a kinetics and mechanistic study on the oxidations of a series of aromatic hydrocarbons. Our goal was to establish the details of the pathway(s) by which the Ru^{IV} oxidants carry out the reactions.

Experimental Section

Materials. Water used throughout was deionized and distilled from alkaline permanganate. Cumene, ethylbenzene, and toluene were all fractionally distilled twice and stored under nitrogen. 4-Isopropylbenzoic acid from Eastman Kodak was very impure and was recrystallized twice from hot 1/1 (v/v) methanol–water. 4-Ethyl- and 4-methylbenzoic acids were used as obtained from the Aldrich Chemical Co. Spectrograde acetonitrile was used as obtained from Burdick & Jackson Laboratories. $RuCl_3 \cdot 3H_2O$ was obtained from Johnson-Matthey Inc., and 2,2′,2″-terpyridine was obtained from G. F. Smith Co. 2,2′-Bipyridine was obtained from the Aldrich Chemical Co., and $AgClO_4$ was purchased from the Alfa Ventron Chemical Co. All simple salts, solvents, and other materials were obtained as reagent grade and used without further purification.

Preparations. $Ru(trpy)Cl_3$, $[Ru(trpy)(bpy)OH_2](ClO_4)_2$, and $[Ru(trpy)(bpy)O](ClO_4)_2 \cdot 2H_2O$ were prepared by literature procedures.[4a,7]

Sodium 4-Alkylbenzoates. 4-Alkylbenzoic acid (10 g) (alkyl = methyl, ethyl, 2-propyl) was added to 100 mL of hot water containing 1 equiv of sodium bicarbonate, and the mixture was stirred until the acid had all dissolved. The solvent was removed with a rotary evaporator and the resultant white powder dried in a vacuum oven for 24 h at 50 °C; yield, >98%.

Measurements. Routine UV–vis spectra were obtained on a Varian 634 spectrophotometer. Kinetic studies were monitored spectrophotometrically with a Varian 634 spectrophotometer. NMR experiments were conducted with a Varian XL-100 spectrometer.

NMR Spectra. All NMR measurements were made in acetonitrile-d_3 or D_2O/H_2O mixtures in a 5-mm tube and referenced to Me_4Si. Quantitative measurements were made by comparing the peak areas of a sample to be determined with the peak areas (with an appropriate factor correcting for differences in proton number) of weighed standards of either sodium acetate or sodium terephthalate.

Kinetic Measurements in Water. Rate data were obtained in a 1-cm cell by monitoring absorbance changes at 477 and 406 nm. The initial concentrations of $Ru(trpy)(bpy)O^{2+}$ were varied from 1×10^{-4} to 3×10^{-4} M. Solutions of the oxidant were generated by electrochemical oxidation of $Ru(trpy)(bpy)OH_2{}^{2+}$ immediately prior to use. Experiments at a pH of 6.8 or 8.9 were conducted by using standard phosphate or bicarbonate buffers, respectively.[8] It should be noted that we have no evidence under our conditions of complications arising from coordination or other reactions of the buffers. The Ru(II) aquo complexes have low affinities for non-back-bonding anions, as shown by the fact that K(25 °C) < 0.05 for the equilibria:

$$Ru(bpy)_2(py)H_2O^{2+} + X^- \rightleftharpoons Ru(bpy)_2(py)X^+ + H_2O \quad (X = Cl, NO_3)$$

Ionic strengths were adjusted by varying buffer concentrations and were varied from 0.10 to 2.02 M. The reactions were initiated by adding aliquots of standardized aqueous alkylbenzoate solution to thermostated solutions of ruthenium complex. Alkylbenzoate concentrations were varied from 0.004 to 0.05 M. Except for solutions where O_2 was deliberately added, the solutions were purged with nitrogen and kept under nitrogen during the course of the kinetic runs.

The kinetic analysis used is somewhat complicated and although it has been discussed in detail elsewhere[6] will be outlined here as well. If an aqueous solution of $Ru(trpy)(bpy)O^{2+}$ is made roughly millimolar in reductant (a pseudo-first-order excess) and the visible region of the spectrum is scanned repeatedly, two stages in the reaction are apparent. The spectral changes observed correspond to a rapid reduction of $Ru(trpy)(bpy)O^{2+}$ to $Ru(trpy)(bpy)OH^{2+}$ followed by a slow reduction of $Ru(trpy)(bpy)OH^{2+}$ to $Ru(trpy)(bpy)OH_2{}^{2+}$. If a trace is obtained by monitoring absorbance change as a function of time at 406 nm, which is an isosbestic point between Ru(II) and Ru(III), and plotted with the assumption of first-order kinetics (ln ΔA vs. t), a straight line is obtained. However, if the reaction is followed at the Ru(IV)/Ru(II) isosbestic point at 363 nm, a first-order plot of the data is curved initially but becomes linear in the later stages. The spectral changes with time are consistent with a three-stage reaction: (1) the rapid reduction of Ru(IV) to Ru(III), which is first order in Ru(IV), (2) an intermediate stage in which Ru(IV) is still the oxidant but the oxidation step is preceded by the rapid disproportionation of Ru(III):

$$2Ru(trpy)(bpy)OH^{2+} \xrightleftharpoons{K=0.050} Ru(trpy)(bpy)O^{2+} + Ru(trpy)(bpy)OH_2{}^{2+}$$

and (3) a third stage in which Ru(III) is reduced to Ru(II) by a path that is first order in Ru(III). The procedure that we have followed involves the following steps: (1) The rate law for the reaction is

$$\text{rate} = k_{IV}[Ru(IV)][S] + k_{III}[Ru(III)][S]$$

where [S] is the substrate concentration and k_{III} and k_{IV} are rate constants for oxidation by Ru(III) and Ru(IV), respectively. (2) The rate law can be written as

$$(dz/dt)/f_{IV}[S] = 2k_{IV} + 2k_{III}(f_{III}/f_{IV})$$

where z is a reaction variable, the number of electrons added per Ru(IV), and f_{III} and f_{IV} are the fractions of the total Ru concentration at time t as Ru(III) and Ru(IV). (3) As described previously,[6] f_{III} and f_{IV} can be determined from the disproportionation equilibrium, known molar extinction coefficients at 477 nm, and mass balance. dz/dt can be determined from the slopes of absorbance vs. time curves. (4) k_{III} and k_{IV} can be determined from the slopes and intercepts of plots of $(dz/dt)/(f_{IV}[S])$ vs. (f_{III}/f_{IV}). Straight lines were fitted to data points by using a simple linear least-squares program available for a Texas Instruments 59 programmable calculator. Each observed rate constant was determined from a plot comprised of at least six absorbance–time readings. Each actual rate constant was determined from a plot comprised of at least three different observed rate constant–concentration points. Thus each reported rate constant was determined from the average of at least 18 separate measurements. Experimental uncertainties were estimated from the instrument manufacturer's reported error limits and the scatter observed for different individual measurements on a given system.

