J. Am. Chem. Soc. 1981, 103, 512-516

Electrogenerated Chemiluminescence. 37. Aqueous Ecl Systems Based on Ru(2,2′-bipyridine)$_3$$^{2+}$ and Oxalate or Organic Acids

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Abstract: An aqueous system for electrogenerated chemiluminescence (ecl) based on the reaction of electrogenerated $Ru(bpy)_3^{3+}$ with strong reductants produced as intermediates in the oxidation of oxalate ion is described. The bright orange chemiluminescence, which could also be generated by reaction of chemically produced Ru(III) species with oxalate, corresponded to emission by $Ru(bpy)_3^{2+*}$; ecl efficiency (photons emitted/$Ru(bpy)_3^{3+}$ generated) was ~2% in deaerated solution. Ecl by reaction of the 1+ and 3+ Ru species could also be obtained in partially aqueous solutions containing at least 20% acetonitrile. Chemiluminescence was also observed with other organic acids (pyruvic, malonic, lactic), when the intermediates produced on their oxidation by Ce^{4+} reacted with $Ru(bpy)_3^{3+}$.

Introduction

The numerous investigations of chemiluminescence arising from excited-state production in energetic electron-transfer reactions of electrogenerated reactants (electrogenerated chemiluminescence or ecl) have almost always involved nonaqueous solvent media such as *N*,*N*-dimethylformamide or acetonitrile (MeCN).[1] Indeed even small amounts of water will frequently quench the ecl reaction and studies are usually carried out under rigorously dry conditions utilizing vacuum line or drybox techniques.[2] The major difficulties with designing ecl systems in aqueous solutions are (a) the very low solubility of the organic compounds which are the radical ion precursers, (b) the reactivity of the radical ions with water, and (c) the limited potential range of water. However, aqueous ecl systems would be of interest, especially for the design of practical ecl devices (e.g., displays). In many cases, the lifetime of an ecl device appears to be governed by the presence of trace impurities (e.g., water) in the solvent and supporting electrolyte.

A very good candidate for aqueous ecl is the $Ru(bpy)_3^{2+}$ (where bpy = 2,2′-bipyridine) system. This system involves water-soluble species, and previous studies[3] have shown that in MeCN solutions intense ecl results from the reaction of the 3+ and 1+ species.

$$Ru(bpy)_3^{3+} + Ru(bpy)_3^{+} \rightarrow Ru(bpy)_3^{2+*} + Ru(bpy)_3^{2+} \quad (1)$$

$$Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{2+} + h\nu \quad (2)$$

An investigation of the temperature dependence of the ecl efficiency (photons emitted per redox event) suggested that the production of the excited state by the redox reaction (1) occurs with an efficiency near 100%.[4] In addition to the annihilation mode of ecl with $Ru(bpy)_3^{3+/+}$, chemiluminescence involving reaction of the +3 species with other reducing agents is possible.[5,6] Thus the simultaneous oxidation of $Ru(bpy)_3^{2+}$ and oxalate ion in MeCN at a Pt electrode produces light emission. The mechanism proposed for this emission was based on the oxidation of oxalate ion to form the strong reducing agent $CO_2^{-}\cdot$, which ultimately yields an electron transfer to $Ru(bpy)_3^{3+}$ to produce an excited state.

We report here aqueous ecl systems involving $Ru(bpy)_3^{2+}$ and a preliminary study of coupled reactions ("oxidative reductions") of oxalate and several organic acids which were revealed by the ecl investigations.

Experimental Section

Electrochemical measurements were performed in a simple three-electrode cell, using Pt wire or a glassy carbon disk (Tokai Carbon Co., Tokyo, Japan) working electrodes (geometric area, 0.20 cm^2), a Pt auxiliary electrode, and either a mercury sulfate reference electrode [(MSE) Hg/Hg_2SO_4/1.0 M H_2SO_4; +0.67 V vs. NHE[7]] or a silver wire quasi reference electrode.[8] The electrochemical and ecl experiments generally used the instrumentation and techniques previously described.[3,5] Ecl and fluorescence spectra were measured on an Aminco-Bowman spectrophotofluorometer. $Ru(bpy)_3(ClO_4)_2$ was prepared from the chloride (G. F. Smith Chemical Co.).[3b] Oxalic acid (Mallinckrodt, A.R.), sodium oxalate (Allied Chemical), sodium sulfate (Fisher Scientific Co., certified ACS), cerium(III) sultate (Alfa Products, 99.9%), ceric ammonium sulfate (G. F. Smith Chemical Co.), lead dioxide (Allied Chemical), tetramethylammonium chloride (Southwestern Analytical Chemicals, polargraphic grade), and acetonitrile (MCB, spectroquality) were all used without further purification. All solutions were prepared with triple-distilled water.

