

Chemically Catalyzed Net Electrochemical Oxidation of Alcohols, Aldehydes, and Unsaturated Hydrocarbons Using the System (trpy)(bpy)Ru(OH₂)²⁺ / (trpy)(bpy)RuO²⁺

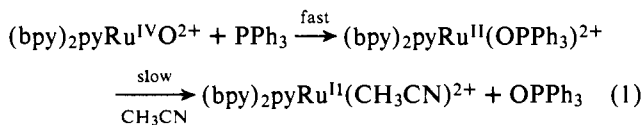
Bruce A. Moyer, Mark S. Thompson, and Thomas J. Meyer*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received June 11, 1979

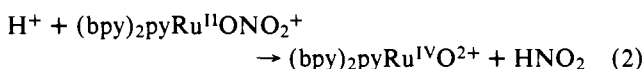
Abstract: A mild electrocatalytic technique has been developed for the oxidation of selected alcohols, aldehydes, and unsaturated hydrocarbons at 25–50 °C using as catalysts the systems (bpy)₂pyRu(OH₂)²⁺ / (bpy)₂pyRuO²⁺ and (trpy)(bpy)Ru(OH₂)²⁺ / (trpy)(bpy)RuO²⁺. The organic compounds were dissolved or dispersed in an aqueous buffer solution of the catalyst, and the net oxidations were carried out using conventional three-electrode electrolysis cells at applied potentials which were sufficient to cause the oxidation of Ru(II) to Ru(IV) (0.6–0.8 V vs. SCE). Background currents in the absence of catalyst were negligible. Using the electrocatalytic approach, 2-propanol and ethanol were oxidized to acetone and acetate, respectively, and acetaldehyde was oxidized to acetate. Toluene was oxidized to benzoate anion, *p*-xylene to terephthalate dianion, and *p*-phthalate anion to terephthalate quantitatively, in all three cases without the appearance of intermediates. Ethylene is unreactive, but cyclohexene was oxidized first to 2-cyclohexen-1-one and then to *p*-benzoquinone, which decomposes in solution. The (trpy)(bpy)Ru(OH₂)²⁺ catalyst is greater than 75% recoverable after 100 catalytic cycles.

Oxo complexes of transition metals such as MnO₄⁻, RuO₄, and CrO₃ are strong oxidants and are often used in synthetic organic chemistry as general-purpose, stoichiometric oxidizing agents.^{1,2} Although these reagents and others have proven to be extremely useful in the laboratory, they are often limited in effectiveness by undesirable selectivity patterns and by the impracticality of using them catalytically.³ In addition, there is little beyond changing the reaction conditions that can be done to alter their reactivity in particular chemical oxidations.

We recently reported that the net 2e⁻ oxidation of the complex *cis*-(bpy)₂pyRu(OH₂)²⁺ (bpy is 2,2'-bipyridine) in aqueous solution results in the reversible formation of the monooxo Ru(IV) complex ion, (bpy)₂pyRuO²⁺, which is a moderately strong oxidant⁴ (Scheme I). Given the presence of the oxo group and the implied capability of behaving as a 2e⁻ acceptor via the Ru(IV)/(II) couple, it was our thought that (bpy)₂pyRuO²⁺ could share some of the reactivity features exhibited by MnO₄⁻, CrO₃, etc., while retaining the inherent advantages common to polypyridine complexes of ruthenium: (1) high structural stability, (2) facile electron transfer,⁷ (3) a rich synthetic chemistry with which to make appropriate synthetic modifications,⁸ and (4) a demonstrated ability to catalyze net redox reactions.⁹ Previous work has shown that a net 2e⁻ oxidation involving (bpy)₂pyRuO²⁺ may take the form of an oxygen transfer in the oxidation of triphenylphosphine to triphenylphosphine oxide:⁴

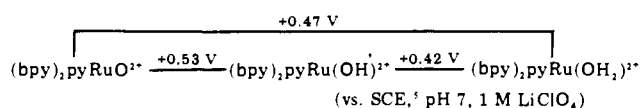


In a related reaction, (bpy)₂pyRu(OH₂)²⁺ is oxidized by HNO₃ via what may be a reverse oxygen transfer step to give HNO₂ and Ru(IV):^{9a}



Initial experiments with the Ru(IV) ion, (bpy)₂pyRuO²⁺, in aqueous solution showed that (bpy)₂pyRu(OH₂)²⁺ rapidly forms in the presence of certain organic compounds. Owing to the reversibility of the Ru(IV)/(III)/(II) couples in aqueous solution (Scheme I), the implied reactivity was important because it suggested that the oxidation of selected organic compounds could be made catalytic in the presence of an ex-

