An analytically pure sample was obtained by preparative GC: bp 108–110 °C (45 mm); IR (CHCl$_3$) 3260, 2975, 1385, 1264, 1077, 1010 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.05 (d, 12 H), 3.17 (m, 2 H), 3.82 (s, 4 H), 5.35 (br s, 2 H, exchanged with D$_2$O); ^{13}C NMR (CDCl$_3$) δ 71.8, 50.5, 19.0; mass spectrum, m/e (relative intensity) 176 (0.30, M$^+$), 161 (16), 104 (28), 102 (77), 76 (6.7), 75 (11), 72 (46), 60 (29), 59 (6.9), 58 (100), 56 (21). Anal. Calcd for C$_8$H$_{20}$N$_2$O$_2$: C, 54.52; H, 11.44; N, 15.89. Found: C, 54.20; H, 11.53; N, 15.51.

N,N'-Dimethyl-1,2-bis(aminooxy)ethane (6). To a stirred solution of 8 (4.47 g, 38.5 mmol) and borane–pyridine complex (25.9 mL, 0.257 mol) in EtOH (100 mL) maintained at less than 5 °C was added 20% ethanolic HCl (210 mL) dropwise over a 1.5-h period under N$_2$. After addition was complete, the mixture was stirred for 24 h at room temperature. The mixture was made basic with neat Na$_2$CO$_3$ and then filtered. The solvent was removed under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$ (100 mL) and dried (MgSO$_4$). The solvent was removed under reduced pressure to give a liquid residue that was vacuum distilled to give 1.49 g of a colorless liquid. ^{1}H NMR showed the liquid to be a mixture of 6 (23% yield) and other unidentified products. Compound 6 was isolated by preparative GC: bp 80–84 °C (50 mm); IR (CHCl$_3$) 3290, 2960, 1470, 1073, 964 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.70 (s, 6 H), 3.82 (s, 4 H), 5.56 (br s, 2 H, exchanged with D$_2$O); ^{13}C NMR (CDCl$_3$) δ 71.7, 39.2; mass spectrum, m/e (relative intensity) 120 (0.17, M$^+$), 90 (6.7), 89 (6.6), 75 (4.6), 74 (100), 73 (2.6), 72 (3.6), 62 (2.7), 61 (3.2), 60 (10), 58 (4.6). Anal. Calcd for C$_4$H$_{12}$N$_2$O$_2$: C, 39.99; H, 10.07; N, 23.31. Found: C, 39.84; H, 10.45; N, 23.52.

Acetone O,O'-1,2-Ethanediylbisoxime (7). Acetone (8.28 mL, 0.112 mol) was added dropwise to a stirred solution of 1,2-bis(aminooxy)ethane (5.16 g, 56.0 mmol) in H$_2$O (100 mL) at room temperature. The mixture was stirred for 7 h. The mixture was extracted with CH$_2$Cl$_2$ (5 × 100 mL). The extracts were dried (MgSO$_4$) and the solvent was removed under reduced pressure to give a crude yellow liquid. Vacuum distillation gave 8.83 g of 7 as a colorless liquid (92% yield): bp 99–100 °C (35 mm); IR (CHCl$_3$) 2990, 1650, 1371, 1076, 946 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.84 (s, 12 H), 4.17 (s, 4 H); ^{13}C NMR (CDCl$_3$) δ 154.9, 71.7, 21.8, 15.6; mass spectrum, m/e (relative intensity) 173 (0.99, M$^+$ + H), 172 (0.17, M$^+$), 117 (4.8), 116 (81), 100 (15), 74 (3.4), 73 (5.5), 70 (16), 57 (9.0), 56 (100), 55 (2.5), 54 (3.5).

Formaldehyde O,O'-1,2-Ethanediylbisoxime (8). Aqueous formaldehyde (37%, 7.6 mL, 94 mmol) was added dropwise to a stirred solution of 1,2-bis(aminooxy)ethane (4.33 g, 47.0 mmol) in CH$_2$Cl$_2$ (40 mL) at room temperature. The reaction was mildly exothermic. After stirring for 10 min, H$_2$O (15 mL) was added. The layers were separated and the aqueous layer was saturated with NaCl and extracted with CH$_2$Cl$_2$ (5 × 25 mL). The combined

extracts were dried (MgSO$_4$) and the solvent was removed under reduced pressure to give 4.5 g of 8 as a colorless liquid (82% yield): IR (CHCl$_3$) 2940, 1617, 1356, 1061, 957 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.28 (s, 4 H), 6.71 (AB quartet, J_{AB} = 8 Hz, ν_{AB} = 36 Hz, 4 H); ^{13}C NMR (CDCl$_3$) δ 137.6, 72.2; mass spectrum, m/e (relative intensity) 117 (0.55, M$^+$ + H), 116 (0.18, M$^+$), 91 (9.1), 89 (4.5), 88 (100), 72 (28), 71 (29), 70 (3.0), 61 (63), 59 (4.3), 58 (84).

