Inverted Region Electron Transfer Demonstrated by Electrogenerated Chemiluminescence at the Liquid/Liquid Interface

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We describe several transinterface electron-transfer processes occurring at the benzonitrile (PhCN)/water interface that produce excited states. When an electrode was moved very close to the interface or even through the interface to produce an electrode/thin layer organic phase/aqueous solution configuration, the electrogenerated radical species formed in the PhCN phase (C12−$Ru(bpy)_3^{3+}$, DPA^+, or TH^+) diffused to the liquid/liquid interface to react with (oxidize) a coreactant ($C_2O_4^{2-}$) soluble only in the aqueous solution, leading to the formation of a strongly reducing radical species ($CO_2^{\bullet-}$). The electron transfer from $CO_2^{\bullet-}$ in the aqueous solution to the oxidized species in the organic phase across the liquid/liquid interface produced an electronically excited state which then emitted light. The appearance of an ECL signal in these systems supports the suggestion of Marcus inverted region behavior in very exothermic heterogeneous electron-transfer reactions at the liquid/liquid interface.

Introduction

One of the remarkable predictions made in Marcus electron transfer (ET) theory is the existence of an inverted region,[1] where, under conditions that the free energy ($\Delta G°$) of a very exothermic reaction is greater than the reorganization energy, the ET rate decreases with increasing $\Delta G°$. The earliest experimental verifications of the existence of the inverted region were in studies of electrogenerated chemiluminescence (ECL) reactions.[2,3] ECL arises from an energetic ET reaction between electrogenerated redox species, represented by $A^{\bullet-}$ and $D^{\bullet+}$, which are often radical ions, to form an excited state (A* or D*) that leads to emission:

$$A + e^- \rightarrow A^{\bullet-} \tag{1}$$

$$D - e^- \rightarrow D^{\bullet+} \tag{2}$$

$$A^{\bullet-} + D^{\bullet+} \rightarrow A + D^* \text{ (or } A^* + D) \tag{3}$$

$$D^* \rightarrow D + h\nu \text{ (or } A^* \rightarrow A + h\nu) \tag{4}$$

Basically, in the highly exoergic ET reaction (eq 3), the intersection of the potential energy surface of the reactants with that of the electronic ground-state products produces a large energetic barrier compared to the intersection with respect to one producing an excited state so that the rate of formation of the ground-state products then becomes slow relative to the formation of the excited states. In other words, formation of ground-state species in the high-energy electron-transfer reaction would necessitate production of highly excited vibrational states and the dissipation of the reaction energy as excess heat. Alternatively, the formation of an electronic excited state allows the later dissipation of the reaction energy in the form of an emitted photon (eq 4). Thus, the existence of efficient ECL processes is a good indication of inverted region behavior.

An alternative means of production of ECL utilizes a coreactant species (such as $C_2O_4^{2-}$ or $S_2O_8^{2-}$) in solution, where an ET reaction of an intermediate generated from the coreactant leads to ECL.[4−6] For example, in the system of tris(2,2′-bipyridinyl)ruthenium [$Ru(bpy)_3^{2+}$] and $C_2O_4^{2-}$, the proposed ECL processes are as follows:

$$Ru(bpy)_3^{2+} - e^- \rightarrow Ru(bpy)_3^{3+} \tag{5}$$

$$Ru(bpy)_3^{3+} + C_2O_4^{2-} \rightarrow Ru(bpy)_3^{2+} + C_2O_4^{\bullet-} \tag{6}$$

$$C_2O_4^{\bullet-} \rightarrow CO_2 + CO_2^{\bullet-} \tag{7}$$

$$Ru(bpy)_3^{3+} + CO_2^{\bullet-} \rightarrow Ru(bpy)_3^{2+*} + CO_2 \tag{8}$$

$$Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{2+} + h\nu \tag{9}$$

Marcus has suggested that classical ET theory should be applicable to reactions at the liquid/liquid interface.[7] However, there have been few experimental studies of ET at the interface between two immiscible electrolyte solutions (ITIES).[8] Recently, we have been investigating these processes using scanning electrochemical microscopy (SECM)[9] and have shown that it is a powerful tool for the characterization of ET occurring at the ITIES via a bimolecular reaction between redox species confined to the two different solutions. These studies demonstrated that the ET rate is a function of the potential drop across the interface and that ET theories are applicable to the ITIES. For the first time, inverted region behavior of the heterogeneous high-energy ET process at a liquid/liquid interface with an organized monolayer of surfactant was observed.[9c] More recently, we have suggested similar behavior for a monolayer-free interface.[10]

Here, we describe several ECL processes occurring at the PhCN/water interface. Hydrophobic radical ion precursors of the emitting species were electrogenerated in the organic solution, while the hydrophilic coreactant ($Na_2C_2O_4$) was dissolved in the aqueous solution. When an electrode was brought very close to the liquid/liquid interface through the PhCN layer, an ECL reaction at the ITIES was observed. These ECL processes could also be expressed by eqs 5−9, with reactions 6 and 8 taking place at the ITIES. Figure 1 schematically shows the processes.