For the aromatic hydrocarbon oxidations described here, $k_{III} \ll k_{IV}$, and it was only possible to establish an upper limit for k_{III}, $k_{III} < 10^{-4}$ M^{-1} s^{-1}. The limit quoted here is based on the assumption of a k_{III} path which is first order in Ru(III) and first order in substrate, which is the case for the oxidation of 2-ropanol by Ru(III).[6]

An alternate procedure was adopted for the analysis of the kinetics data in acetonitrile. In acetonitrile the oxidation by Ru(IV) is much slower than are the reactions in water, and the initial Ru(IV) → Ru(III) conversion is followed by an even slower conversion of Ru(III) to Ru(II). The half-time for the latter reaction even with large excesses of added substrate was near the half-time for "spontaneous" conversion of $Ru(bpy)_2(py)OH^{2+}$ to Ru(II), presumably by oxidation of CH_3CN or of an

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[5] Moyer, B. A.; Sipe, B. K.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 1475.
[6] Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4106.
[7] Thompson, M. S.; Meyer, T. J., submitted for publication.
[8] Weast, R. C., Ed. "Handbook of Chemistry and Physics": CRC Press: Cleveland, OH, 1976.

impurity in the solvent. Because of the apparent slowness of the reaction between Ru(III) and added hydrocarbon, we were unable to obtain an intrinsic rate constant for these reactions. The procedure that was followed to obtain k_{IV} values was to plot absorbance time data as ln (ΔA) vs. t where ΔA is the absorbance change after time t. These plots had both a linear portion and an initial curved portion. By a plot of the natural logs of the differences between the ln (ΔA) plot and the linear portion extrapolated to time = 0, a straight line was obtained and the slope of the difference plot was taken to be the rate constant for the first step.[10]

Stoichiometry. The stoichiometry of the oxidation of 4-isopropylbenzoate determined by the electrocatalytic technique is discussed elsewhere.[4a,9] In this experiment, 110 mg of sodium 4-isopropylbenzoate in pH 6.8 aqueous solution at 30 °C was oxidized at 0.80 V vs. SCE in the presence of $Ru(trpy)(bpy)O^{2+}$ until the current had fallen to $\sim$1% of its initial value. The organic product was isolated by acidification of the aqueous solution followed by extraction of the organic product with 10 × 20-mL aliquots of diethyl ether. The ether was stripped off on a rotary evaporator, leaving behind a white powder.

Kinetics in Acetonitrile with $Ru(bpy)_2pyO^{2+}$ as Oxidant. In an attempt to ascertain the role of solvent in the reaction, the kinetics of oxidation of the hydrocarbons toluene and 2-propylbenzene were studied in acetonitrile. It was necessary to use the pyridine complex because of the instability of $Ru(trpy)(bpy)O^{2+}$ in acetonitrile.[6] The reactions were carried out by dissolving $Ru(bpy)_2(py)O^{2+}$ as the perchlorate salt in acetonitrile and adding 2-propylbenzene (cumene) or toluene by syringe. In the cases where the effects of added nucleophile were studied, stock solutions containing the nucleophiles were made up and used instead of the neat acetonitrile solution. No attempt was made to deoxygenate the solutions. Except for experiments where LiBr was present, absorbance changes with time were monitored at 488 nm, which is an isosbestic point between the spectra of $Ru(bpy)_2(py)OH_2^{2+}$ and $Ru(bpy)_2(py)(CH_3CN)^{2+}$. The details of the kinetic analysis were described in the previous section. In the presence of lithium bromide, the kinetics were monitored at 487 nm, which is an isosbestic point under these conditions where $Ru(bpy)_2(py)Br^+$ forms in the solution by anation.

For determination of the nature of the initial Ru(II) product, the reaction between $Ru(bpy)_2(py)O^{2+}$ and cumene was quenched by the addition of 1 μL of 64% hydrazine after the Ru(IV) was approximately 75% reduced, and the spectrum of the resulting solution was scanned rapidly in the visible region in order to ascertain the relative amounts of $Ru(bpy)_2(py)OH_2^{2+}$ (λ_{max} = 471 nm) and $Ru(bpy)_2(py)CH_3CN^{2+}$ (λ_{max} = 440 nm).

Results

Stoichiometry Measurements. The electrocatalytic procedure used for the oxidation of sodium 4-isopropylbenzoate was described above. In the experiment 137 C was passed for 110 mg of reactant. A ^1H NMR spectrum of the isolated product in D_2O made sufficiently basic to dissolve the white solid showed a singlet at 1.5 ppm plus a multiplet in the region 7–8 ppm, with no evidence for unreacted starting material. The observed spectrum is consistent with that expected for the anion, $p\text{-}^-O_2CC_6H_4COH(CH_3)_2$. Comparisons of NMR peak areas with the methyl resonance of the acetate ion added as an internal reference showed the presence of 4.6×10^{-4} mol of product. On the basis of the number of coulombs passed in the electrocatalytic reaction and the stoichiometric factor of 2 in the oxidation, the yield of isolated product was 87%, based on the stoichiometry of the reaction in eq 1. Given the experimental uncertainty in the analysis and isolation procedures, the yield of 87% probably represents a quantitative conversion to within experimental error.