Acetone O-[2-[(N-Isopropylamino)oxy]ethyl]oxime (15). To a stirred solution of 7 (1.16 g, 6.74 mmol), NaBH$_3$CN (565 mg, 8.99 mmol), and bromocresol green solution (few drops) in MeOH (20 mL) was added 2 N HCl/MeOH at room temperature to maintain the yellow color of the indicator. After 3 h of addition, the yellow color remained constant and the mixture was allowed to stir for 24 h. The solvent was removed under reduced pressure to give a residue that was dissolved in H$_2$O (10 mL). The pH was raised to >9 with 6 N KOH and the basic solution was extracted with CHCl$_3$ (5 × 30 mL). The extracts were dried (MgSO$_4$) and the solvent was removed under reduced pressure to give 968 mg of a colorless liquid that contained the desired monohydroxyl-amine monooxime 15 (33% yield) along with 5 and 7. Compound 15 was isolated by preparative TLC (silica gel, 1:2 cyclohexane/ethyl acetate). An analytically pure sample was obtained by preparative GC: IR (CHCl$_3$) 3260, 2980, 1650, 1373, 1078 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.04 (d, J = 7 Hz, 6 H), 1.36 (s, 6 H), 3.17 (sept, J = 7 Hz, 1 H), 3.37 (m, 2 H), 4.15 (m, 2 H), 5.27 (br s, 1 H, exchanged with D$_2$O); ^{13}C NMR (CDCl$_3$) δ 154.9, 73.1, 71.5, 51.5, 21.8, 20.0; mass spectrum, m/e (relative intensity) 174 (M$^+$, 0.09), 159 (2.2) 118 (2.4), 100 (18), 74 (8.0), 73 (12), 70 (23), 59 (3.1), 58 (18), 57 (7.9), 56 (100), 54 (4.8). Anal. Calcd for C$_8$H$_{18}$N$_2$O$_2$: C, 55.15; H, 10.41; N, 16.08. Found: C, 55.25; H, 10.62; N, 15.86.

Novel Electrocatalytic Procedure for the Oxidation of Alcohols, Aldehydes, Cyclic Ketones, and C–H Bonds Adjacent to Olefinic or Aromatic Groups

Mark S. Thompson, Wagner F. De Giovani, Bruce A. Moyer, and Thomas J. Meyer*

Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514

Received February 22, 1984

A novel electrocatalytic procedure is described for the oxidation of primary and secondary alcohols, cyclic ketones, and C–H bonds adjacent to aromatic or olefinic groups. The procedure involves the use of the Ru^{IV} oxidant [Ru(trpy)(bpy)(O)]$^{2+}$ (trpy is 2,2′,2″-terpyridine; bpy is 2,2′-bipyridine) in water at pH 6.8 or in dimethyl sulfone–water mixtures and is based on an electrochemical "shuttle" mechanism in which the Ru^{IV} complex is regenerated by electrochemical oxidation of [Ru^{II}(trpy)(bpy)(H$_2$O)]$^{2+}$.

Introduction

In principle, the use of electrolytic techniques for carrying out organic redox reactions has many appealing features.[1] In practice, complications can arise from high

overvoltages and an absence of selectivity. Both reactivity characteristics have their origins in the intrinsic properties of the electrode–solution interface. An alternate approach involves the use of homogeneous or surface-attached catalysts where the redox chemistry occurs at the catalyst and the role of the electrode is to provide a source of oxidizing or reducing equivalents at a controlled potential. An obvious advantage of this approach is that the reactivity

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characteristics of the electrocatalytic system are controlled by individual chemical sites whose reactivity properties can be studied separately and modified according to the demands of the reaction.

In other work it has been shown that polypyridyl complexes of ruthenium and osmium have an extensive redox chemistry based in part on higher oxidation states such as Ru(IV), e.g., $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ (bpy is 2,2'-bipyridine, py is pyridine) and Os(VI), e.g., $[Os(bpy)_2(O)_2]^{2+}$.[2,3] Complexes of this type have been shown to act as catalytic or stoichiometric reagents for the interconversion of nitrate and nitrite,[4] the oxidation of water to oxygen,[5] the interconversion of nitrite and ammonia,[6] and the oxidation of Cl^- to chlorine.[7] Mechanistic studies have suggested that the $Ru^{IV}{=}O$ group can function via a number of mechanistic pathways including O atom transfer,[4,8] hydride transfer,[9,10] and H atom transfer.[11]

Here we describe the use of the Ru(IV) complex $[Ru^{IV}(trpy)(bpy)(O)]^{2+}$ (trpy is 2,2',2''-terpyridine) as a catalyst for the electrocatalytic oxidation of alcohols, aldehydes, cyclic ketones, and C–H bonds adjacent to olefinic or aromatic groups. Part of this work has already appeared in a preliminary account[12a] and the reactivity characteristics of the Ru complexes have been described in a recent review article.[12c]

Experimental Section

Materials. Water was deionized and distilled from alkaline potassium permanganate. Toluene, isopropyl alcohol, and acetaldehyde were fractionally distilled immediately prior to use. *p*-isopropylbenzoic acid as obtained from Eastman Kodak Co. was impure and recrystallized twice from hot methanol/water. Ethanol used in oxidative experiments was Aaper "gold seal" and was used without purification. Deuterium oxide was 99.8% atom D and was obtained from the Alfa Ventron Chemical Co. All other materials, salts, and solvents were purchased as reagent grade chemicals and used without further purification.

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 stirred until it 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. UV–vis spectra were obtained in quartz cells on a Bausch & Lomb 210 UV or a Varian 634 spectrophotometer. The electrochemical apparatus used for coulometric experiments consisted of a PAR 173 Galvanostat/Potentiostat and a PAR 179 digital coulometer. The determination of hydrogen by gas chromatography was carried out by using a two foot column packed with alumina and cooled with a dry ice–isopropyl alcohol bath. IR spectra were obtained in sodium chloride solution cells

on a Beckman IR 4250 spectrophotometer. NMR measurements were made in a 5-mm tube on either a Varian XL100 or a Perkin-Elmer R24B spectrometer and resonances are reported vs. Me₄Si as an external standard.