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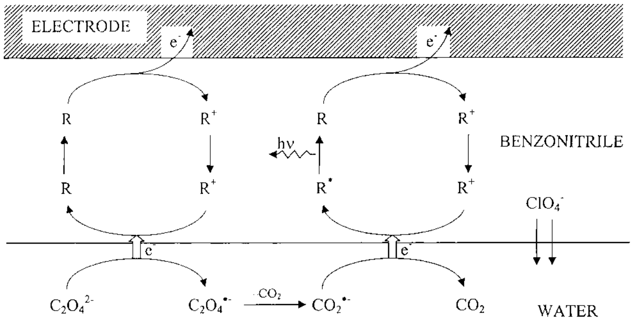

Figure 1. Schematic diagram of the ECL processes occurring at the liquid/liquid interface, where R represents the luminescent species. Electroneutrality was maintained by transfer of perchlorate ions across the interface. For luminescent species (such as C12−Ru(bpy)$_3^{2+}$ and DPA) which can be reduced to radical anions by $CO_2^{\bullet -}$, homogeneous annihilation reactions between radical cation and anion species may also lead to light emission (see text).

Experimental Section

Chemicals. 9,10-Diphenylanthracene (DPA), thianthrene (TH), and PhCN (99%) from Aldrich (Milwaukee, WI), $Na_2C_2O_4$ from J. T. Baker (Phillipsburg, NJ), and $NaClO_4$ from EM Science (Cherry Hill, NJ) were used as received. Tetrabutylammonium perchlorate ($TBAClO_4$, Fluka Chemica, Switzerland) was recystallized twice from acetone/ether and dried under vacuum overnight. The synthesis of the derivative of tris(2,2′-bipyridine)ruthenium(II) followed the procedure reported previously.[11] Tris(2,2′-bipyridine)ruthenium(II) chloride hexahydrate (min. 98%) from Strem Chemicals (Newburyport, MA) was used, and the resulting derivative was (bpy)$_2$−Ru^{II}[bpy-(COOC$_{12}$H$_{25}$)$_2$](ClO$_4$)$_2$, the cation of which will be represented as C12−Ru(bpy)$_3^{2+}$ in following text. All aqueous solutions were prepared from deionized water (Milli-Q, Millipore).

Electrode and Electrochemical Cells. Pt wires of 12.5 and 50 μm radius (Goodfellow, Cambridge, U.K.) were heat-sealed in glass capillaries under vacuum and then beveled to produce SECM tips as described previously.[9] A 0.6 mm diameter Pt disk electrode was used as the working electrode when the ECL intensity was low. These electrodes were polished with 0.05 μm alumina and rinsed with ethanol and water and then dried before each experiment. A three-electrode configuration was employed in all experiments with a 0.2 mm diameter Pt wire serving as the counter electrode and a 0.5 mm diameter Ag wire as a quasireference electrode (AgQRE). A 2 mL glass vial mounted on a vibration-free stage was used as the electrochemical cell. The ITIES was formed by pouring 0.8 mL of an aqueous solution (bottom layer) and 0.7 mL of PhCN solution (top layer) into the vial. Both solutions had been deareated by bubbling N_2 for 15 min. During the experiments, a N_2 atmosphere was maintained above the solutions. Both the counter and reference electrodes were in the organic phase. The concentration of ClO_4^- in both phases was much higher than that of the luminescent species oxidized at the working electrode during the experiment. Therefore, the potential drop across the ITIES did not change significantly throughout the experiment.

Apparatus and Procedure. The SECM instrument consists of a combination of electrochemical components (cell and potentiostat) and those used in a scanning tunneling microscope for manipulating a tip at high resolution (piezoelectric drivers) and acquiring the data (computer/interface). The SECM instrument has been described in detail previously.[12] The ECL intensity was measured with a photomultiplier tube (PMT) installed under the electrochemical cell. Before SECM measurements, the tip electrode was positioned in the top (PhCN) phase and the steady-state voltammogram of the luminescent species was recorded. Then, the tip was biased at a potential corresponding to the plateau current of the oxidation wave. As the tip was approached to the liquid/liquid interface, the tip current, i_T, and PMT output were recorded as a function of d, the distance between the tip and the ITIES. The coordinate of the ITIES ($d = 0$) was determined from the sharp change of i_T that occurred when the tip moved across the ITIES.