Results and Discussion

(A) The $Ru(bpy)_3^{2+}$–Oxalate System. Electrochemical measurements. Current-potential curves for the $Ru(bpy)_3^{3+/2+}$ reversible couple and the anodic oxidation of oxalate at a Pt electrode in 1.0 M H_2SO_4 are presented in Figure 1a–c. Oxalate is irreversibly oxidized to CO_2 at Pt at potentials within the platinum oxide region. Although this reaction has been investigated before[9] and the only product in aqueous solution is CO_2, the detailed mechanism is uncertain. The oxalate oxidation wave is known to be completely suppressed on an oxide-covered Pt surface,[9] as is also demonstrated by the voltammogram in Figure 1c. The electroactive species is usually assumed to be the adsorbed undissociated acid, which is oxidized according to the overall eq 3.

$$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^- \quad (3)$$

In the simultaneous oxidation of oxalate and $Ru(bpy)_3^{2+}$, in 1.0 M H_2SO_4 at a reduced Pt electrode (Figure 1d), the oxidation peaks of both species occur at nearly the same potential. This results in a single broad oxidation peak. On the other hand, with a Pt electrode which has been preoxidized (an oxide-covered electrode), one observes only the reversible $Ru(bpy)_3^{3+/2+}$ couple

$$Ru(bpy)_3^{3+} + e^- \rightleftarrows Ru(bpy)_3^{2+} \quad (4)$$

Carbon electrodes (both pyrolytic graphite and glassy carbon) show behavior similar to that of oxide-covered Pt electrodes toward

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[1] See, for example: (a) Faulkner, L. R. *Methods Enzymology* **1978**, *57*; (b) Faulkner, L. R.; Bard, A. J. *Electroanal. Chem.* **1977**, *10*.

[2] An exception is the ecl in the luminol-oxygen system by: Epstein, B.; Kuwana, T. *Photochem. Photobiol.* **1965**, *4*, 1157; *Ibid.* **1967**, *6*, 605.

[3] (a) Tokel, N. E.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 2862. (b) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *Ibid.* **1973**, *95*, 6582.

[4] (a) Wallace, W. L.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 1350. (b) Itoh, K.; Honda, K. *Chem. Lett.* **1979**, 99.

[5] Chang, M.; Saji, T.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 5399.

[6] Lytle, F. E.; Hercules, D. M. *Photochem. Photobiol.* **1971**, *13*, 123.

[7] Reichman, B.; Bard, A. J. *J. Electrochem. Soc.* **1979**, *126*, 583.

[8] Keszthelyi, C. P.; Tachikawa, H.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 1522.

[9] (a) Lingane, J. J. *J. Electroanal. Chem.* **1959/1960**, *1*, 379. (b) Giner, J. *Electrochim. Acta* **1961**, *4*, 42. (c) Anson, F. C.; Schulz, F. A. *Anal. Chem.* **1963**, *35*, 1115. (d) Johnson, J. W.; Wroblowa, H.; Bockris, J. O'M. *Electrochim. Acta* **1964**, *9*, 639.

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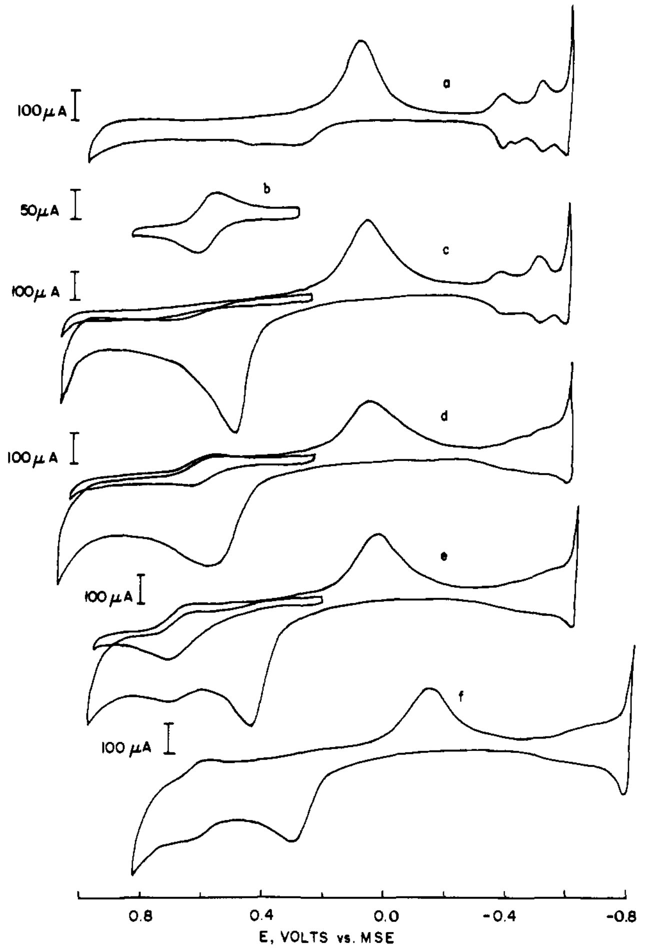