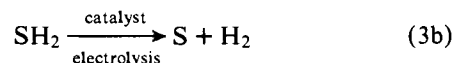
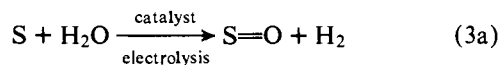
Scheme I



ternal source of oxidizing equivalents capable of regenerating (bpy)₂pyRuO²⁺. In the experiments described here, an electrochemical "shuttle" mechanism was adopted to reoxidize Ru(II) continuously at an electrode as it formed following the oxidation of some simple organic compounds.

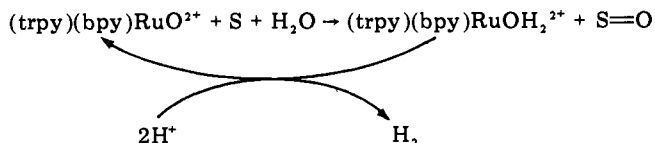
It became obvious early in our experiments that over an extended period of time the pyridyl system was unstable. The origin of the instability is the slow loss of the pyridine ligand with the ultimate appearance of a deep green, oxo-bridged dimer,¹⁰ possibly (bpy)₂(OH₂)RuORu(py)(bpy)₂⁴⁺. The instability problem was easily overcome by turning to the complex (trpy)(bpy)Ru(OH₂)²⁺^{8a} (trpy is 2,2',2''-terpyridine), where substitutional instability is apparently avoided by the chelate effect. The trpy system has been fully characterized and has the same pattern of redox chemistry shown in Scheme I except that the Ru(IV)/(III) and Ru(III)/(II) potentials are 0.61 and 0.48 V vs. SCE.

In Scheme II is shown in a simplified way the type of catalytic cycle that we have used in our experiments. In the scheme, S is an organic substrate, which in the example shown undergoes a net 2e⁻ oxidation. The balancing chemical reaction in the second electrode compartment is the reduction of H⁺ to 1/2H₂. In the net sense, either water acts as the primary oxidant in the electrochemically driven oxidation of S to S=O (eq 3a) or the organic compound undergoes a net oxidative dehydrogenation (eq 3b):¹¹



The experiments were carried out at 25–50 °C using phos-

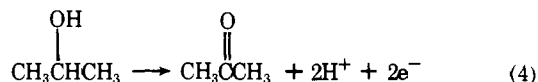
Scheme II



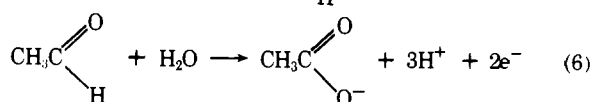
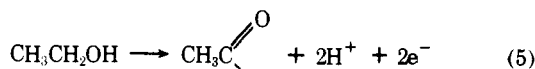
phate (pH ~7) or borate (pH ~9) buffer solutions¹² in the range 0.1–1.0 M under a nitrogen atmosphere. Catalyst concentrations (using the ClO₄⁻ salts) were approximately millimolar, and the organic compounds were present in from 5- to 2000-fold excess over catalyst. When not miscible with the aqueous buffer solution, the organic compounds were dispersed neat or as a solution using a water-immiscible inert solvent with rapid stirring. Three-compartment electrochemical cells⁶ were employed using Pt gauze or reticulated vitreous carbon working electrodes¹³ and Ag/AgCl or SCE (saturated calomel electrode) reference electrodes.⁶ Electrolyses were carried out at potentials sufficient to oxidize Ru(II) to Ru(IV) (0.6–0.8 V vs. SCE depending on the pH).⁴ Catalytic currents varied from 1 to 35 mA, and background currents in the absence of catalyst were negligible.

In an initial experiment designed to test the feasibility of the electrocatalytic procedure, triphenylphosphine dissolved in cyclohexane (cyclohexane is inert to attack by Ru(III) or Ru(IV) under the conditions of the experiments) was dispersed in a phosphate buffer solution of (bpy)₂pyRu(OH₂)²⁺ and oxidized electrochemically until the current had fallen to about 1% of the initial value. Subsequent IR analysis for triphenylphosphine oxide using the ν(P=O) peak¹⁴ at 1195 cm⁻¹ confirmed that essentially complete conversion of the triphenylphosphine (initially present at approximately fivefold excess over catalyst) had occurred, in agreement with the number of electrochemical equivalents passed during the electrolysis. However, a visible spectrum of the aqueous solution from which all of the organic material had been removed showed that the decomposition reaction mentioned above had occurred to an appreciable degree and all of the remaining experiments described here utilized the (trpy)(bpy)Ru(OH₂)²⁺/(trpy)(bpy)RuO²⁺ system. In the experiments which follow, the turnover numbers per catalyst molecule were dictated by experimental patience rather than catalyst stability.