Apparatus and General Techniques. The electrochemical cells used were of a standard three-compartment variety[13] or of a cylindrical, two-compartment design which has been described elsewhere.[12b] The working and auxiliary electrodes were made of platinum gauze connected to platinum wires. The reference electrode was a saturated sodium calomel electrode (SSCE). The electrolyses were carried out under a nitrogen atmosphere.

Aqueous solutions were used throughout and the temperature was held at 25 °C unless otherwise specified. A constant pH of 6.8 was maintained by using 0.1 M or 1 M 1:1 $HPO_4^{2-}/H_2PO_4^-$, 0.5 M. The buffer also served as electrolyte. Concentrations of $[Ru(trpy)(bpy)OH_2]^{2+}$ in the cell were typically millimolar and the total volume of the electrolysis solution was roughly 10 mL. Generally, the organic substrate was present in 10- to 1000-fold excess over the ruthenium complex. For water insoluble compounds such as toluene, a two-phase system was used in which a solubilizing agent (dimethyl sulfone) was added to enhance exchange between the aqueous and organic phases. Unless otherwise specified, the coulometric measurements and the analyses based on UV–vis and NMR measurements have an estimated uncertainty of ∼±10%.

The electrolyses were performed at a fixed applied potential of 0.8 V vs. the SSCE, which is sufficient to generate the Ru(IV) oxidant, $Ru(trpy)(bpy)O^{2+}$, from $Ru(trpy)(bpy)H_2O^{2+}$. At pH 7, the formal potential for the $Ru^{IV/II}$ couple, $Ru(trpy)(bpy)O^{2+}/Ru(trpy)(bpy)H_2O^{2+}$ is 0.56 V. In a typical experiment, a solution containing the buffer component and the substrate to be oxidized were added to the cell. A potential of 0.8 V was applied across the cell until a stable "background" current was reached. The ruthenium complex was added as $[Ru(trpy)(bpy)H_2O]^{2+}$ which led to catalytic currents typically in the range of 5–50 μamps. The electrolyses were continued to exhaustion or for a period long enough to obtain sufficient product for analysis. In some cases NMR analyses were made directly on the reaction solution. In other cases the product was isolated and analyzed in a separate step.

Catalyst Stability. After extended electrolyses (500 catalyst turnovers) of alcohols, aliphatic aldehydes, and crotonic acid an appreciable amount of a green material having λ_{max} ∼680–690 nm appears in the solution. The same material is observed to form if $[Ru(trpy)(bpy)O]^{2+}$ is allowed to stand in a solution of 1 M pH 6.8 phosphate buffer for several days in the absence of any substrate. By reduction of the green solution electrolytically at 0 V (vs. SCE), the broad band at 680–690 nm disappears and a new band appears at 481 nm. If this solution is allowed to stand for a day the absorption band at 481 nm becomes sharper and shifts to 477 nm, which is a visible absorption λ_{max} for $[Ru(trpy)(bpy)OH_2]^{2+}$. The electrolytic/stand cycle returns the catalyst to $[Ru(trpy)(bpy)OH_2]^{2+}$ in 90–100% yield based on the known extinction coefficients in the region 200–700 nm. From work on related systems, the green material is no doubt an oxo-bridged dimer. For example, the dimer, e.g., $[(bpy)_2(H_2O)Ru]_2O^{4+}$, is known and has been characterized structurally.[14b] Reduction of this formally Ru(III)–Ru(III) dimer in water at potentials below 0 V is known to occur via reduction of the Ru(III)–Ru(III) form to Ru(III)–Ru(II) followed by a breakdown in the dimeric structure to give the associated Ru(II) monomers.[14]

An additional catalyst loss step occurs to a noticeable extent in catalyzed oxidations involving a substrate in which a methyl group adjacent to a benzene ring is oxidized to a carboxylate group. For example, under our conditions, during an electrocatalytic run involving ∼1000 two-electron turnovers in the oxidation of *p*-toluate anion to terephthalate dianion, the catalytic current slowly falls and spectrophotometric studies show that the catalyst is converted into a product having a broad visible absorption band

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Table I. Results of Electrocatalytic Oxidations Based on Ru(trpy)(bpy)O²⁺ [a]

substrate (concn)	oxidative coulombs passed	products (% yield ±10%)	analysis method
2-propanol (2 mL/10 mL)	118	acetone (102%)	distillation, UV
ethanol (2 mL/10 mL)	464	acetaldehyde (14%)[b]	^{1}H NMR
		acetate ion (60%)	^{1}H NMR
acetaldehyde (1.5 mL/10 mL)	289	acetate ion (100%)	^{1}H NMR
sodium 4-methylbenzoate (207 mg/10 mL)[c]	618	terephthalate ion (100%)	^{1}H NMR of the acid following acidification and ether extraction
toluene (1 mL/10 mL)[d]	88	benzoate ion	IR and ^{1}H NMR following acidification and ether extraction
crotonic acid (236 mg/10 mL)[e] (*trans*-CH₃CH=CHCO₂H)	1036	fumarate ion (86%)	^{1}H NMR
Na⁺ p-⁻O₂CC₆H₄CH(CH₃)₂	122	p-⁻O₂CC₆H₄C(OH)(CH₃)₂ (87%)	^{1}H NMR
Na⁺ p-⁻O₂CC₆H₄CH₂CH₃ (213 mg/10 mL)	407	p-⁻O₂CC₆H₄C(O)CH₃ (81%)	^{1}H NMR

[a] At room temperature, pH 6.8 (0.1 M in HPO₄²⁻/H₂PO₄⁻ buffer), and ~1 mM in catalyst unless otherwise noted. [b] The major loss mechanism appears to be via vaporization of acetaldehyde during the extended (~14 h) electrolysis period. [c] At 50 °C. [d] In a solution containing 50% by volume dimethyl sulfone as a solubilizing agent. The product was not determined quantitatively. [e] At 30 °C.

with λ_{max} ~515 nm. A small amount of the oxo-bridged dimer mentioned above was also formed.