Figure 1. Current–potential curves at steady state for a Pt electrode (sweep rate, 200 mV/s): (a) 1.0 M H_2SO_4; (b) 1.0 mM $Ru(bpy)_3(ClO_4)_2$, 1.0 M H_2SO_4; (c) 3.0 mM $H_2C_2O_4$, 1.0 M H_2SO_4; (d) 3.0 mM $H_2C_2O_4$, 1.0 mM $Ru(bpy)_3(ClO_4)_2$, 1.0 M H_2SO_4; (e) Same as d but 0.1 M H_2SO_4; (f) same as d at pH 4.5 (adjusted by addition of NaOH to 0.1 M H_2SO_4).

oxalate and $Ru(bpy)_3^{2+}$ oxidation; i.e., there is a very large overpotential for oxalate oxidation on carbon compared to that on reduced Pt. The potential at which oxalate oxidation occurs depends upon the pH and becomes less positive with an increase in pH. Thus in 0.1 M H_2SO_4 (pH ~1.8) the cyclic voltammogram of a solution containing both oxalate and $Ru(bpy)_3^{2+}$ shows separated waves (Figure 1e). A further increase in the pH causes an even greater separation (Figure 1f). Moreover, at an oxidized electrode in the presence of oxalate, the anodic current for $Ru(bpy)_3^{2+}$ was larger and the cathodic current on the reverse scan was smaller than in its absence (Figure 1e). This results from the reaction of the 3+ species with oxalate, which under these conditions is not oxidized directly at the electrode.

While the mechanism for the oxidation of oxalate by $Ru(bpy)_3^{3+}$ or at an electrode has not been established, the previous ecl results[5] and the fact that Ru(III) is usually a one-electron oxidant suggest reaction 5 followed by rapid decomposition of $C_2O_4^{-}\cdot$. (For oxalic

$$Ru(bpy)_3^{3+} + C_2O_4^{2-} \rightarrow Ru(bpy)_3^{2+} + C_2O_4^{-}\cdot \qquad (5)$$

acid, $pK_{a1} = 1.23$ and $pK_{a2} = 4.19$,[10] so that the predominant forms in acidic solution are $H_2C_2O_4$ and $HC_2O_4^-$.) Thus at an oxidized Pt electrode oxalate is oxidized exclusively by reaction with $Ru(bpy)_3^{3+}$, thus producing in the diffusion layer near the electrode a mixture of the 2+ and 3+ Ru species as well as intermediates from the oxidation of oxalate. The catalytic oxidation of oxalate by $Ru(bpy)_3^{3+}$ does not occur in 1 M H_2SO_4, however.

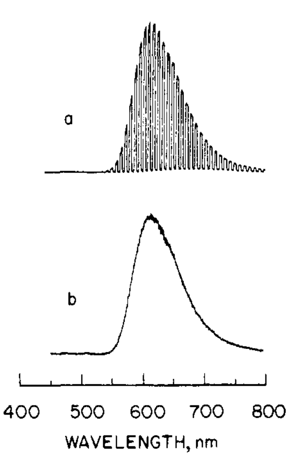

Figure 2. (a) Ecl emission spectrum of Pt electrode in a solution of 1.0 mM $Ru(bpy)_3(ClO_4)_2$ and 50 mM $Na_2C_2O_4$ at pH 5.0, with cyclic square wave excitation, between 0.2 and 0.7 V vs. MSE at 0.2 Hz. (b) Luminescence emission spectrum of 1.0 mM $Ru(bpy)_3(ClO_4)_2$ in 0.1 M H_2SO_4, with photoexcitation at 500 nm.

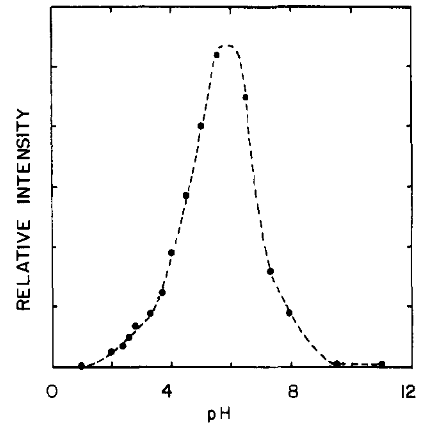

Figure 3. Dependence of the ecl intensity (at 610 nm) on the pH. The solution contained 1.0 mM $Ru(bpy)_3(ClO_4)_2$ and 6.0 mM $H_2C_2O_4$, with the pH adjusted by addition of NaOH to 0.1 M H_2SO_4.

Electrogenerated Chemiluminescence. When a potential which is more positive than the potential for the oxidation of $Ru(bpy)_3^{2+}$ is applied to a Pt or carbon electrode in an aqueous solution containing as low as 1.0 mM $Ru(bpy)_3^{2+}$ and various concentrations of oxalate at pH ≥2, orange light is emitted from the electrode surface. No ecl occurs in 1.0 M H_2SO_4. The ecl can be produced either by repetitively pulsing the electrode potential between a potential sufficiently positive for $Ru(bpy)_3^{2+}$ oxidation and a more negative rest potential to allow renewal of the depleted oxalate near the electrode surface or by applying a constant positive potential with stirring of the solution. With high oxalate concentration stirring is unnecessary. The ecl intensity is quite strong (clearly visible to the non-dark-adapted eye) even at low concentrations (e.g., 5 mM) of oxalate at $7 \gtrsim pH \gtrsim 4$. Removal of oxygen from the solution is not necessary, but deaeration with nitrogen for several minutes increases the ecl intensity. This light emission is clearly attributable to the excited state, $Ru(bpy)_3^{2+}*$, since the ecl and luminescence spectra are essentially identical (Figure 2).