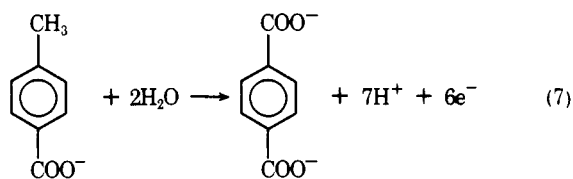
Alcohols and Aldehydes. 2-Propanol was converted quantitatively to acetone (with respect to electrochemical equivalents passed) as shown by distillation of the solution after approximately 100 catalytic cycles and subsequent UV analysis (λ_{max} 265 nm, ε 18.5).¹⁵ The oxidation half-reaction is eq 4.



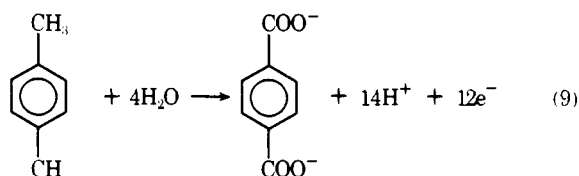
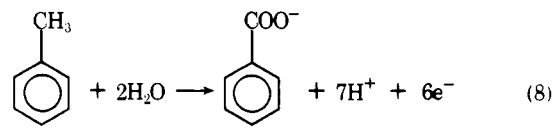
In the experiment, 2-propanol was in large excess, mostly to ensure more rapid catalyst turnover, and only 10–20% was oxidized. For the primary alcohol, ethanol, NMR analysis for acetate ion and UV analysis for acetaldehyde after approximately 100 catalytic cycles (5% of the ethanol consumed) showed that acetate and acetaldehyde each accounted for about 50% of the current passed under the conditions used (50 °C, phosphate buffer). By itself, acetaldehyde is readily oxidized to acetate quantitatively, but its intermediacy in the oxidation of ethanol suggests that under suitable conditions it should be isolable as the final product. The oxidation half-reactions are eq 5 and 6.



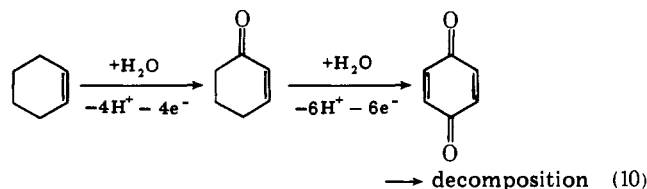
Aromatic Hydrocarbons. *p*-Toluic acid undergoes a quantitative 6e⁻ oxidation to terephthalate as shown by NMR analysis of the product solution after 100 catalytic cycles (eq 7). Similarly, toluene and *p*-xylene undergo respective 6e⁻ and



12e⁻ conversions without the noticeable buildup of intermediates (eq 8 and 9).



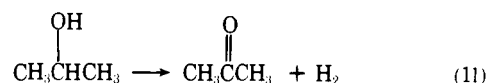
Olefins. A related type of reactivity occurs with cyclohexene where an allylic oxidation occurs at a carbon adjacent to the double bond to form 2-cyclohexen-1-one accounting for approximately 15% of the current passed as determined by NMR. Also detectable in the mixture by NMR were hydroquinone and minor amounts of unidentified products. Since hydroquinone is itself readily oxidized at the electrode to *p*-benzoquinone under the experimental conditions employed,^{16–18} its presence can be explained as a product of the decomposition of *p*-benzoquinone which is unstable toward disproportionation reactions in pH 7 aqueous buffer solutions at 50 °C¹⁹ (eq 10).



IR, NMR, and GC analysis gave no evidence for attack at the double bond which would otherwise be indicated by formation of products such as cyclohexene oxide, cyclohexanediol, 2-hydroxycyclohexanone, 1,2-cyclohexanedione, or adipic acid.^{1,2} As might then be expected, ethylene is unreactive toward oxidation under similar conditions.