Kinetics. All kinetic runs were carried out at 25.0 ± 0.1 °C at μ = 0.32 (0.1 M Li₂SO₄). The reactions were followed spectrophotometrically by using either conventional mixing techniques or a stopped-flow spectrometer by observing spectral changes with time.[9,10] Spectral monitoring is convenient because [Ru(trpy)(bpy)O]²⁺ is transparent in the visible while [Ru^{III}(trpy)(bpy)OH]²⁺ and [Ru^{II}(trpy)(bpy)H₂O]²⁺ have characteristic absorption bands in the visible, λ_{max} 380 nm and 477 nm, respectively.[12,15] The reactions were followed at 406 nm which is an isosbestic point for [Ru(trpy)(bpy)OH]²⁺ and [Ru(trpy)(bpy)OH₂]²⁺ since at that wavelength the initial, rapid Ru(IV) → Ru(III) step can be studied without interference from the subsequent slower oxidation of the substrate by [Ru(trpy)(bpy)OH]²⁺. In all cases oxidation by Ru(III) was considerably slower than oxidation by Ru(IV). We have not acquired rate constant data for the Ru(III) oxidations.

Cyclohexanol. Oxidation of cyclohexanol by [Ru(trpy)(bpy)O]²⁺ was studied under pseudo-first-order conditions at six different concentrations in the range 1.0×10^{-2} to 7.0×10^{-2} M and at three different pH values—4.7, 6.8, and 8.4—by using acetate, H₂PO₄⁻/HPO₄²⁻, and bicarbonate buffers, respectively. Plots of ln ΔA vs. t, where ΔA is the absorbance change between time ∞, and time t, were linear showing first-order kinetics in Ru(IV). The dependence of k_{obsd} on the concentration of cyclohexanol was linear showing first-order kinetics in cyclohexanol. k_{obsd} was independent of pH in the range 4.7–8.4 and of the concentration of Ru(IV). The second-order rate constant for the oxidation by Ru(IV) was k = $(6.3 \pm 0.3) \times 10^{-2}$ M⁻¹ s⁻¹.

Cyclohexanone. The kinetics of the oxidation of cyclohexanone by Ru(IV) were first order in cyclohexanone, first order in Ru(IV) and independent of pH in the range pH 4.7–6.8. The second-order rate constant was k = $(2.1 \pm 0.2) \times 10^{-2}$ M⁻¹ s⁻¹.

2-Hydroxycyclohexanone. The kinetics were studied only at pH 6.7. The rate law was first order in 2-hydroxycyclohexanone and first order in Ru(IV). Assuming the rate law to be independent of pH gave k = (11.3 ± 1.0) M⁻¹ s⁻¹.

1,2-Cyclohexanedione. The kinetics were studied at pH 6.7 by using a stopped-flow spectrometer. The reaction was first order in both substrate and Ru(IV) and k = (1170 ± 27) M⁻¹ s⁻¹, assuming that the reaction is independent of pH.

Gas Chromatography. Experiments based on the determination of products using gas chromatography were carried out by using a Gow Mac Series 550 dual column GC with a thermal conductivity detector. The carrier gas was helium and the column material, 110 in., was 10% Carbowax 20M Chrom W 60/80. Unless otherwise specified, the column temperature was 90 °C, the injector and detector temperatures 250 °C, and the rate of flow of the carrier gas was 20 mL/min.
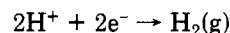
Results

The conditions for the electrocatalytic oxidation of isopropyl alcohol are mentioned in detail below. For the

remaining electrolyses, the same conditions were used unless otherwise noted.

Isopropyl Alcohol. The mechanistic details of the oxidation of isopropyl alcohol by [Ru^{IV}(trpy)(bpy)O]²⁺ and by [Ru^{III}(trpy)(bpy)OH]²⁺ have been reported.[9] Electrolysis of an aqueous solution which was 0.1 M in isopropyl alcohol, 1 mM in [Ru(trpy)(bpy)H₂O]²⁺, and 0.1 M in HPO₄²⁻/H₂PO₄⁻ buffer was carried out at 0.8 V (vs. SCE). Under our conditions, steady-state catalytic currents of 10 μA were obtained by using the cylindrical cell design mentioned above. The electrolysis was continued until 118 coulombs had passed as shown by integrating the area under the current–time curve. The amount of acetone formed (102 ± 10%) was determined by distillation and UV analysis, λ_{max} 265 nm ϵ = 16.4 M⁻¹ cm⁻¹.[16]

In a second experiment, the oxidation was extended to 1005 coulombs and the amount of acetone determined in situ by ^{1}H NMR. A singlet was observed at 2.05 ppm (vs. external Me₄Si) for the methyl protons of acetone, and peak area measurements relative to sodium terephthalate added as an internal standard gave a yield of 88 ± 10%.