No emission is observed at potentials where only oxidation of oxalate occurs; potentials sufficiently positive to cause $Ru(bpy)_3^{2+}$ oxidation are required. In addition, in the repetitive pulsing mode, a shift in the rest potential to sufficiently negative values to cause the removal of the oxide layer (which is present on the Pt surface at the potential for oxidation of $Ru(bpy)_3^{2+}$) results in a substantial decrease in the emission intensity. The ecl intensity is strongly dependent on the pH, as shown in Figure 3. Note that these measurements were made in unbuffered solutions, so that the pH at the electrode surface during oxidation was somewhat lower than

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[10] Weast, W. C. "Handbook of Chemistry and Physics", 51st ed.; CRC Press: Cleveland, Ohio, 1970; p D-120.

in the bulk solution. Addition of buffers, e.g., acetate, decreased the ecl intensity. However, over a pH range of 4–6 with an acetate buffer of the same total acetate concentration the trend in the variation of ecl intensity with pH was qualitatively the same as in the unbuffered solutions.

The ecl efficiency was estimated by comparing the ratio of the integrated light intensity to electric charge passed for the present system to that of the $Ru(bpy)_3^{2+}$–acetonitrile nonaqueous system, whose ecl efficiency is known.[4] In an aqueous deaerated solution of 1.0 mM $Ru(bpy)_3(ClO_4)_2$ and 50 mM $Na_2C_2O_4$, the ϕ_{ecl} calculated in this manner, taking into account that each ecl event requires the transfer of two electrons, was ~2%. In a nondeaerated solution, ϕ_{ecl} decreased to about one-third of this value.

The mechanism of this ecl reaction clearly involves reaction of $Ru(bpy)_3^{3+}$ and an intermediate formed on oxidation of oxalate. The excited state cannot be produced via reaction 5 since the free energies of the $Ru(bpy)_3^{3+/2+}$ and $C_2O_4^{2-}/CO_2$ couples are insufficient.[11] At the applied electrode potential for the ecl generation (more positive than that of the $Ru(bpy)_3^{3+/2+}$ couple), the Pt electrode is covered with an oxide layer, which prevents the direct oxidation of oxalate on the electrode (see Figure 1c). On the other hand, at pH values above ~3, the generated $Ru(bpy)_3^{3+}$ oxidizes the oxalate (as shown in Figure 1e) near the electrode, according to (5). This can be followed by

$$C_2O_4^{-}\cdot \rightarrow CO_2 + CO_2^{-}\cdot \qquad (6)$$

The intermediate radical $CO_2^{-}\cdot$, which results from the one-electron oxidation of oxalate, is a strong reducing agent and can produce the excited state by reacting directly with the 3+ species

$$CO_2^{-}\cdot + Ru(bpy)_3^{3+} \rightarrow CO_2 + Ru(bpy)_3^{2+*} \qquad (7)$$

followed by (2) or possibly by

$$CO_2^{-}\cdot + Ru(bpy)_3^{2+} \rightarrow CO_2 + Ru(bpy)_3^{+} \qquad (8)$$

followed by (1) and (2).

We consider here both (7) and (8) as possible routes for generation of the excited state, although (8) was shown to be more favorable in MeCN.[5]

At lower pHs where the predominant species in solution is $HC_2O_4^-$, one would expect a reaction sequence similar to (5)–(8) with the reactive intermediate now being $CO_2H\cdot$, which would be a weaker reducing agent than $CO_2^{-}\cdot$ This will account for the pH dependence shown in Figure 3, where the increase in the ecl intensity occurs in the vicinity of pK_{a2} of the oxalic acid and roughly follows the fractional concentration of $C_2O_4^{2-}$ in solution. Another factor which may contribute to the increase in intensity with the pH is the shift of the potential for oxidation of oxalate, as shown in Figure 1. The decrease in the ecl intensity above pH 6 is most likely caused by the increasing importance of the oxygen evolution reaction at the electrode, which is shifted to less positive potentials with increasing pH. The increasing importance of the reaction of $Ru(bpy)_3^{3+}$ with water (or hydroxide ion) in this pH region[12] may also play a role in this decrease. Very weak emission exists even at pH values above 10; this is probably caused by the known light-emitting reduction of $Ru(bpy)_3^{3+}$ with OH^- ions.[6]

Note that each oxalate species directly oxidized on the electrode is wasted with respect to the ecl. Since $CO_2^{-}\cdot$ (or $CO_2H\cdot$) is a much stronger reducing agent than $C_2O_4^{2-}$ (or $HC_2O_4^-$), when this intermediate is formed at the electrode surface it will immediately transfer the second electron to the electrode to produce CO_2. The oxide layer on the Pt surface thus prevents the direct oxidation of oxalate at the electrode. This accounts for the experimental observation that the ecl intensity decreases when the oxide layer is repeatedly removed in the pulsed-mode ecl experiments. In this respect, carbon electrodes have the same advantage as oxidized Pt electrodes, since they show a large overpotential for the electrooxidation of oxalate so that it occurs at more positive potentials than those for the reversible oxidation of $Ru(bpy)_3^{2+}$.