Stoichiometries were not determined for the reactions between $Ru(trpy)(bpy)O^{2+}$ and $p\text{-}^-O_2CC_6H_4CH_2CH_3$ or $p\text{-}^-O_2C_6H_4CH_3$ in water or for the reaction between $Ru(bpy)_2(py)O^{2+}$ and $C_6H_5CH_3$ in acetonitrile. However, it should be noted that extended electrocatalytic oxidation of these substrates based on $Ru(trpy)(bpy)O^{2+}$ leads to the quantitative production of $p\text{-}O_2CC_6H_4C(O)CH_3$, $p\text{-}^-O_2CC_6H_4CO_2^-$, or $C_6H_5CO_2^-$, respectively, within experimental error.[4] Further, initial results show that the oxidations occur in a series of two-electron steps, $ArCH_3 \rightarrow ArCH_2OH \rightarrow ArCHO \rightarrow ArCO_2^-$, and that for $ArCH_3$, the rate constants for the alcohol to aldehyde and aldehyde to acid conversions are within an order of magnitude of each other. As a consequence, we feel justified in assuming that the reaction between $Ru(trpy)(bpy)O^{2+}$ and large excesses of the aromatic hydrocarbons in water are probably well-defined two-electron oxidations, as shown here for the 4-isopropylbenzoate anion.

Spectral Changes and Search for Intermediates. An aqueous solution containing $Ru(trpy)(bpy)O^{2+}$ was made roughly millimolar in 4-isopropylbenzoate, and the absorption spectrum of the solution was scanned repeatedly between 350 and 700 nm. In the initial stages of the reaction, an isosbestic point was present at 363 nm. After several scans the isosbestic point at 363 nm had disappeared, to be replaced by an isosbestic point at 406 nm, which remained for the duration of the experiment. The two isosbestic points match exactly those that appear in the electrochemical reduction of $Ru(trpy)(bpy)O^{2+}$ to $Ru(trpy)(bpy)OH^{2+}$ and of $Ru(trpy)(bpy)OH^{2+}$ to $Ru(trpy)(bpy)OH_2^{2+}$ in water. The observed spectral changes are consistent with the reduction of Ru(IV) to Ru(III), as discussed later, most probably by reaction 4 followed by reaction 5. The initial, rapid reduction of Ru(IV) is followed

$$Ru(trpy)(bpy)O^{2+} + p\text{-}^-O_2CC_6H_4CH(CH_3)_2 + H_2O \rightarrow Ru(trpy)(bpy)OH_2^{2+} + p\text{-}^-O_2CC_6H_4COH(CH_3)_2 \quad (4)$$

$$Ru(trpy)(bpy)O^{2+} + Ru(trpy)(bpy)OH_2^{2+} \overset{K=200}{\rightleftharpoons} 2Ru(trpy)(bpy)OH^{2+} \quad (5)$$

$$2Ru(trpy)(bpy)OH^{2+} + H_2O + p\text{-}^-O_2CC_6H_4CH(CH_3)_2 \rightarrow 2Ru(trpy)(bpy)OH_2^{2+} + p\text{-}^-O_2CC_6H_4COH(CH_3)_2 \quad (6)$$

by the very slow reduction of $Ru(trpy)(bpy)OH^{2+}$ to $Ru(trpy)(bpy)OH_2^{2+}$. The Ru(IV) complex is still present in small amounts during the later stages of the reaction due to the disproportionation reaction, which is the reverse of eq 5. A significant point that arises from the spectral study is that if there are any intermediates during the reaction, they do not build up to appreciable concentrations or are too short-lived to be observed spectrophotometrically.

A hydrazine quenching experiment was carried out in acetonitrile in order to search for O atom transfer. The reaction between $Ru(bpy)_2(py)O^{2+}$ and isopropylbenzene under kinetic conditions was quenched by adding hydrazine after the reaction had been allowed to proceed to $\sim$75% completion. After the addition of hydrazine, the spectrum was rapidly scanned. The addition of hydrazine results in the rapid reduction of both $Ru(bpy)_2(py)O^{2+}$ and $Ru(bpy)_2(py)OH^{2+}$ to $Ru(bpy)_2(py)OH_2^{2+}$. After correction for the extent of acetonitrile complex formation by solvolysis,

$$Ru(bpy)_2(py)OH_2^{2+} + CH_3CN \rightarrow Ru(bpy)_2(py)CH_3CN^{2+} + H_2O \quad (7)$$

$$(t_{1/2}(25\ ^\circ C) = 8\ \text{min})$$

it is apparent that $Ru(bpy)_2(py)OH_2^{2+}$ and $Ru(bpy)_2(py)OH^{2+}$ are the dominant (>90%) reduced forms in solution at this point in the reaction. This result plus the fact that the organic product is *not* the corresponding alcohol (see below) shows that O atom transfer from Ru(IV) to the hydrocarbon does *not* occur. If O atom transfer had occurred, the products would have been cumyl alcohol and the Ru(II)–acetonitrile complex.

Kinetics. For the oxidation by Ru(IV) in water, the reaction is first order in $[Ru(trpy)(bpy)O^{2+}]$ and first order in [4-isopropylbenzoate]. The dependence on the benzoate anion was shown by varying its concentration from 4.5 to 50×10^{-3} M (note Figure 1). At 24.3 °C for the oxidation by Ru(IV), $k_{IV} = (12.2 \pm 1.2)\ M^{-1}\ s^{-1}$. As can be seen from the data in Table I, k_{IV} is not sensitive to the presence of O_2 in an air-saturated solution or to ionic strength variations in the range μ = 0.20–2.02. k_{IV} is also independent of changes in pH in the range 6.8–8.9. A detailed pH study was not undertaken because of the insolubility of the conjugate acid of 4-isopropylbenzoate, which restricts the acid

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[9] (a) Thompson, M. S.; Meyer, T. J., manuscript in preparation. (b) Thompson, M. S. Ph.D. Dissertation, University of North Carolina, Chapel Hill, NC, 1981.

[10] Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981.

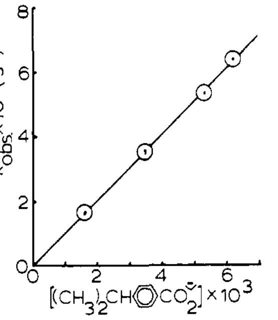

Figure 1. Variation of k_{obsd} for the oxidation of 4-isopropylbenzoate by Ru(trpy)(bpy)O^{2+} as a function of 4-isopropylbenzoate concentration at 24.3 °C in water ($\mu = 0.20$).

