

## References and Notes

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- (5) Concentrated solutions containing the two ions are unstable over a period of time. With time, a new band grows in at  $\sim 1190$  nm and the near-infrared spectrum shifts to longer wavelengths. The new absorption band may arise because of the formation of a mixed-valence cyano-bridged ion, a possibility which is currently under investigation. The spectrum in Figure 1 was obtained by rapid mixing in a Cary 17 spectrophotometer so that the extent of the subsequent reaction was negligible.
- (6) The value for  $K_{IP}$  was arrived at using the following equations<sup>7</sup>

$$K_O = \frac{4\pi Na^3}{3000} \exp(-U(a)/kT)$$

$$U(a) = Z_1 Z_2 e^2 / Da(1 + \kappa a)$$

$$\kappa = \left( \frac{8\pi Ne^2 \mu}{1000 Dk_B T} \right)^{1/2}$$

where  $N$  is Avogadro's number,  $Z_1$  and  $Z_2$  are the ion charges,  $e$  is the unit electron charge,  $\mu$  is the ionic strength,  $k_B$  is Boltzmann's constant,  $a$  is the distance of closest approach ( $\sim 8.5$  Å),<sup>8</sup> and  $D$  is the bulk dielectric constant.  $K_{IP}$  and  $\mu$  were arrived at by iterative calculations starting from the formal concentrations of the metal ions employed.
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- (8) Estimated from crystallographic data on  $Fe(CN)_6^{4-}$ <sup>8a</sup> and  $Ru(NH_3)_6^{3+}$ <sup>8b</sup> and the known van der Waals radii for N and H:<sup>8c</sup> (a) A. G. Sharpe, "The Chemistry of Cyano Complexes of the Transition Metals", Academic Press, New York, N.Y., 1976, p 104; (b) H. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971); (c) "Handbook of Chemistry and Physics", 53rd ed, CRC, Cleveland, Ohio, 1973, p D146.
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- (10) Studies currently in progress indicate that it will be possible to make solution measurements on a number of ion pairs between complexes of Ru(III) and  $Fe(CN)_6^{4-}$ ,  $Ru(CN)_6^{4-}$ , or  $Os(CN)_6^{4-}$ .
- (11) Calcd for  $[Ru(NH_3)_5py]_4[Fe(CN)_6]_3 \cdot 7H_2O$ : C, 25.03; H, 5.16; N, 32.26. Found: C, 24.62; H, 4.90; N, 31.86. Calcd for  $[Ru(NH_3)_5py]_4[Ru(CN)_6]_3 \cdot 7H_2O$ : C, 23.29; H, 4.80; N, 30.03. Found: C, 23.19; H, 4.60; N, 29.80. Calcd for  $[Ru(NH_3)_6]_4[Fe(CN)_6]_3 \cdot 5H_2O$ : C, 14.04; H, 5.33; N, 38.23. Found: C, 14.07; H, 5.30; N, 38.00. Calcd for  $[Ru(NH_3)_6]_4[Ru(CN)_6]_3 \cdot 5H_2O$ : C, 12.90; H, 4.90; N, 35.13. Found: C, 12.88; H, 4.65; N, 32.86.
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### Photoelectrochemical Cells Based on Electron-Transfer Quenching of Excited States

Sir:

Electron-transfer quenching of molecular excited states is a common reaction<sup>1</sup> and one which can lead to significant conversion of excited-state energy into stored chemical redox energy on a transient basis. The excited states of metal complexes like  $Ru(bpy)_3^{2+}$  ( $bpy$  is 2,2'-bipyridine) are especially appealing in this regard because the complexes absorb light appreciably in the visible, well-characterized, ground-state, one-electron oxidation and reduction products are known, and the excited states have been shown to undergo both oxidative and reductive quenching (e.g., eq 1 and 2).

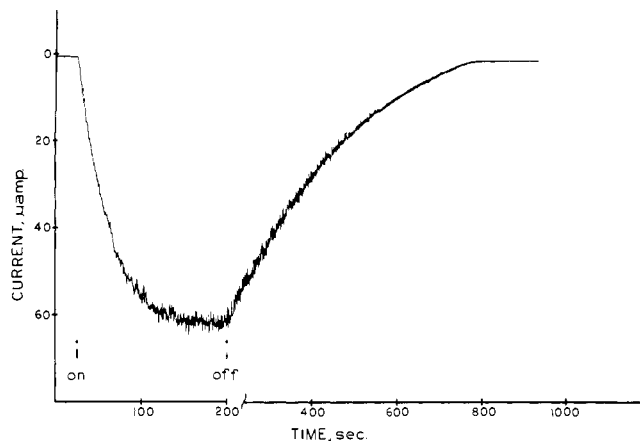
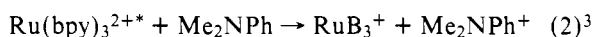
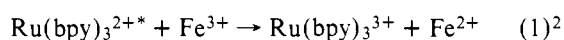
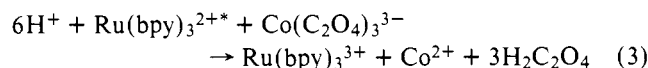


Figure 1. Time dependence of the photocurrent following irradiation at 453 nm of a cell consisting of  $[Ru(bpy)_3^{2+}] = 8.6 \times 10^{-8}$  M and  $[Co(C_2O_4)_3^{3-}] = 2.5 \times 10^{-3}$  M in 1 N  $H_2SO_4$  in the photolyzed cell compartment and  $[Fe^{2+}] = [Fe^{3+}] = 0.01$  M in 1 N  $H_2SO_4$  in a second compartment.