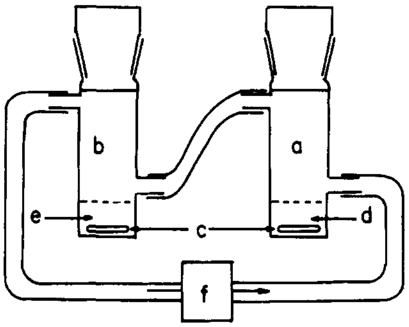

Figure 4. Flow system for continuous light generation: a and b, glass compartments; c, magnetic stirrer; d, solid BaC_2O_4; e, solid PbO_2; f, peristaltic pump.

Solution Chemiluminescence Reactions. Light emission from the same system can be generated not only at an electrode surface but also in homogeneous solution by chemical reaction. Quantitative oxidation of an orange solution of $Ru(bpy)_3^{2+}$ in 0.1 M H_2SO_4, either electrochemically or with PbO_2, produces a green solution of $Ru(bpy)_3^{3+}$. Addition of sodium oxalate (or oxalic acid) powder to this solution immediately results in a very strong orange luminescence. In agreement with the ecl results, only a very low-intensity emission is generated if the same experiment is performed in 1.0 M H_2SO_4. These experiments suggest that the ecl emission is indeed the result of a homogeneous reaction between $Ru(bpy)_3^{3+}$ and oxalate.

Chemiluminescent Systems. The $Ru(bpy)_3^{2+}$–oxalate aqueous ecl system presents some important advantages for possible practical applications. It is an aqueous, very stable, and intense ecl system, relatively insensitive to the presence of oxygen or organic and inorganic impurities. The main disadvantage is that it is not a regenerative system, since oxalate is consumed. Still, because oxalate does not react directly at an oxidized Pt electrode, one can keep an ecl system operating for prolonged periods of time by having a sufficiently large amount of oxalate in the solution. In a typical experiment, a constant anodic current of 6.8 mA cm^{-2} was applied to a Pt flag electrode (area, 0.22 cm^2) in a solution containing 1.0 mM $Ru(bpy)_3(ClO_4)_2$ and 0.25 M $Na_2C_2O_4$ in acetate buffer (pH 4.8). A strong, constant ecl was observed (without stirring) for 20 h, at which time the experiment was terminated.

Another possibility is to make use of a chemical oxidizing agent in a light-generating device. This was done with the flow system shown in Figure 4. The solution flowing in a closed circuit was 1.0 mM $Ru(bpy)_3Cl_2$ in 0.1 M H_2SO_4, and the solids in the two compartments were gently stirred. The slightly soluble BaC_2O_4 in compartment a provides a constant supply of oxalate ions to compartment b, where they react with $Ru(bpy)_3^{3+}$ that was produced by oxidation of $Ru(bpy)_3^{2+}$ by PbO_2. As a result, one observes a constant light emission from compartment b. The use of a slightly soluble oxalate and two separate compartments was dictated by the desire to minimize loss of oxalate and PbO_2 by direct reaction between the two species. Here again the light emission lasted until the oxalate and PbO_2 were consumed.

(B) The $Ru(bpy)_3^{3+/+}$ Regenerative System. $Ru(bpy)_3^{2+}$ provides a regenerative ecl system in acetonitrile,[3] when a Pt electrode potential is pulsed between the oxidation and reduction potentials of the complex

$$Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e^- \qquad (9)$$

$$Ru(bpy)_3^{2+} + e^- \rightarrow Ru(bpy)_3^{+} \qquad (10)$$

followed by (1) and (2). This, however, cannot be achieved in water. $Ru(bpy)_3^+$ is not generated, even at a glassy carbon electrode, which shows a large overpotential for hydrogen evolution. Figure 5 presents the electrochemical behavior of $Ru(bpy)_3^{2+}$ in aqueous solution on glassy carbon electrode. The behavior (on the reduction side) is similar to that with a mercury cathode. On the anodic side, one observes the reversible oxidation

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(11) Latimer, W. M. "Oxidation Potentials", Prentice-Hall: New York, 1952.

(12) Creutz, C.; Sutin, N. *Proc. Natl. Acad. Sci. U.S.A.*, **1975**, *72*, 2858.