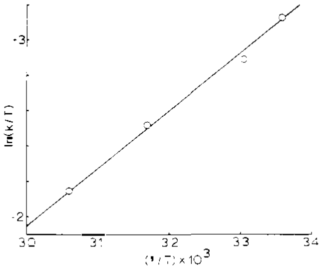

Figure 2. Plot of ln (k/T) vs. $1/T$ for the oxidation of 4-isopropylbenzoate anion by Ru(trpy)(bpy)O^{2+} in water ($\mu = 0.2$ M).

Table I. Representative Rate Constants for the Oxidation of Aromatic Hydrocarbons by Ru(trpy)(bpy)O^{2+} in Water at 24.3 °C, pH 6.8

expt	substrate	k_{IV}, M^{-1} s^{-1}	μ, M^c
1	p-$^-O_2CC_6H_4CH(CH_3)_2$	12.3 ± 1.2	0.20
2	p-$^-O_2CC_6H_4CH(CH_3)_2$	11.9 ± 1.2^a	0.20
3	p-$^-O_2CC_6H_4CH(CH_3)_2$	10.3 ± 1.0	0.66
4	p-$^-O_2CC_6H_4CH(CH_3)_2$	12.6 ± 1.3	1.34
5	p-$^-O_2CC_6H_4CH(CH_3)_2$	12.8 ± 1.3	2.02
6	p-$^-O_2CC_6H_4CH(CH_3)_2$	10.5 ± 1.1	0.10
7	p-$^-O_2CC_6H_4CH_2CH_3$	3.4 ± 0.30^b	0.20
8	p-$^-O_2CC_6H_4CH_3$	0.43 ± 0.04^b	0.20

[a] In an air-saturated solution. All other experiments were carried out in deaerated solutions. [b] Observed rate constants; note text for possible ambiguities arising from subsequent reactions so that $k_{IV} \leq k_{obsd}$. [c] Ionic strength variations were made by varying the concentrations of the buffer components Na_2HPO_4 and NaH_2PO_4.

range, and because of the instability of the oxidant at higher pH values.[11]

As described in the Experimental Section, the kinetic treatment used to treat the absorbance–time data yields rate constants for the Ru(III) pathway as well as for the Ru(IV) pathway. However, in water the rate constant for oxidation by Ru(III) is too small to be measurable. Assuming that as for the oxidation of 2-propanol by Ru(trpy)(bpy)O^{2+}[6] the oxidation of the hydrocarbons is first order in both Ru(IV) and substrate, we estimate that $k_{III} < 10^{-4}$ M^{-1} s^{-1} at 24.3 °C and $\mu = 0.20$ M.

For the oxidation of 4-isopropylbenzoate anion by Ru(trpy)(bpy)O^{2+}, activation parameters were determined from the slope and intercept of a plot of ln (k/T) vs. $1/T$ over the temperature range 24–44 °C (Figure 2). The values were $\Delta H^{\ddagger} = 7 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = 32 \pm 4$ eu.

Substituent Effects. The commerical unavailability of deuterium-substituted derivatives of 4-isopropylbenzoic acid and difficulties encountered in the preparation of the materials prevented the measurement of kinetic isotope effects. However, it was possible to investigate the variation of rate constants with alkyl substituent for the series of anions where the alkyl group was CH_3, CH_2CH_3, or $CH(CH_3)_2$. Representative results are shown in Table I. It should be noted that the observed rate constants for the oxidations where R = CH_3 or CH_2CH_3 represent upper limits for the actual rate constants for conversion of the alkyl group to the alcohol. This is so because, as noted above, the final products of the oxidations under electrocatalytic conditions are p-toluic acid and the p-carboxylate of acetophenone, respectively. If the oxidation steps past the initial stage, which gives p-$^-O_2CC_6H_4CH_2OH$ or p-$^-O_2CC_6H_4CHOHCH_3$, are competitive with the initial step, the stoichiometric assumption used in the kinetic analysis, $k_{IV} = {}^1/_2 k_{IV}$(obsd), is incorrect, and $k_{IV} \geq {}^1/_2 k_{IV}$(obsd). However, preliminary results suggest that the subsequent oxidations of the alcohols to the carbonyls are considerably less than 10^2 faster than the initial reaction. Consequently, under our conditions where there was always a large pseudo-first-order excess ($>10^2$) of substrate, the rate constants probably represent the intrinsic values for the initial two-electron steps shown in eq 8 and 9.

Table II. Rate Constant and Related Comparisons for Oxidations by Ru(IV)

substrate	k_{IV}, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Ru(trpy)(bpy)O^{2+} as Oxidant in H_2O ($\mu = 0.2$ M)^a at 24–25 °C			
p-$^-O_2CC_6H_4CH(CH_3)_2$	12.2 ± 1.2	7 ± 1	−32 ± 4
p-$^-O_2CC_6H_4CH_2CH_3$	3.4 ± 0.3		
p-$^-O_2CC_6H_4CH_3$	0.43 ± 0.04		
$(CH_3)_2CHOH^b$	0.067 ± 0.07	9 ± 1	−34 ± 4
Ru(bpy)$_2$(py)O^{2+} as Oxidant in CH_3CN at 24–25 °C			
$C_6H_5CH(CH_3)_2$	0.026 ± 0.003		
$C_6H_5CH_3$	0.00005		
$(CH_3)_2CHOH^b$	0.0087 ± 0.009	8 ± 1	−42 ± 5

[a] Ionic strength was maintained by the added buffer, NaH_2PO_4/Na_2HPO_4. [b] For the oxidation of $(CH_3)_2CHOH$ to $(CH_3)_2CO$, note ref 6.

$$H_2O + p\text{-}^-O_2CC_6H_4CH_2CH_3 + \text{Ru(trpy)(bpy)O}^{2+} \rightarrow p\text{-}^-O_2CC_6H_4C(OH)HCH_3 + \text{Ru(trpy)(bpy)}_2\text{OH}_2^{2+} \quad (8)$$

$$H_2O + p\text{-}^-O_2CC_6H_4CH_3 + \text{Ru(trpy)(bpy)O}^{2+} \rightarrow p\text{-}^-O_2CC_6H_4C(OH)H_2 + \text{Ru(trpy)(bpy)OH}_2^{2+} \quad (9)$$

In terms of substitutional effects, the point to note about the data in Table I is the increase in k_{IV} with increased substitution at the α-carbon.