Our initial results clearly point to a functional group selectivity for the ruthenium catalyst. Under reaction conditions where alcohols, aldehydes, and unsaturated hydrocarbons are readily oxidized, there is little or no reactivity with cyclohexane, diethyl ether, acetone, acetate anion, benzoate anion, dimethyl sulfone, or ethylene. However, the list of reactions may well be extended or modified by making rather obvious changes in such variables as temperature (possibly to 100 °C), pH, method of oxidation,²⁰ or, probably most significantly, in the chemical makeup of the catalyst itself. In the presence of excess reactant, the (trpy)(bpy)Ru(OH₂)²⁺ catalyst proved durable (recoverable to greater than 75%) for up to at least 100 2e⁻ catalytic cycles in all of the reactions studied.

Final Comments. In itself, our electrocatalytic approach provides a controlled way to use electrolytic techniques for the oxidation of selected organic functional groups at relatively low potentials, advantages which are seldom available in direct electrode oxidations.¹⁸ Further, the second product of the electrolysis is H₂, and it was shown to be evolved quantitatively for the case of 2-propanol where the net reaction is¹¹ eq 11.



Neglecting the voltage drop across the cell, the overall applied electrical potential between the working and counter electrodes necessary to drive this reaction (or any of the others previously discussed) using the (trpy)(bpy)Ru(OH₂)²⁺ catalyst is approximately 1.2 V, which is the potential difference between the H⁺/H₂ and Ru(IV)/(III) couples at pH 7. Given the thermodynamics of the combustion of H₂ in air, eq 11 has been carried out in the net sense with a near energy balance.²¹ Perhaps more importantly, it follows that, if a reversible, high current density O₂ electrode can be developed and coupled with the catalyzed oxidations reported here, the resulting cells could be made to operate spontaneously, in effect becoming chemical synthesis fuel cells.

Acknowledgment is made to the National Science Foundation for support of this research through Grant CHE77 04961.

References and Notes

- (1) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Reading, Mass., 1972.
- (2) Wiberg, K. B., Ed. "Oxidation in Organic Chemistry", Trahanovsky, W. S., Ed. Academic Press: New York, 1965; Part A. *Ibid.*, 1973; Part B. Trahanovsky, W. S., Ed. *Ibid.*, 1978; Part C.
- (3) It is possible to use MnO₄⁻, RuO₄, or CrO₃ as catalysts in special cases, but not in general applications. The strong primary oxidants that must be used to recycle the systems to their oxidized states frequently influence the course of the net chemical oxidation independent of the catalyst.^{1,2}
- (4) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3601; submitted.
- (5) SCE is the saturated calomel electrode. Potentials referenced to the SCE may be approximately referenced to the NHE (normal hydrogen electrode) by adding 0.24 V, ignoring junction potentials.⁶
- (6) Sawyer, D. T.; Roberts, J. L., Jr. "Experimental Electrochemistry for Chemists"; Wiley: New York, 1974.
- (7) Braddock, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 3158. Braddock, J. N.; Cramer, J. L.; Meyer, T. J. *Ibid.* **1975**, *97*, 1972. Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *Ibid.* **1977**, *99*, 1064. Young, R. C.; Keene, F. R.; Meyer, T. J. *Ibid.* **1977**, *99*, 2468.
- (8) (a) Dwyer, F. P.; Goodwin, H. A.; Gyarfas, E. C. *Aust. J. Chem.* **1963**, *16*, 42. (b) *Ibid.* **1963**, *16*, 544. Adeyemi, S. A.; Miller, F. J.; Meyer, T. J. *Inorg. Chem.* **1972**, *11*, 994. Krause, R. A. *Inorg. Chim. Acta* **1977**, *22*, 209. Meyer, T. J.; Salmon, D. J.; Sullivan, B. P. *Inorg. Chem.* **1978**, *17*, 3334. Connor, J. A.; Meyer, T. J.; Sullivan, B. P. *Ibid.* **1979**, *18*, 1388. Durham, B.; Walsh, J. L.; Carter, C. L.; Meyer, T. J. *Ibid.*, in press.
- (9) (a) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 1326. (b) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *Ibid.* **1977**, *99*, 4821.
- (10) Weaver, T. R.; Adeyemi, S. A.; Brown, G. M.; Eckberg, R. P.; Hatfield, W. E.; Johnson, E. C.; Murray, R. W.; Untereker, D.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 3039.
- (11) While we have shown that (bpy)₂pyRuO₂²⁺ may act as a potential oxygen donor,^{4,9a} its general reactivity patterns undoubtedly include a number of mechanistic possibilities shared by other oxo complexes.^{1,2}
- (12) Bates, R. G. "Determination of pH", 2nd ed.; Wiley: New York, 1973. The buffer serves the dual purpose of maintaining constant pH and acting as supporting electrolyte.⁶
- (13) RVC Products Co., Ann Arbor, Mich.
- (14) Cotton, F. A.; Barnes, R. D.; Bannister, E. *J. Chem. Soc.* **1960**, 2199.
- (15) "DMS UV Atlas of Organic Compounds", Vol. II; Plenum Press: New York, 1966.
- (16) Clark, W. M. "Oxidation-Reduction Potentials of Organic Systems"; Williams and Wilkins: Baltimore, Md., 1960.
- (17) Papouchado, L.; Petrie, G.; Sharp, J. H.; Adams, R. N. *J. Am. Chem. Soc.* **1968**, *90*, 5620. Finley, K. T. "The Chemistry of Quinoid Compounds", Part 2; Patai, S., Ed.; Interscience: New York, 1974; Chapter 17.
- (18) Ross, S. D.; Finkelstein, M.; Rudd, E. F. "Anodic Oxidation"; Academic Press: New York, 1975. Balzer, M. M., Ed. "Organic Electrochemistry"; Marcel Dekker: New York, 1973.
- (19) At 50 °C in phosphate buffer solution, *p*-benzoquinone by itself rapidly undergoes decomposition to give hydroquinone (as shown by NMR) plus insoluble products, consistent with observations in the catalysis experiments. Although the ultimate fate of the *p*-benzoquinone that is probably being formed in the catalytic oxidation of cyclohexene is uncertain, previous work^{17,18} has demonstrated that quinone compounds are particularly susceptible to attack by nucleophiles, including water. In the case of hydrolysis of benzoquinone, the product may well be further oxidized by benzoquinone, thus giving rise to the hydroquinone.
- (20) Instead of the electrochemical method used here to oxidize Ru(II) to Ru(IV), chemical oxidation is possible as in the oxidation of (bpy)₂pyRu(OH₂)²⁺ by HNO₃.^{9a}
- (21) Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall: Englewood Cliffs, N.J. 1952.