Hydrogen Evolution from the Auxiliary Electrode. A third experiment was carried out under the same conditions. The amount of H₂ (by GC) produced (51.0 mL) corresponded stoichiometrically (99.6%) to the following equation:

$$2H^+ + 2e^- \rightarrow H_2(g)$$

Other Substrates. The electrocatalytic oxidations of a series of organic compounds were carried out by using the procedure described above for isopropyl alcohol. The results are summarized in Table I.

Unreactive Substrates. A number of compounds were found to be unreactive in the sense that catalytic currents were not significantly greater than background currents. The list of "unreactive" compounds included the benzoate, acetate, and fumarate anions as well as *tert*-butyl alcohol, naphthalene, acetone, alkanes, terphthalate, *trans*-stilbene, and ethylene coordinated to silver ion. However, the mild conditions—pH 6.8, 25 °C—used in the electrolyses should be recalled since at higher temperatures or in different media, e.g., acetone is reactive at pH 10, the oxidation of some of these compounds may become accessible to the electrocatalytic procedure.

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Cyclohexanol. The electrocatalytic oxidation of cyclohexanol was studied in detail because of the possibility of exploring an extended series of redox steps based on a single compound and because of the possible development of an electrocatalytic procedure for the conversion of cyclohexanol to adipic acid,

$$3H_2O + C_6H_{11}OH \rightarrow O_2C(CH_2)_4CO_2H + 8H^+ + 8e^-$$
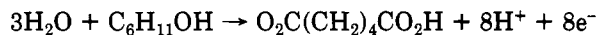
A series of electrocatalytic oxidations were carried out based on cyclohexanol and its successive oxidation products. The conditions for the electrolyses were as described above with the catalyst concentration, $[Ru(trpy)(bpy)H_2O]^{2+}$, at $1-2 \times 10^{-3}$ M in 10 mL of a 1 M $H_2PO_4^-/HPO_4^{2-}$ buffer solution.

(A) Cyclohexanol. An electrolysis solution (10 mL) 0.5 M in cyclohexanol (4.8 mM) was oxidized as previously described until 98.6 coulombs had been passed. The contents of the solution were analyzed by GC where the order of elution was: cyclohexanone, cyclohexanol, 2-hydroxycyclohexanone, 1,2-cyclohexanedione. When *p*-xylene was used as an internal standard, the composition of products in the electrolyzed solution was
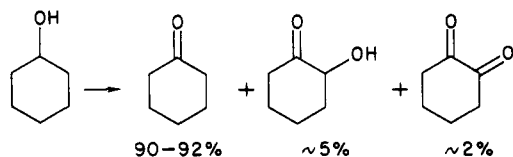
The calculation of % yields was based on total coulombs passed by taking into account the number of equivalents needed for each of the products which are 2, 4, and 6 for the products as shown above.

(B) Cyclohexanone. A solution 1 M in cyclohexanone was electrolyzed until 474 coulombs had passed to give the product distribution shown below, which was determined by GC using cyclohexanol as an internal standard.
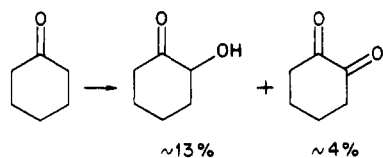

Additional, unknown products were observed in the GC which appeared to represent ~4% of the oxidized cyclohexanone. As noted below, the reason for the low stoichiometric balance arises from further oxidation of 1,2-cyclohexanedione to give products which are not eluted from the GC under our conditions.

(C) 1,2-Cyclohexanedione. A 12-mL solution 0.5 M in $H_2PO_4^-$ and in HPO_4^- which was 3.7×10^{-2} M in 1,2-cyclohexanedione and 1.15×10^{-3} M in $[Ru(trpy)(bpy)H_2O]^{2+}$ was electrolyzed until 48.4 coulombs had passed corresponding to 56% of the initial 1,2-cyclohexanedione, assuming that a two-electron oxidation had occurred or 23% if a four-electron oxidation had occurred. Catalytic currents were noticeably higher for 1,2-cyclohexanedione than for cyclohexanol (×6) or for cyclohexanone (×18) even though the substrate concentration was lower by 10. After the electrolysis was complete a few clear crystals had appeared in the electrolysis solution (mp 160 °C). The electrolysis solution was acidified with 0.1 M HCl and extracted with ether for 24–48 h. The ether extract was treated with diazomethane and the failure to observe a fading in the yellow color of the diazomethane even when present in slight amounts suggested the absence of carboxylic acid groups. No evidence was obtained for the diesters of adipic or glutaric acids, $HO_2C(CH_2)_3CO_2H$, by GC.[18] Evaporation of the ether solution gave a gluelike

material whose infrared spectrum (KBr pellets) was not revealing. ^1H NMR spectra of the extract were obtained both in D_2O and in Me_2SO-d_6. Interpretation of the spectra were complicated by the presence of the starting material which at room temperature in water has been reported to exist predominantly as the hydrate (I) (60%)
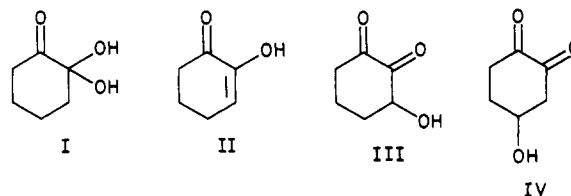