Kinetics and Labeling Studies in Acetonitrile. The oxidations of isopropylbenzene (cumene) and toluene by Ru(bpy)$_2$(py)O^{2+} were studied with acetonitrile as solvent. In acetonitrile the spectral changes observed for the pyridyl complex show a similar pattern to those observed for the terpyridyl complex in water. In order to avoid interference from the acetonitrile solvolysis reaction that follows the redox steps (eq 7), we monitored the kinetics at 448 nm, which is an isosbestic point for Ru(trpy)(bpy)OH$_2^{2+}$ and Ru(trpy)(bpy)(CH$_3$CN)$^{2+}$.

A really striking difference is observed when oxidation rate constants in acetonitrile are compared with those in water (Table II). In acetonitrile the rate constant for oxidation of cumene has decreased by a factor of 500 and the rate constant for oxidation of toluene has fallen by a factor of at least 1000 compared to the related carboxylate oxidations in water (Table II). On the basis of observed substitutent effects in related reactions, the observed changes are greater by a factor of ~100 than might have been predicted for the substitution of hydrogen by a carboxylate at the position para to the alkyl group.[12] The oxidants used in the two media, Ru(trpy)(bpy)O^{2+} in water and Ru(bpy)$_2$(py)O^{2+} in acetonitrile, are different, but with 2-propanol as substrate, the

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(11) Simmons, M., unpublished results.

(12) (a) March, J. "Advanced Organic Chemistry"; McGraw-Hill: New York, 1977. (b) Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191. (c) Chapman, N. B.; Shorter, J., Ed. "Advances in Linear Free Energy Relationships"; Plenum Press: London, 1972.

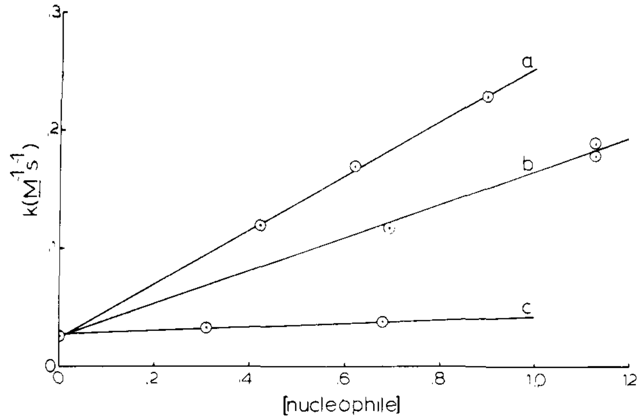


Figure 3. Variation of observed rate constants at 24.3 °C for the oxidation of isopropylbenzene by $Ru(bpy)_2(py)O^{2+}$ in acetonitrile plotted as a function of added nucleophile concentration: (a) water, (b) *tert*-butyl alcohol, (c) lithium bromide.

rate decrease in acetonitrile is only a factor of ~10 rather than 10^3. The rate enhancement in water indicated that solvent could play a very important role in these reactions.

The suggested importance of water led to attempts to establish the role of the solvent and of other nucleophiles on the kinetics of the reaction and to establish if the O atom involved in the oxidation came from the oxidant or from solvent. A batch oxidation of isopropylbenzene by $Ru(bpy)_2(py)O^{2+}$ was carried out in acetonitrile, and a ^1H NMR spectrum of the product solution was obtained. The spectrum was consistent with a single organic product, but it was not 2-phenyl-2-propanol, as shown by a comparison with the ^1H NMR spectrum of an authentic sample of the latter.

In the attempt to ascertain the role of water and of other added nucleophiles, kinetic experiments were performed in acetonitrile in which a fixed concentration of isopropylbenzene (cumene) was oxidized by $Ru(bpy)_2pyO_2^+$ in the presence of varying concentrations of the inert nucleophiles water, *tert*-butyl alcohol, and bromide ion. Figure 3 shows plots of the data obtained for the three nucleophiles. It should be appreciated that experiments of this kind are somewhat limited because of the reactivity of Ru(IV) toward many possible nucleophiles.

For facilitation of comparisons, rate constant and related data are collected in Table II for the oxidations in water and in acetonitrile. Data obtained earlier for the oxidation of 2-propanol are also included in Table II in order to broaden the comparisons.

Discussion

Spectral studies indicate that the reduction of $Ru(trpy)(bpy)O^{2+}$ by 4-isopropylbenzoate anion in water occurs in two and possibly three stages. The initial stage is the net reduction of Ru(IV) to Ru(III), as depicted in eq 4–6. The next stage of the reaction still involves Ru(IV), but the Ru(IV) is formed by disproportionation of Ru(III) into Ru(IV) and Ru(II). In the oxidation of 2-propanol by Ru(IV) studied earlier,[6] the second stage is followed by a third stage, where the intrinsic oxidation of 2-propanol by $Ru(trpy)(bpy)OH^{2+}$ is the dominant reaction. In the current work, the intrinsic reaction between the aromatic anion and Ru(III) is much slower than the oxidation by Ru(IV), and there is no real evidence for the expected third stage of the reaction. From our data it is only possible to place an upper limit of k_{III} and with the assumption that the Ru(III) reaction is first order in both Ru(III) and in substrate, $k_{III} < 10^{-4}\ M^{-1}\ s^{-1}$ (24–44 °C).

Oxidation Mechanism. Using the available results it is possible to reach some reasonable conclusions about the mechanism of oxidation of aromatic hydrocarbons by the Ru(IV) complexes. Under our pH conditions the carboxylate anions $ArCO_2^-$ are the dominant form of the aromatic hydrocarbons in water. The second-order kinetics and apparent lack of a pH effect up to pH 8.9 lead to the conclusion that the reaction occurs between Ru(IV) and $ArCO_2^-$. If a prior association were to occur via the carboxylate end of the substrate via ion pair (eq 10) or actual complex formation (eq 11), it would appear as an ionic strength dependence

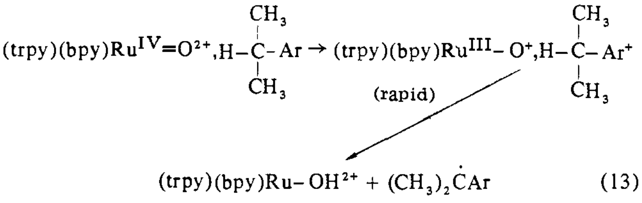
$$(trpy)(bpy)Ru{=}O^{2+} + {}^{-}O_2CAr \overset{K}{\rightleftharpoons} (trpy)(bpy)RuO^{2+},{}^{-}O_2CAr \quad (10)$$

$$(trpy)(bpy)Ru{=}O^{2+} + {}^{-}O_2CAr \rightleftharpoons (trpy)(bpy)Ru(O)[OC(O)Ar]^{+} \quad (11)$$