The redox properties of the excited state  $Ru(bpy)_3^{2+*}$  have been used in electrochemical cells to demonstrate direct excited-state quenching at semiconductor electrodes.<sup>4</sup> The difference in quenching (eq 1) and back-electron-transfer rates,  $Ru(bpy)_3^{3+} + Fe^{2+} \rightarrow Ru(bpy)_3^{2+} + Fe^{3+}$ , has also been utilized in a photogalvanic cell.<sup>5</sup> We would like to point out that there are a number of additional electrochemical-excited-state experimental configurations which can be exploited and that the photoelectrochemical cells which result may be useful in providing models for a variety of approaches to solar energy conversion based on molecular excited states.

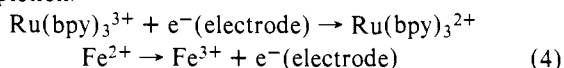
Demas and Adamson<sup>6</sup> have shown that  $Ru(bpy)_3^{2+*}$  undergoes net oxidative quenching by tris(oxalato)cobalt(III) in acid solution to give  $Co^{2+}$  with a quantum efficiency of  $\sim 0.85$ .



Photolysis at 453 nm ( $\pm 10$  nm) of a solution containing  $Ru(bpy)_3^{2+}$  ( $5 \times 10^{-5}$  M) and  $Co(C_2O_4)_3^{3-}$  ( $2 \times 10^{-3}$  M) in 1.0 N  $H_2SO_4$  and a platinum electrode causes a rapid increase in potential as  $Ru(bpy)_3^{3+}$  is produced. The potential increases exponentially and after a few seconds reaches a limiting value of 1.015 V which is that expected for the  $Ru(bpy)_3^{3+/2+}$  couple vs. SCE. At the concentration level used,  $Ru(bpy)_3^{2+}$  absorbs an appreciable amount of light from the ultraviolet through much of the visible region of the spectrum. Making corrections for the amount of light absorbed, essentially identical results were obtained at 405, 500, and 546 nm. The absence of a wavelength dependence is expected since  $Ru(bpy)_3^{2+*}$  is known to form with an efficiency of  $\sim 1$  following photolysis throughout much of the ultraviolet and visible.<sup>7</sup> The initial slopes of the potential curves are dependent on the absorbance of the solution as well as on the output of the irradiating lamp. The long term stability of the cell is limited because of slow oxidation of oxalic acid by  $Ru(bpy)_3^{3+}$ , but there are two points worth noting. The first is that this or a related system may be useful for chemical actinometry since the total number of photons absorbed over a broad wavelength range can be determined by simple potential measurements. The usefulness of the present system below 400 nm is limited by the photoreactivity of  $Co(C_2O_4)_3^{3-}$ ,<sup>8</sup> but other, less photoactive quenchers could also be used.

The second point is that the stored chemical redox energy in the cell can be withdrawn as a current during and following photolysis. In Figure 1 is shown a photocurrent vs. time plot for a photoelectrochemical cell consisting of an illuminated

(453 nm)  $\text{Ru}(\text{bpy})_3^{2+}\text{-Co}(\text{C}_2\text{O}_4)_3^{3-}$  solution as in the previous cell but connected by a salt bridge to a solution containing  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  (0.01 M) in 1 N  $\text{H}_2\text{SO}_4$  and a platinum gauze electrode. The photocurrent arises because of oxidative quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  by  $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$  followed by oxidation of  $\text{Fe}^{2+}$  by  $\text{Ru}(\text{bpy})_3^{3+}$  but through the electrode circuit (eq 4). The photocurrent responds as expected for a diffusion limited electrochemical cell. The current is dependent on electrode area especially in the anode compartment and on the rate of stirring. Currents as high as 60  $\mu\text{A}$  at a light intensity of  $1.5 \times 10^{-9}$  einstein/s were observed which were steady for 15 min or longer. The magnitude of the current is independent of wavelength (at 405, 453, 500, and 546 nm) when differences in absorbance and light intensity are taken into account. Variations in  $[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}]$  over the range  $3 \times 10^{-3}$  to  $5 \times 10^{-4}$  M had no effect on the maximum current over 15-min photolysis intervals, but the initial slopes of the current-time curves did decrease with decreasing  $[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}]$  as expected for a slower rate of quenching of  $\text{Ru}(\text{bpy})_3^{2+}$ .<sup>6</sup> One effect of the diffusion-limited nature of the photocurrents is that significant dark currents are observed when irradiation is stopped. The dark current falls exponentially as eq 4 goes to completion.