and enol (II) (40%) forms.[19] Additional resonances clearly appear in the δ 1–3 region. Our failure to observe the expected OH resonance for III or IV in Me_2SO-d_6[19] suggests that neither is a major product. Comparative integrations of the vinylic triplet for II at 5.9 to the ring C–H resonances at $\sim$C 1–3 show that CH groups are lost in the oxidation product. The 1,2,3-triketone V is known[18] and
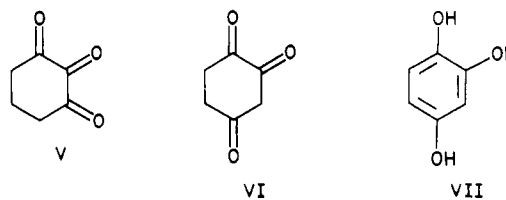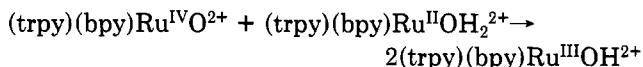

appears *not* to be the product based on a comparison of melting points. It is conceivable that the product is the 1,2,4-triketone VI or its hydrated or enolic forms. We have been unable to find reference to the 1,2,4 triketone or the tautomeric phenolic form VII in the literature.
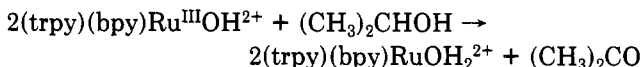
Kinetics. The results of kinetic and mechanistic studies on the oxidation of 2-propanol[9] and a series of aromatic hydrocarbons[10] by $[Ru^{IV}(trpy)(bpy)O]^{2+}$ have been reported. For 2-propanol, for example, the overall mechanism appears to involve an initial two-electron oxidation step,

$$(trpy)(bpy)RuO^{2+} + (CH_3)_2CHOH \rightarrow$$
$$(trpy)(bpy)RuOH_2^{2+} + (CH_3)_2CO$$
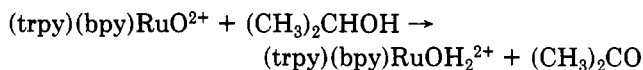
followed by rapid comproportionation.

$$(trpy)(bpy)Ru^{IV}O^{2+} + (trpy)(bpy)Ru^{II}OH_2^{2+} \rightarrow$$
$$2(trpy)(bpy)Ru^{III}OH^{2+}$$

Oxidation of 2-propanol by $[Ru^{III}(trpy)(bpy)OH]^{2+}$, is far slower (1/400).

$$2(trpy)(bpy)Ru^{III}OH^{2+} + (CH_3)_2CHOH \rightarrow$$
$$2(trpy)(bpy)RuOH_2^{2+} + (CH_3)_2CO$$

Rate constant data for the oxidations by $Ru(trpy)(bpy)O^{2+}$ of the components that appear in the cyclohexanol oxidation were obtained. The reactions were all first order in Ru(IV) and in organic, and where studied, were independent of pH. The data are presented in Table II along with selected data obtained from earlier kinetic studies for purposes of comparison.
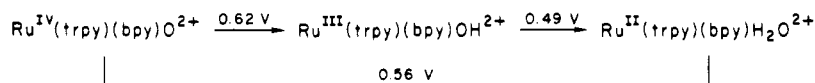
Discussion

Our results show that the electrocatalytic system based on electrolytic regeneration of $[Ru(trpy)(bpy)(O)]^{2+}$ is potentially capable of providing a general and selective

(18) Wolfrom, M. L.; Bobbitt, J. M. *J. Am. Chem. Soc.* **1956**, *78*, 2489.
(19) Bakule, R.; Long, F. A. *J. Am. Chem. Soc.* **1963**, *85*, 2309.

Chart I

(25 °C, μ = 0.10, pH 7.0)

$$Ru^{IV}(trpy)(bpy)O^{2+} \xrightarrow{\text{0.62 V}} Ru^{III}(trpy)(bpy)OH^{2+} \xrightarrow{\text{0.49 V}} Ru^{II}(trpy)(bpy)H_2O^{2+}$$

0.56 V

Table II. Rate Constants for the Oxidation of Selected Substrates by $[Ru^{IV}(trpy)(bpy)(O)]^{2+}$ at 25.0 ± 0.1 °C, pH 6.8, $\mu = 0.32$ M $(Li_2SO_4)^a$

substrate	k, $M^{-1} s^{-1}$	k/H, $M^{-1} s^{-1}$ ^{b}
$(CH_3)_2CHOH$	0.067 ± 0.07	0.067
[cyclohexanol structure]	0.063 ± 0.003	0.0016
[cyclohexanone structure]	$<0.02 \pm 0.002$	<0.005
[2-hydroxycyclohexanone structure]	$<11.3 \pm 1.0$	<11.3
[1,2-cyclohexanedione structure]	$<1170 \pm 200$	<290 (?)
$p\text{-}^-O_2CC_6H_4CH(CH_3)_2$	12.2 ± 1.2	12.2
$p\text{-}^-O_2CC_6H_4CH_2CH_3$	3.4 ± 0.3	1.7
$p\text{-}^-O_2CC_6H_4CH_3$	0.43 ± 0.04	0.14

^{a} In all cases the reactions were carried out with large pseudo-first-order excesses of substrate and the rate constants refer to the net two-electron oxidation of the substrate, e.g., $Ru(trpy(bpy)O^{2+}$ + $C_6H_{11}OH \rightarrow Ru(trpy(bpy)H_2O^{2+}$ + cyclohexanone. The exceptions are cyclohexanone and α-hydroxycyclohexanone where rate constants for the oxidation of the following oxidation products are far more rapid and of 1,2-cyclohexadione where the final product is unknown. For these cases, the observed rate constant includes contributions from subsequent, rapid reactions past the initial two-electron step and the observed second-order rate constants represent an upper limit for the initial step. ^{b} Rate constants corrected for statistical effects obtained by dividing k by the number of equivalent C–H bonds.