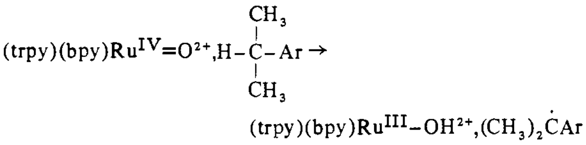
in the observed rate constants since k_{obsd} includes the properties of the preequilibrium. In fact, k_{IV} is independent of ionic strength (Table I). The site of approach of the oxidant on the substrate must be at the hydrocarbon end of the molecule. Since there is no binding site at that end of the molecule, the preassociation step must involve formation of a weak association complex rather than an intermediate, as shown in eq 12.

$$(trpy)(bpy)Ru{=}O^{2+} + p\text{-}RC_6H_4CO_2^- \overset{K'}{\rightleftharpoons} (trpy)(bpy)Ry{=}O^{2+}, p\text{-}RC_6H_4CO_2^- \quad (12)$$

The redox step follows association complex formation. It could involve either one- or two-electron transfer. In the case of one-electron transfer there are two possible limiting mechanisms, outer-sphere electron transfer followed by rapid proton transfer (eq 13) or H atom (H^+-coupled electron transfer, eq 14). The



$$(trpy)(bpy)Ru^{IV}{=}O^{2+},H{-}C(CH_3)_2{-}Ar \rightarrow (trpy)(bpy)Ru^{III}{-}O^{+},H{-}C(CH_3)_2{-}Ar^{+} \xrightarrow{\text{(rapid)}} (trpy)(bpy)Ru{-}OH^{2+} + (CH_3)_2\dot{C}Ar \quad (13)$$



$$(trpy)(bpy)Ru^{IV}{=}O^{2+},H{-}C(CH_3)_2{-}Ar \rightarrow (trpy)(bpy)Ru^{III}{-}OH^{2+},(CH_3)_2\dot{C}Ar \quad (14)$$

reactions in eq 13, 14 would be followed by rapid one-electron oxidation of the organic radicals by Ru(III) or Ru(IV).

However, the available evidence suggests that the mechanism involves a concerted, two-electron step involving hydride transfer. From the data in Table I there is no observed dependence of K_{IV} on the prersence or absence of O_2. As observed in the one-electron oxidation of 2-propanol by $Ru(trpy)(bpy)OH^{2+}$,[6] capture of a radical intermediate by O_2 would have the effect of changing the observed value of k_{IV} by affecting the stoichiometry in eq 3. The observation is consistent with a two-electron step but does not rule out an initial one-electron step followed by a second, rapid, one-electron transfer before the radical can separate in solution (e.g., eq 14 followed by eq 15).

$$\begin{aligned}(trpy)(bpy)Ru{-}OH^{2+},Ar\dot{C}(CH_3)_2 &\rightarrow (trpy)(bpy)RuOH^{2+} + Ar\overset{+}{C}(CH_3)_2\\ &\xrightarrow{+H_2O} (trpy)(bpy)RuOH_2^{2+} + ArC(OH)(CH_3)_2\end{aligned} \quad (15)$$

One-electron steps suffer from the instability of the initial product. For example, from estimated redox potentials, $\Delta G \sim +32$ kcal/mol for the reaction in eq 16.[5,11,13,14]

$$Ru(trpy)(bpy)O^{2+} + p\text{-}{}^{-}O_2C_6H_4CH(CH_3)_2 \rightarrow Ru(trpy)(bpy)O^{+} + p\text{-}{}^{-}O_2C_6H_4CH(CH_3)_2^{+\cdot} \quad (16)$$

Using this value as the minimum value for $\Delta G^{\ddagger}$ and $K' = 1$ (eq 12) gives $kK' = (k_BT/h)\exp{-\Delta G^{\ddagger}/RT} = 2 \times 10^{11}\ M^{-1}\ s^{-1}$,

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(13) Fleischmann, M.; Pletcher, D. *Tetrahedron Lett.* **1968**, 6255.

(14) Latimer, W. M. "Oxidation Potentials" 2nd ed.; Prentice-Hall: New York, 1962.

which is many orders of magnitude below the observed value for k_{IV}. The increase in k_{IV} with increasing alkyl substituents is certainly consistent with a buildup of positive charge at the α-carbon atom during the redox step but is also the order expected, for example, for a H atom transfer step on the basis of the stability of the resulting radicals.[12a]

However, there is other, very clear, evidence that points to a two-electron step in the oxidation of the aromatic hydrocarbons. The oxidations that have been studied stoichiometrically, eq 1–3, give quantitative yields of the expected two-, four-, or six-electron oxidation products, within experimental error. There is no evidence, for example, for radical coupling products. Also worth considering are the observations that k_{IV} is dramatically dependent on solvent when related reactions in acetonitrile and water are compared (Table II) and that added nucleophiles appear in the rate law in acetonitrile (Figure 3). Both observations are consistent with a hydride transfer mechanism in which the loss of the hydride group and buildup of positive charge are compensated for by electron pair donation from the added nucleophile to the central carbon atom during the oxidation. It is hard to reconcile such observations on the basis of one-electron steps.