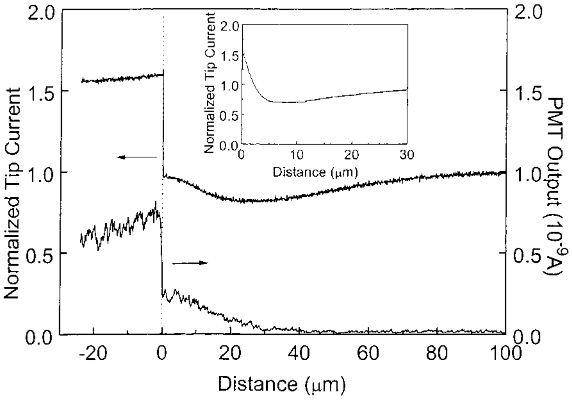

Figure 2. Current−distance and PMT output−distance curves for a 50 μm radius Pt electrode approaching and moving across the PhCN/water interface in the C12−Ru(bpy)$_3^{2+}$ (PhCN)/oxalate (aq) system. Tip potential, 1.3 V vs AgQRE. Tip scan rate, 5 μm/s. Inset shows the current−distance curve obtained with a 12.5 μm radius Pt tip in the same system; tip scan rate, 1 μm/s. Positive distances correspond to the tip approaching the phase boundary; negative distances correspond to thin layer formation in water.

Results and Discussion

To achieve high resolution, the probe tip used in SECM is usually a disk ultramicroelectrode with a radius of 12.5 μm or even smaller. The small tip can be brought precisely to the liquid/solid, liquid/liquid or liquid/gas interface. In the present experiments, however, the ECL intensity was so low that it was difficult to detect with such a small ultramicroelectrode. Therefore, a 50 μm radius electrode was used as the probe. It also behaved like a microelectrode with a fairly stable, diffusion-controlled tip current in a solution containing electrolyte and redox species. Three different systems were examined.

C12−Ru(bpy)$_3^{2+}$ (PhCN)/Oxalate (aq). To avoid the dissolution of the luminescent species in the aqueous solution, C12−Ru(bpy)$_3^{2+}$ was used instead of Ru(bpy)$_3^{2+}$ in this system, 5 mM C12−Ru(bpy)$_3^{2+}$ + 0.1 M $TBAClO_4$ (PhCN)//0.1 M $Na_2C_2O_4$ + 0.1 M $NaClO_4$ (aq). Figure 2 shows the tip current and ECL intensity curves as a 50 μm radius electrode approached the interface from the PhCN side. The tip potential was held at 1.3 V vs AgQRE, and the tip current was controlled by the diffusion of C12−Ru(bpy)$_3^{2+}$ to the electrode and its oxidation to the +3 state. When the tip was brought to the interface within a distance comparable to the radius of the electrode, the diffusion layer of C12−Ru(bpy)$_3^{2+}$ touched the liquid/liquid boundary and feedback effects became important. The tip current first decreased because the liquid/liquid interface blocks the diffusion of C12−Ru(bpy)$_3^{2+}$ to the tip. Then, when the tip was closer, positive feedback appeared and the tip current increased. The feedback current was due to the bimolecular reaction at the interface as C12−Ru(bpy)$_3^{3+}$ reacted with oxalate in the aqueous phase (e.g., eqs 6−8). C12−Ru(bpy)$_3^{3+}$ could also react with H_2O at the interface (formation of O_2 or hydrolylated products of C12−Ru(bpy)$_3^{2+}$), e.g.:

$$2\mathrm{C12{-}Ru(bpy)_3}^{3+} + \mathrm{H_2O} \rightarrow 2\mathrm{C12{-}Ru(bpy)_3}^{2+} + {}^{1}/_{2}\mathrm{O_2} + 2\mathrm{H}^+ \quad (10)$$

Under the experimental conditions, the PMT background output was around 20 pA. When the electrode was far from the interface, no ECL signal was detected. However, when a larger Pt electrode (0.6 mm radius) was used with $\mathrm{C12{-}Ru(bpy)_3}^{2+}$ in PhCN, a very weak background ECL was detected. Weak emission upon the oxidation of $\mathrm{Ru(bpy)_3}^{2+}$ has also been observed in aqueous solutions without coreactant and was attributed to the oxidation of $\mathrm{Ru(bpy)_3}^{3+}$ by some trace impurity.[13] This background ECL signal could not be detected at the 50 μm radius Pt electrode. When the tip was brought very close to the liquid/liquid interface (the distance between the tip and the interface was smaller than 50 μm), an ECL signal appeared and increased rapidly as the tip approached the interface.