Total integrated currents in the  $\text{Ru}(\text{bpy})_3^{2+}/\text{Co}(\text{C}_2\text{O}_4)_3^{3-}\text{-Fe}^{2+}/\text{Fe}^{3+}$  cell were used to calculate quantum yields for  $\text{Fe}^{3+}$  production. The yields for 3-min photolysis intervals were  $0.82 \pm 0.02$  which is in good agreement with the value found by Demas and Adamson for eq 3 showing that the redox equivalents produced photochemically in the  $\text{Ru}(\text{bpy})_3^{2+}/\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$  half-cell are transferred quantitatively through the cell to the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  solution. The quantum yields fall with longer irradiation times (0.74 for 6 min) since the oxalic acid concentration increases with time (eq 3) and oxalic acid begins to compete effectively for  $\text{Ru}(\text{bpy})_3^{3+}$ .

The experiments described here are of limited practical value because of the nature of the chemical systems involved. However, they do serve as prototypes for possible applications in (1) chemical actinometry, (2) photochemical fuel cells or photochemical synthesis cells based on more realistic net quenchers than  $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$  (like  $\text{O}_2$ ), and (3) photochemical water-splitting systems where the necessary catalytic oxidative and reductive parts of the redox chemistry can be dealt with separately and combined in an electrochemical cell. In such cells, it should be possible to obtain photocurrents and  $\text{H}_2$  and  $\text{O}_2$  evolution from separate cell compartments.

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## Highly Discriminative Binding of Nucleoside Phosphates by a Lipophilic Diammonium Salt Embedded in a Bicyclic Skeleton

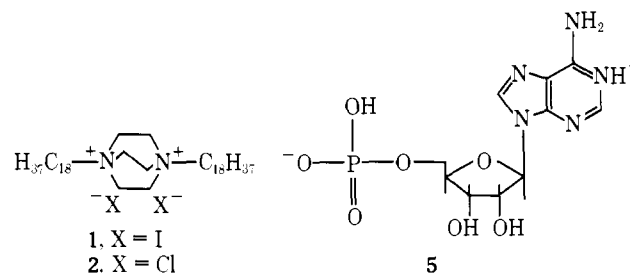
Sir:

Organized interconversions among nucleoside phosphates, AMP, ADP, and ATP are especially important in the sense that chemical energy supplied from outside is stored through the formation of high energy phosphate linkages. Their coupled cleavages provide energy sources for biosynthetic reactions which reverse catabolic pathways and which drive active transport through the cell membrane against electrochemical gradients.

The first crucial key to understanding these processes depends upon the knowledge of how enzymes recognize and discriminate between mono-, di-, and triphosphates. A specific or highly selective ion-ion interaction has been suggested to operate between phosphate and ammonium groupings at the binding site of ATPase<sup>1</sup> or various kinases.<sup>2</sup> The ion-ion and/or ion-dipole interaction is also one of the determining factors in the recognition of neurotransmitters.<sup>3</sup> Thus the investigation of the ion-ion interaction in a medium less polar than water is important to understand these biologically important phenomena.

Here we wish to report that a lipophilic diammonium salt embedded in a rigid bicyclic structure can specifically bind ADP under the condition of no appreciable binding of AMP. This is the first example of artificial molecules which successfully discriminate among nucleoside phosphates.

The diammonium salt was obtained by heating 1,4-diazabicyclo[2.2.2]octane, Dabco (1.0 g, 8.9 mmol), and stearyl iodide (20 g, 53 mmol), in 50 mL of DMF at 70 °C for 2 days. After removing excess stearyl iodide and monoammonium salt, the remaining solid was recrystallized from dimethylformamide to give white crystals of *N,N'*-distearyldiammonium diiodide of Dabco in 83% yield (6.5 g), mp 234–237 °C.<sup>4</sup> The iodide was converted to the corresponding chloride **2** using silver oxide followed by treatment with hydrochloric acid.<sup>5</sup>



An aqueous solution of adenosine phosphates (0.2 and 1.0  $\times 10^{-4}$  M, 8 mL) was shaken at 25 °C with a chloroform solution (8 mL) of **2** (2.5 molar equivalent) or trioctylmethylammonium chloride (Adogen 464) **3** (5.0 molar equiv) at specified pH values, 3.0, 5.0, and 8.0 where AMP (or ADP) is dissociated to the mono(di)anionic species containing protonated adenine, **5**, the mono(di)anionic, and di(tri)anionic forms, respectively, as the predominant species in aqueous solution.<sup>7</sup> The concentrations of phosphate remaining in aqueous solution (and/or extracted into the chloroform layer) were determined by UV spectroscopy from which apparent equilibrium constants were calculated and listed in Table I.

The diammonium salt **2** exhibits a remarkably high selectivity toward the binding of ADP compared with that of AMP. The selectivity ratios of binding,  $K_{\text{ADP}}/K_{\text{AMP}}$ , amounted to 79 and 28 at pH 3 and 5, respectively, at relatively higher concentrations of the diammonium salt and the phosphate. These results strongly support our basic concept that two cationic centers rigidly spaced by embedding them in the rigid bicyclic skeleton should be complementary to vicinal **6** (ADP