procedure for the oxidation of a series of organic molecules. The ability of the Ru system to act as a catalyst arises from two key factors: (1) its inherent reactivity characteristics, most notably through an accessibility to multiple electron-transfer pathways; (2) its coordinative stability in a series of adjacent oxidation states.
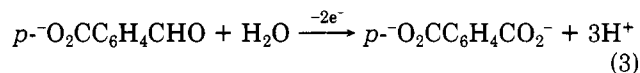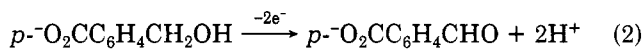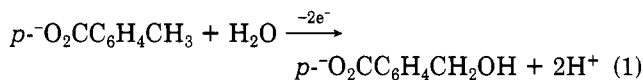
Coordinatively, the advantage of the trpy–bpy system is that the coordination sphere remains intact in each of its three oxidation state components, $Ru(trpy)(bpy)H_2O^{2+}$, $Ru(trpy)(bpy)OH^{2+}$, and $Ru(trpy)(bpy)O^{2+}$. The only significant changes occur at the oxo–aquo "active site", e.g., $Ru(trpy)(bpy)(H_2O)^{2+} \xrightarrow{-2e^-, -2H^+} Ru(trpy)(bpy)(O)^{2+}$ which allows the system to be recycled through the different oxidation states in a facile way. This is in contrast to oxidants like MnO_4^- or CrO_3 where significant changes in coordination number and structure occur upon reduction, e.g., $CrO_3 \rightarrow Cr(H_2O)_6^{3+}$. Such changes in structure can cause severe restrictions in the ability of a system to be recycled in a facile way and restricts their use in catalytic applications.

The reactivity feature of the catalytic system is its ability to carry out what are ostensibly difficult redox steps in a relatively facile manner. It can be appreciated from the Latimer-type diagram (Chart I) that thermodynamically speaking, the system is not strongly oxidizing. For the oxidations of 2-propanol to acetone and of C–H bonds adjacent to aromatic groups, e.g., $C_6H_5CH(CH_3)_2 \rightarrow C_6H_5COH(CH_3)_2$, by $Ru^{IV}{=}O$, the available mechanistic information suggests that the redox pathways involved are

two electron in nature and involve hydride transfers.[9,10] The Ru^{IV} site clearly has a two-electron capability via the Ru(IV)/Ru(II) couple, and it is interesting to note from the redox potential data that because the potentials for the Ru(IV)/(III) and Ru(III)/(II) couples are so close, there is only a slight thermodynamic preference for Ru(IV) as a one-electron oxidant, $E°'(Ru(IV)/(III)) = 0.62$ V compared to Ru(IV) as a two-electron oxidant, $E°'(Ru(IV)/(III) = 0.56$ at pH 7. The rate constant data available to date show that Ru(IV) is a much more facile oxidant toward organic substrates than is Ru(III) and that Ru(IV) is the reactive entity in the oxidations.

Because the catalyzed oxidations are dominated by Ru(IV) and it appears to function as a two-electron oxidant, one-electron pathways leading to radicals appear to be avoided, which is important on two counts. The first is that it probably helps to explain the nearly quantitative yields of oxidized products since side reactions such as radical coupling are avoided. In addition, it is probably an important element in catalyst stability, since the polypyridyl ligands do appear to be susceptible to attack by radicals. However, it should be appreciated that alternate redox pathways are available to the system and for substrates where one-electron intermediates are more accessible. H atom or outer sphere pathways may appear.

Another notable feature about the Ru(IV) complex as a catalytic system, although not systematically exploited here, is the clear element of functional group specificity that exists in its reactions. Perhaps the point is made most clearly by the rate constant data in Table II and by the results of some of the electrocatalytic experiments where, for example, for $p\text{-}^-O_2CC_6H_4CH_2CH_3$, selective oxidation at the carbon adjacent to the aromatic ring was observed. In addition, in the catalyzed oxidations of substrates like 4-methylbenzoate or of crotonic acid, the fact that the intermediate alcohols or aldehydes, e.g., eq 1–3, do *not* appear suggests that they must be oxidized at significantly more rapid rates than the starting hydrocarbon.

$$p\text{-}^-O_2CC_6H_4CH_3 + H_2O \xrightarrow{-2e^-} p\text{-}^-O_2CC_6H_4CH_2OH + 2H^+ \quad (1)$$

$$p\text{-}^-O_2CC_6H_4CH_2OH \xrightarrow{-2e^-} p\text{-}^-O_2CC_6H_4CHO + 2H^+ \quad (2)$$

$$p\text{-}^-O_2CC_6H_4CHO + H_2O \xrightarrow{-2e^-} p\text{-}^-O_2CC_6H_4CO_2^- + 3H^+ \quad (3)$$
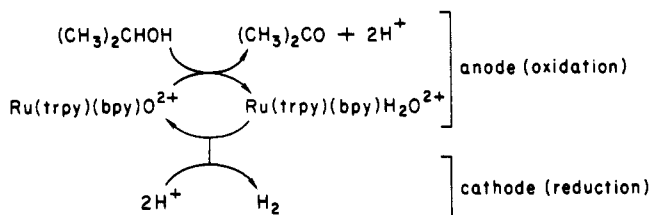
Clearly, even with the limited kinetic data available, there are notable differences in oxidative rate constants for different functional groups, perhaps the most dramatic being the enhanced rate constants for oxidation of C–H bonds adjacent to aromatic groups compared to secondary alcohols. With the acquisition of more rate data, including activation parameters so that temperature can be made a useful variable, it may be possible to establish a means for developing functional group specificity based on kinetic factors and so to develop general electrocatalytic procedures for selective oxidations in complex molecules. In this regard, it should be noted that the catalyst described here represents the first member of what should become a broad class of related oxidative catalysts. There is an extensive background synthetic chemistry for complexes of this type[20] and using it will allow systematic ligand variations

to be made while at the same time maintaining the $Ru^{IV}{=}O$ "active" site intact.