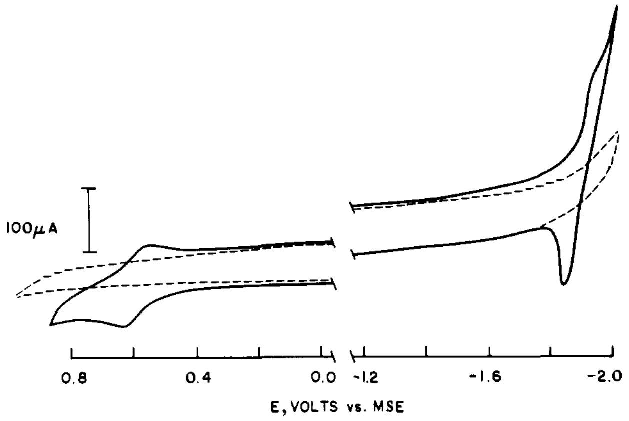

Figure 5. Current–potential curve at steady state for a glassy carbon disk electrode (sweep rate, 200 mV/s) in a solution containing 1.0 mM $Ru(bpy)_3(ClO_4)_2$ in aqueous 0.1 M Na_2SO_4. Dashed curve shows background current in 0.1 M Na_2SO_4.

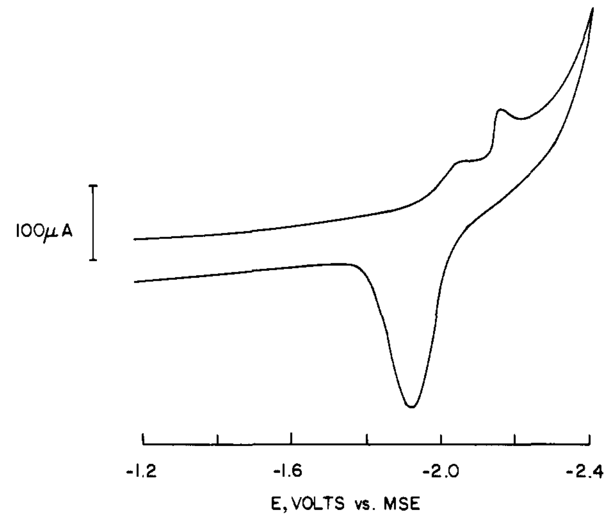

Figure 6. Current–potential curve at steady state for a glassy carbon electrode (sweep rate, 200 mV/s) in H_2O–CH_3CN (1:1 by volume) containing 1.0 mM $Ru(bpy)_3(ClO_4)_2$ and 0.1 M tetramethylammonium chloride.

of $Ru(bpy)_3^{2+}$ (eq 9). On the cathodic side, no reduction wave corresponding to the formation of $Ru(bpy)_3^{+}$ is observed. The cathodic peak preceding the catalytic hydrogen evolution is probably a two-electron reduction leading to formation of $Ru(bpy)_3^0$ accompanied by decomposition and precipitation of Ru^0 species on the electrode. This is evident from the shape of the peaks and also by the observation of decomposition product. If the electrode is held at the cathodic peak potential, the formation of a black precipitate in the solution is seen. No ecl is generated on pulsing the electrode potential between the anodic and cathodic peak potentials.

Upon addition of acetonitrile to the aqueous solution, the electrochemical behavior of the system changes, as shown in Figure 6. A second, more positive reduction peak now appears, which probably corresponds to reaction 10. The height of this $Ru(bpy)_3^{+}$ peak gradually becomes smaller with decreasing percentages of acetonitrile in the solution.

Bright ecl is generated upon pulsing the potential of a glassy carbon electrode between the oxidation peak and the first reduction peak of $Ru(bpy)_3^{2+}$ in an aqueous solution of 1.0 mM $Ru(bpy)_3^{2+}$, which contains at least 20% acetonitrile. Below 20% acetonitrile no ecl is observed. When the negative potential pulse extends to the second reduction peak region, the light emission decreases or even disappears. This aqueous ecl system is not stable for long periods of operation, however. The light intensity decreases during operation and finally stops, within 5–30 min. This is probably the result of the instability of the 1+ complex toward further reduction or decomposition in aqueous solution.