The observation that the rate constant ratio for oxidation of $p\text{-}^{-}O_2CC_6H_4CH(CH_3)_2$ by $Ru(trpy)(bpy)O^{2+}$ compared to $Ru(trpy)(bpy)OH^{2+}$ is large, $k_{IV}/k_{III} > 10^5$, must also be considered. In 2-propanol, where the Ru(IV) oxidation involves a two-electron step and the Ru(III) oxidation a one-electron step, the ratio is smaller, $k_{IV}/k_{III} = 670$. Oxidations by Ru(III) must occur by one-electron steps. If a low-lying one-electron step exists for Ru(IV), it is considerably slower than the two-electron step that is actually observed. It can be inferred from the observed rate constant ratio for 2-propanol that for a one-electron step for Ru(IV), $k_{IV}(\text{1-electron})/k_{III} \leq 70$. A relatively small discrimination between $Ru(trpy)(bpy)O^{2+}$ and $Ru(trpy)(bpy)OH^{2+}$ in terms of one-electron steps is expected, given the similarities in the one-electron redox potentials, $E_{1/2}(Ru^{IV/III}) - E_{1/2}(Ru^{III/II}) = 0.14$ V, and in the properties of the two oxidants. It is hardly consistent with the ratio $k_{IV}/k_{III} > 10^5$ obtained for the aromatic hydrocarbons. As noted below, there is also a clear similarity in the pattern of activation parameters between the 2-propanol and 4-isopropylbenzoate anion oxidations, which is consistent with related mechanisms for the two cases.

Details of the Redox Step. The weight of available evidence supports the view that the oxidation of aromatic hydrocarbons by Ru(IV) occurs via a two-electron step. The same conclusion was reached earlier for the oxidation of 2-propanol, and it is of some interest to compare the two types of reactions. There are clear similarities between the reactions including the following: similar rate laws, absence of a pH effect if over a narrow pH range, absence of an ionic strength dependence, and the similarities in activation parameters—small $\Delta H^{\ddagger}$ values and large negative $\Delta S^{\ddagger}$ values (Table II). In fact, one of the most extraordinary features of the data in Table II is the fact that the aromatic hydrocarbons are *more reactive* by a considerable degree than is 2-propanol. This represents a striking change from the usual pattern of reactivity for most oxidants. It is unfortunate that we have not been able to acquire H/D kinetic isotope effect data for the aromatic oxidations. For 2-propanol $k_H/k_D = 18 \pm 3$, with the majority of the effect (5–6) coming from substitution of D for H at the α-C–H bond.

Even though there are similarities, there are also clear differences between the two types of reactions. In the case of the alcohol, the substrate already contains the oxygen atom demanded by the stoichiometry $(CH_3)_2CHOH \rightarrow (CH_3)_2CO$. Labeling experiments have shown that O atom transfer does *not* occur in the 2-propanol to acetone oxidation. For the aromatic hydrocarbons the reaction stoichiometry includes an oxygen atom demand, e.g., $p\text{-}^{-}O_2CC_6H_4CH(CH_3)_2 \rightarrow p\text{-}^{-}O_2CC_6H_4C(OH)(CH_3)_2$, which must be satisfied by either the solvent or the oxidant. From the hydrazine quenching experiment described above for the oxidation of isopropylbenzene by Ru(IV) and the fact that $C_6H_5C(OH)(CH_3)_2$ is *not* the product of the oxidation, O atom transfer does not occur to a significant extent in acetonitrile. However, from the rate constant data in Table II and the effects of added nucleophiles shown in Figure 3, it is clear that the solvent or an added nucleophile plays a major role in the reaction. This role is more profound than simply providing an electron-pair scavenger for a carbocation once formed. When the oxidation of 2-propanol by $Ru(trpy)(bpy)O^{2+}$ in water with oxidation by $Ru(bpy)_2(py)O^{2+}$ in acetonitrile is compared, there is a rate decrease of 8. When the ratios of $p\text{-}^{-}O_2CC_6H_4CH(CH_3)_2$ with $C_6H_5CH(CH_3)_2$ and $p\text{-}^{-}O_2CC_6H_4CH_3$ with $C_6H_5CH_3$ are compared, they are ~500 and >900, as noted previously. In acetonitrile, the added nucleophiles H_2O, *tert*-butyl alcohol, or Br^- enter the rate directly through rate terms of the form $k[PhCH(CH_3)_2][Ru(bpy)_2(py)O^{2+}][\text{nucleophile}]$, with $k_{H_2O} = 2.5$, $k_{t\text{-}BuOH} = 1.7$, $k_{Br^-} \sim 0.4\ M^{-2}\ s^{-1}$ at 24.3 °C. The variations in these k values and their appearance in the rate law show a direct intervention of the added nucleophiles in the activation process. A detailed interpretation would have to include a preequilibrium step involving association between the substrate, Ru(IV), and the added nucleophile:

$$Ru(trpy)(bpy)O^{2+},Ar\text{–}R + H_2O \rightleftharpoons Ru(trpy)(bpy)O^{2+},Ar\text{–}R,H_2O$$

Nonetheless, it is clear that the added nucleophiles are directly involved in the reactions. A reasonable view of their role is as "assisting" in the loss of the hydride ion. An alternate and equivalent view would be that charge neutralization at the central carbon atom occurs by electron-pair donation as hydride transfer occurs to $Ru^{IV}{=}O$.

Although not testable kinetically, the same situation no doubt exists in the pure solvents. It is interesting to note that in acetonitrile when the added water concentration is 1 M, oxidation of $C_6H_5CH(CH_3)_2$ by $Ru(bpy)_2(py)O^{2+}$ is within a factor of ~2 of the rate constant for oxidation of $p\text{-}^{-}O_2CC_6H_4CH(CH_3)_2$ by $Ru(trpy)(bpy)O^{2+}$ in water. From the kinetics data and Figure 3, acetonitrile is clearly the worst of the nucleophiles studied. Acetonitrile is known to act as a trap toward carbocations,[15] and we presume that it is also involved in assisting the hydride transfer. Although we have not made a positive identification, a reasonable possibility is that the organic product in acetonitrile is the acetamide arising from hydrolysis of the initial acetonitrile–carbocation adduct by trace water in the solution

$$C_6H_5CH(CH_3)_2 \xrightarrow[+CH_3CN]{-H:^-} C_6H_5C(CH_3)_2NCCH_3^+ \xrightarrow[-H^+]{+H_2O} C_6H_5C(CH_3)_2NHC(O)CH_3$$

Conclusions and Comments

In eq 17 and 18 are shown schematic attempts to illustrate the details of the redox steps in the oxidations of 2-propanol and the aromatic hydrocarbons by Ru(IV). For the aromatic hydrocarbons, cumene is used as the example and the added nucleophile shown is water. Given the small values of $\Delta H^{\ddagger}$ and large negative $\Delta S^{\ddagger}$ values, important features of both reactions probably include the following: (1) the critical involvement of α-C—H and Ru=O stretching vibrations; (2) strong electron-vibrational coupling along the appropriate energy surface, induced by strong electronic wave-function mixing between the Ru=O group and appropriate molecular orbitals of the substrate—in this overlap the O atom functions as a lead-in atom or bridge[16] between the substrate and the Ru(IV) acceptor site; (3) specific orientational demands, imposed by alignment of the $Ru{=}O^{2+}$ and α-C—H groups, and in the aromatic oxidations by the involvement of the nucleophile. In addition, both reactions involve "template" mechanisms in which the bound oxo group is *not* transferred, and this has important implications for applications in catalysis.