As a final note on the rate constant data in Table II, the greatly enhanced rate constant for oxidation of 1,2-cyclohexanedione is worth noting. As pointed out above this substrate exists predominantly in the hydrate and enol forms and its enhanced reactivity toward other oxidants has been attributed to the enol.[21]
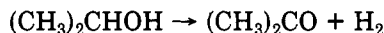
Some comments also need to be made in a general way concerning the electrocatalytic approach to organic oxidations. As exploited here, the procedure involves an electrochemical shuttle mechanism, as shown below using 2-propanol as the example,

$$(CH_3)_2CHOH \qquad (CH_3)_2CO \ + \ 2H^+$$
$$Ru(trpy)(bpy)O^{2+} \qquad Ru(trpy)(bpy)H_2O^{2+}$$ anode (oxidation)
$$2H^+ \qquad H_2$$ cathode (reduction)

In the above scheme, the oxidized form of the catalyst couple oxidizes the organic substrate to its oxidized form in solution. The necessary oxidizing equivalents to maintain the catalytic cycle enter the solution via oxidation of $[Ru(trpy)(bpy)H_2O]^{2+}$ to $[Ru(trpy)(bpy)O]^{2+}$ at the electrode. In the net sense, the electrolyses involve either the electrochemically driven oxidation of the substrate by water, e.g.,
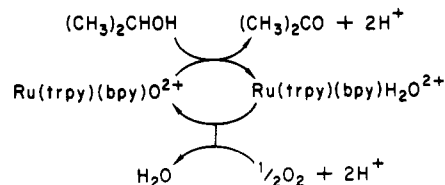
$$H_2O \ + \ p\text{-}^-O_2OC_6H_4CH(CH_3)_2 \ \rightarrow$$
$$p\text{-}^-O_2CC_6H_4COH(CH_3)_2 \ + \ H_2$$
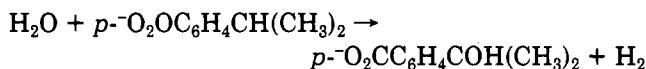
or a net oxidative dehydrogenation, e.g.,

$$(CH_3)_2CHOH \ \rightarrow \ (CH_3)_2CO \ + \ H_2$$

It is interesting to note that in the electrolyses the product in the second cell compartment is H_2 which was shown to form quantitatively in the oxidation of 2-propanol. This is an important point, since, as noted earlier, given the thermodynamcs of the combustion of H_2

in air, the electrolyses are carried out with a near energy balance.[12a] In addition, if a reversible high energy density O_2/H_2O electrode can be developed and used as the source of oxidizing equivalents, the resulting cells would function as synthesis fuel cells, as shown below, once again using 2-propanol as the example,

$$(CH_3)_2CHOH \qquad (CH_3)_2CO \ + \ 2H^+$$
$$Ru(trpy)(bpy)O^{2+} \qquad Ru(trpy)(bpy)H_2O^{2+}$$
$$H_2O \qquad {}^1\!/_2O_2 \ + \ 2H^+$$

The background chemistry is available for the attachment of catalytic sites like those described here to polymers, polymer beads, and to electrode surfaces.[22] As a consequence, it should be possible in the future to develop systems in which catalytic sites are held in open, porous structures, where oxidative regeneration is carried out chemically, or on electrode surfaces, electrochemically. There are obvious advantages to be gained in such systems including the ability to recycle the catalyst and to pass the dissolved organic substrate over a fixed bed containing the catalytic sites.

Registry No. $[Ru^{IV}(trpy)(bpy)(O)]^{2+}$, 73836-44-9; $[Ru^{IV}(trpy)(bpy)OH_2]^{2+}$, 20154-63-6; $CH_3CH(OH)CH_3$, 67-63-0; EtOH, 64-17-5; CH_3CHO, 75-07-0; $Me\text{-}p\text{-}C_6H_4CO_2Na$, 17264-54-9; $PhCH_3$, 108-88-3; $trans\text{-}CH_3CH{=}CHCO_2H$, 107-93-7; $i\text{-}Pr\text{-}p\text{-}C_6H_4CO_2Na$, 1009-60-5; $Et\text{-}p\text{-}C_6H_4CO_2Na$, 2046-83-5; $CH_3C(O)CH_3$, 67-64-1; $CH_3C(O)O^-$, 71-50-1; $^-O_2C\text{-}p\text{-}C_6H_4CO_2^-$, 3198-29-6; $PhCO_2^-$, 766-76-7; $(E)\text{-}^-O_2CCH{=}CHCO_2^-$, 142-42-7; $(CH_3)_2C(OH)\text{-}p\text{-}C_6H_4CO_2^-$, 92096-49-6; $CH_3C(O)\text{-}p\text{-}C_6H_4CO_2^-$, 22583-64-8; cyclohexanol, 108-93-0; cyclohexanone, 108-94-1; 2-hydroxycyclohexanone, 533-60-8; 1,2-cyclohexanedione, 765-87-7.

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