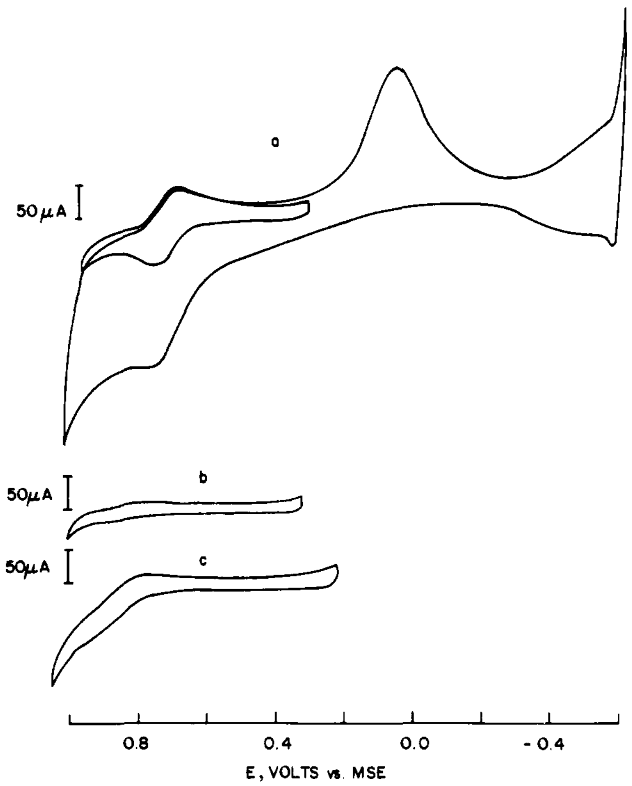

Figure 7. Current–potential curves at steady state for a Pt electrode (sweep rate, 200 mV/s) in 0.1 M H_2SO_4: (a) 5.0 mM sodium pyruvate and 1.0 mM $Ru(bpy)_3(ClO_4)_2$; (b) 0.58 mM $Ce_2(SO_4)_3$; (c) 0.58 mM $Ce_2(SO_4)_3$ and 5.0 mM sodium pyruvate.

(C) Emission with Other Organic Acids. Figure 7a presents the electrochemical behavior of the system $Ru(bpy)_3^{2+}$–pyruvate at a Pt electrode in 0.1 M H_2SO_4. As in the case of oxalate, the oxidation of pyruvate is suppressed by the presence of an oxide layer on the electrode. The potentials for oxidation of the two species are almost identical on a reduced Pt electrode, and the $Ru(bpy)_3^{2+}$ oxidation on oxide-covered Pt is reversible. No ecl is generated upon stepping the potential to values past the peak. All of these observations are similar to the case of $Ru(bpy)_3^{2+}$–oxalate in 1.0 M H_2SO_4. The electrochemical behavior of $Ce^{4+/3+}$ is shown in Figure 7b. Ce^{3+} is reversibly oxidized in 0.1 M H_2SO_4; the peaks appear small because the concentration is low. The results of addition of sodium pyruvate to this system are presented in Figure 7c. On the oxidized Pt, the Ce^{3+} now produces a much larger anodic current, with a very small reverse peak because of the reaction of Ce^{4+} with pyruvate. Since the potential for the oxidation of Ce^{3+} is more positive than that for $Ru(bpy)_3^{2+}$ oxidation in this system, Ce^{4+} is a better oxidant than $Ru(bpy)_3^{3+}$ so that reactions 11–13 are now possible.

$$Ce^{3+} \rightarrow Ce^{4+} + e^- \qquad (11)$$

$$Ce^{4+} + CH_3COCO_2^- \rightarrow Ce^{3+} + CH_3COCO_2\cdot \qquad (12)$$

$$CH_3COCO_2\cdot \rightarrow CH_3CO\cdot + CO_2 \qquad (13)$$

Addition of $Ru(bpy)_3^{2+}$ to this solution and repetitively pulsing to the Ce^{3+} oxidation potential result in the generation of the characteristic orange luminescence at the electrode. No ecl is observed on pulsing only to the $Ru(bpy)_3^{2+}$ oxidation potential. This suggests that the intermediate radical, $CH_3CO\cdot$, is a strong enough reducing agent to participate in electron-transfer reactions with the $Ru(bpy)_3^{3+}$ similar to (7) or (8). The product of the oxidation of $CH_3CO\cdot$ will be the carbonium ion, which will immediately react with water. This is in agreement with the results on the electrooxidation of pyruvic acid in H_2O[13] or methanol,[14]

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(13) Fichter, V. Fr.; Lurie, S. *Helv. Chim. Acta* **1933**, *16*, 885.

where the main products were reported to be acetic acid and methyl acetate, respectively.

Light emission is also observed when a Ce(IV) salt is added to a solution of $Ru(bpy)_3Cl_2$ and sodium pyruvate or when sodium pyruvate is added to a solution of $Ru(bpy)_3Cl_2$ containing an excess of Ce^{4+}. In both cases, an orange light emission immediately appears. The same chemical experiment generates light emission with lactic and malonic acids and probably will occur with other organic acids or salts that can be rapidly oxidized by Ce^{4+}.

Note that one can produce ecl with the $Ru(bpy)_3^{2+}$–oxalate system in 1.0 M H_2SO_4 by adding Ce^{3+} to the solution. The light emission is weak in this case because of the low solubility of Ce(III)–oxalate. A strong emission occurs upon addition of Ce^{4+} to a mixture of oxalate and $Ru(bpy)_3^{2+}$ in 1.0 M H_2SO_4 in the chemical experiment. An interesting point is that in the same system ($Ru(bpy)_3^{2+}$, oxalate, 1.0 M H_2SO_4) addition of PbO_2 causes only a very low intensity light emission, which develops slowly, in spite of the fact that PbO_2 oxidizes both oxalate and $Ru(bpy)_3^{2+}$ very rapidly. This difference in behavior between Ce(IV) and PbO_2 can be explained by the proposed mechanism. Ce^{4+}, which is a one-electron oxidant, reacts with oxalate to form the reactive intermediate very efficiently. On the other hand, on the solid PbO_2 the oxalate undergoes a direct two-electron oxidation which is ineffective for light emission. The low level light emitted by adding PbO_2 is probably only the result of the very slow reaction between $Ru(bpy)_3^{3+}$ and oxalate in 1.0 M H_2SO_4.