Substitution and Cleavage in the Reaction of Some Benzyl(carbonyl)metal Complexes with Trifluoroacetic Acid

Stewart N. Anderson, Christopher J. Cooksey, Steven G. Holton, and Michael D. Johnson*

Contribution from the Department of Chemistry, University College, London WC1H 0AJ, England. Received September 7, 1978

Abstract: Several benzyl(carbonyl)metal complexes, including benzyldicarbonylcyclopentadienyliron(II) (**1**), undergo substantial deuteration in the ortho and para positions prior to acidolysis of the carbon-metal bond in [2H₁]trifluoroacetic acid. Comparison of the rates of substitution with that for substitution in anisole shows that the metallomethyl substituents, e.g., CH₂Fe(CO)₂(C₅H₅), have large negative substituent constants indicative of very strong hyperconjugative electron donation in the transition states for substitution reactions. There is no evidence that electrophilic attack on the aromatic ring causes cleavage of the carbon-metal bond. The kinetics of the anaerobic acidolysis of **1** and of its 4-fluoro derivative in trifluoroacetic acid and in [2H₁]trifluoroacetic acid in chlorinated solvents show that the acidolysis is first order with respect to acid and to substrate, is influenced by the nature of the cosolvent, and has a very high kinetic isotope effect, *k*_H/*k*_D = 15–25. It is suggested that these results are indicative of an attack on the metal prior to cleavage of the carbon-metal bond.

Studies of the acidolysis of σ -bonded organotransition metal complexes have repeatedly demonstrated that the proton is a relatively poor electrophile for attack at saturated carbon. The study of the cleavage of organochromium(III),¹ organocobalt(III),² organomanganese(I)^{4,5} and organoiron(II)^{5,6} complexes (**1–6**, respectively) in aqueous acidic solution has demonstrated that a wide range of electrophiles, including Hg(II), Tl(III), Hg(I), NO⁺, and halogens, are capable of displacing one or more of the above metals from carbon under conditions in which the proton, though present in appreciably

higher concentration than the other electrophile, plays no direct part in the reaction. Indeed, the pyridylmanganese complex **3** undergoes acidolysis by an *unimolecular* process, and the pyridyliron complex **6** is unchanged after several months, in 4 mol dm⁻³ aqueous perchloric acid at 65 °C under anaerobic conditions.⁷ In the case of some organochromium(III) complexes there is evidence for a pathway that is first order in acid, but this is usually accompanied by a competing unimolecular path that is zero order in acid.⁸

In principle, an electrophile such as the proton may attack