The rate enhancements for the aromatic hydrocarbons compared to 2-propanol are notable. From available thermochemical data, ΔG values for the initial two-electron step giving $Ru(trpy)(bpy)OH^+$ and $(CH_3)_2C{=}OH^+$ or $C_6H_5C(OH_2)(CH_3)_2^+$

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(15) Eberson, L.; Nuberg, K. *Tetrahedron Lett.* 1966, 2389.
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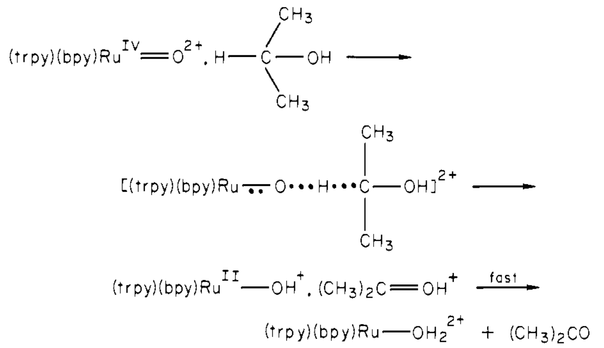
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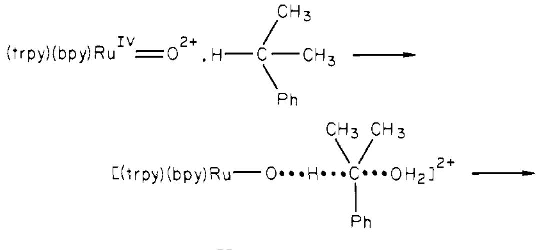
(18)

in water are within a few kilocalories of each other within the range −20 to −25 kcal/mol.[9b] Given the similarity in ΔG between the two reactions, if the same σ-C–H "lead-in" pathway exists for both substrates, a deciding factor in determining relative rates could be the electronic influence of the adjacent phenyl group. On an energy surface dominated by hydride transfer and the buildup of positive charge, electronic stabilization by the adjacent phenyl group could play a major role in determining rate constants. The importance of an adjacent aryl group is easily seen synthetically, as shown, for example, by the selective α-carbon oxidation of the ethylbenzene derivative in eq 2.

Given the proven catalytic capabilities of the $Ru(trpy)(bpy)O^{2+}$, $Ru(trpy)(bpy)OH_2^{2+}$ couple, the rate information obtained here has important implications for synthesis, and the following points are worth noting: (1) Rate discriminations based on functional group types that point to a clear element of oxidative selectivity are beginning to emerge. (2) For substrates like aromatic hydrocarbons, where groups must be added as a consequence of oxidation, strong solvent or added nucleophile effects are to be expected. (3) In weakly nucleophilic solvents the addition of added nucleophiles could lead to oxidatively catalytic pathways like

$$ArCHR_2 + D \xrightarrow{-H:^-} ArC(D^+)R_2$$

and a general route for the direct oxidative insertion of the added group D into the substrate.

Acknowledgement is made to the National Science Foundation under Grant CHE-8002433 for support of this research.

Registry No. p-$NaO_2CC_6H_4CH(CH_3)_2$, 1009-60-5; p-$NaO_2CC_6H_4CH_2CH_3$, 2046-83-5; p-$NaO_2CC_6H_4CH_3$, 17264-54-9; $C_6H_5CH(CH_3)_2$, 98-82-8; $C_6H_5CH_3$, 108-88-3; $Ru(trpy)(bpy)O^{2+}$, 73836-44-9.

Oxidation of Hydrocarbons. 11. Kinetics and Mechanism of the Reaction between Methyl (*E*)-Cinnamate and Quaternary Ammonium Permanganates

Donald G. Lee* and Keith C. Brown

Contribution from the Department of Chemistry, The University of Regina, Regina, Saskatchewan, Canada S4S 0A2. *Received December 21, 1981*

Abstract: A study of the reaction of methyl (*E*)-cinnamate with quaternary ammonium permanganates in methylene chloride solutions has been completed. The rate of reaction is fastest for those ions which permit the interionic distance in the quaternary ammonium ion pair to be minimized. The Hammett ρ value for the reaction is 0.95 at 20 °C, and an inverse secondary deuterium isotope effect is observed at the β-position but not at the α-position. The sign of the ρ value for this reaction is in direct contrast to the reported value (−0.6) for the oxidation of alkyl vinyl ethers in aqueous dioxane solutions. On the other hand, the fact that the activation parameters for the two reactions are almost identical suggests that the reaction mechanisms cannot be widely divergent. An attempt has been made to visualize a mechanism in which the reactions can proceed through similar intermediates but via either an electron-rich or an electron-deficient transition state depending on the demands of the substituents. The apparent change in mechanism is considered to be simply a reflection of nature's ability to find the lowest energy surface between two points.

Introduction

The mechanism of the reaction between carbon–carbon double bonds and permanganate ion has been a subject of interest for nearly one century.[1] Wagner,[2] noting that the oxidation of unsaturated dicarboxylic acids by basic permanganate solutions resulted in the syn addition of two hydroxyl groups to the double bond, suggested that the intermediate in the reaction could be a cyclic manganate(V) diester, **1**, which would undergo hydrolysis with liberation of a diol in aqueous alkaline solutions (eq 1).

In more modern times Wiberg and Saegebarth[3] substantiated this mechanism by showing, with the aid of isotopic tracers, that

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[1] Stewart, R. "Oxidation Mechanisms"; W. A. Benjamin: New York, 1964; p 62.

[2] Wagner, G. *J. Russ. Phys. Chem. Soc.* **1895**, *27*, 219.

[3] Wiberg, K. B.; Saegebarth, K. A. *J. Am. Chem. Soc.* **1957**, *79*, 2822.

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