Conclusions

A new aqueous chemiluminescent and ecl system based on $Ru(bpy)_3^{2+}$ and a suitable organic acid or salt (e.g., $C_2O_4^{2-}$) is described. The system produces quite bright emission and may be useful in practical ecl devices. The system is an example of a coupled chemical reaction[15] with the observation of light emission as a probe of the reaction mechanism. The Ce^{3+}–oxalate system (or one with another organic acid or salt) provides a unique electrochemical system for carrying out a reduction under oxidizing conditions at the electrode surface (an "anodic or oxidative reduction"). Upon applying a sufficiently positive potential to an oxidized Pt (or carbon) electrode, one promotes the one-electron oxidation of the acid by the Ce^{4+}, creating an intermediate (e.g., $CO_2^{-}\cdot$) which is a strong reducing agent. This intermediate has a sufficiently long lifetime in aqueous solution to be able to reduce other molecules in the solution (e.g., $Ru(bpy)_3^{3+}$ in the light-emitting reaction in 1.0 M H_2SO_4). This system can therefore, in principle, be used for electroreductions in aqueous solution under conditions of mild anodic potential and at a Pt electrode.

Acknowledgment. The support of this research by the Army Research Office is gratefully acknowledged.

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Synthesis of "Face to Face" Porphyrin Dimers Linked by 5,15-Substituents: Potential Binuclear Multielectron Redox Catalysts[1a]

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Received January 25, 1980

Abstract: As part of the development of binuclear transition-metal complexes capable of facilitating multielectron redox reactions of small molecules (such as O_2 and N_2), we have devised an efficient and synthetically flexible route to 5,15-disubstituted porphyrins which affords multigram quantities of isomerically pure porphyrins without recourse to chromatography. The 5,15-substituents are principally amine ($(CH_2)_nNHR$ ($n = 1, 2, 3$; R = H, CH_3)) and acid chloride ($(CH_2)_nC(O)Cl$ ($n = 1, 2$)) groups. Reactions of the two types of substituted porphyrins lead to a new class of "face to face" porphyrins with interporphyrin amide bridges of varying length (4–7 atoms). An amine-linked dimer has been produced by the reduction of an appropriate amide linkage. Purely hydrocarbon-linked dimers have also been prepared by the direct coupling of bis(dipyrrylmethanes) bridged by aliphatic $(CH_2)_n$ ($n = 4, 6$) chains. The dimeric porphyrin compounds have been fully characterized by their visible and NMR spectra. The crystal and molecular structure of the bis(copper(II)) complex of one of the amide-linked dimers, the first such determination of a "face to face" porphyrin, is reported. Crystal data for $Cu_2C_{74}N_{10}O_2H_{86}\cdot 2H_2O\cdot C_7H_8$: space group C_{2h}^5—$P2_1/c$; $a = 11.878$ (6) Å, $b = 13.304$ (7) Å, $c = 23.725$ (13) Å, $\beta = 114.60$ (2)° at −140 °C; $Z = 2$. A crystallographic center of symmetry is imposed on the dimer. The structure was refined on all data including $F_o^2 < 0$ (4663 observations) to values for R and R_w on F^2 of 0.103 and 0.152. For the portion of data having $F_o^2 > 3\sigma(F_o^2)$ (3213 observations) the values for R and R_w on F are 0.063 and 0.073. The spectral properties of these new porphyrin dimers are discussed with reference to the structural analysis. A striking feature of the structure is a shear-like displacement of one porphyrin unit with respect to the other by an average distance of 4.95 Å. The Cu···Cu separation is 6.332 (4) Å and the interplanar separation of the two porphyrin rings is 3.87 Å. In solution at ambient temperatures, conformational changes involving motions of the two porphyrin rings cause considerable line broadening in the ^1H NMR spectra of all 5,15-bridged dimers. However, at temperatures above 90 °C conformational equilibria are sufficiently rapid to produce well-resolved spectra.

Introduction

We have been interested in the development of new catalysts for the direct, four-electron electrochemical reduction of O_2 to H_2O at potentials approaching the thermodynamic value of +1.23 V (vs. the normal hydrogen electrode). In a broader context such catalysts may also promote multielectron-transfer reactions for other small molecules such as dinitrogen. In a recent paper we discussed our approach to the design of multielectron redox

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[1] (a) For a more detailed treatment of materials in this paper see: Schmittou, Eric R. Ph.D. Dissertation, Stanford University, 1979. (b) Natural Sciences and Engineering Council of Canada Postdoctoral Fellow, 1976–1978. (c) National Science Foundation Predoctoral Fellow, 1973–1976.

0002-7863/81/1503-516$01.00/0