Before the electrode touched the interface, the increase of the tip current began to slow. Studies with the SCEM and quartz crystal microbalance (QCM) substrate have shown that the approaching tip, especially at fast *z*-direction scan rates, produces a hydrodynamic disturbance at the substrate.[14] While this effect is small at a solid/liquid interface, it causes a larger disturbance at the ITIES and slightly pushes the interface away from the advancing tip. The approach curves varied with the *z*-direction scan rate and showed larger instabilities of the ITIES at faster approach rates. In the present experiment, a rather large electrode (50 μm radius) was used, and this caused a larger disturbance to the interface than the smaller tips usually used in SECM, so the approach curve deviated from the theoretical behavior. When a 12.5 μm radius electrode served as a probe and a slower approach rate was employed, this problem essentially disappeared (Figure 2, inset).

To make sure that the ECL did not result from a small amount of oxalate dissolving at the interface into the PhCN, the liquid/liquid interface was left undisturbed for several days and then the above experiment was repeated. The result remained the same as shown in Figure 2. Even using the 0.6 mm radius Pt electrode, no ECL signal larger than the background was detected when the electrode was far from the interface. This indicated that the coreactant species ($\mathrm{C_2O_4}^{2-}$) did not diffuse into the PhCN phase to generate ECL by a homogeneous reaction in that phase.

When the tip penetrated the PhCN/water boundary, the ECL signal did not disappear right away. On the contrary, its intensity increased by about 3 times at first and then decreased slowly, lasting for a fairly long time. At the same time, the tip current also increased significantly. This current was not due to the direct oxidation of $\mathrm{C_2O_4}^{2-}$ or $\mathrm{H_2O}$ at the electrode, because when a tip, whose potential was held at 1.3 vs AgQRE, was moved through an air/aqueous solution (containing 0.1 M $\mathrm{Na_2C_2O_4}$, pH = 6.0) interface, the tip current was about 10 times larger than that observed here. In our previous studies, we observed that, when an SECM tip penetrated a liquid/liquid interface, a thin layer of a liquid on the electrode was carried into the other liquid phase forming a trapped thin layer.[9b,15] This SECM thin layer cell technique has been used to carry out the fast heterogeneous kinetic measurements of $\mathrm{C_{60}}$ with a layer of 1,2-dichlorobenzene or PhCN as thin as 10−20 nm trapped inside a Hg pool.[15b] In the present experiment, after the tip penetrated the liquid/liquid interface, a layer of PhCN solution remained at the tip surface. Because the layer was very thin, the feedback current increased significantly, and consequently, a higher ECL intensity was observed. This phenomenon also implied that, when a bigger electrode was used as the SECM tip, the liquid/liquid boundary could not be detected with high sensitivity. In an earlier report, an ultramicroelectrode with a radius as small as 25 nm was used to estimate the thickness of the benzene/water interface with a result of several nanometers or less.[9a] The long-lasting ECL signal and the fairly stable tip current after the tip moved through the interface indicated good stability of this system.

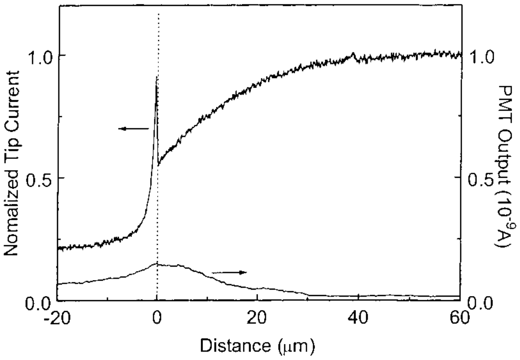

Figure 3. Current−distance and PMT output−distance curves for a 50 μm radius Pt electrode approaching and moving across the PhCN/water interface in the DPA (PhCN)/oxalate (aq) system. Tip potential, 1.3 V vs AgQRE. Tip scan rate, 5 μm/s. Positive and negative distances have the same meaning as in Figure 2.

DPA (PhCN)/Oxalate (aq). Figure 3 shows the approach curve of tip current and PMT output for the system 5 mM DPA + 0.1 M $\mathrm{TBAClO_4}$ (PhCN)//0.1 M $\mathrm{Na_2C_2O_4}$ + 0.1 M $\mathrm{NaClO_4}$ (aq). Near the interface, negative feedback occurred. The reactions of $\mathrm{DPA}^{\bullet+}$ with $\mathrm{C_2O_4}^{2-}$ could also be expressed by eqs 6−8 (replacing $\mathrm{Ru(bpy)_3}^{3+}$ by $\mathrm{DPA}^{\bullet+}$). At the PhCN/water interface, $\mathrm{DPA}^{\bullet+}$ can also react with $\mathrm{H_2O}$ as follows:[16]

$$\mathrm{DPA}^{\bullet+} + \mathrm{H_2O} \rightarrow \mathrm{DPA(OH)}^{\bullet} + \mathrm{H}^+ \quad (11)$$

$$\mathrm{DPA(OH)}^{\bullet} + \mathrm{DPA}^{\bullet+} \rightarrow \mathrm{DPA(OH)}^{+} + \mathrm{DPA} \quad (12)$$

$$\mathrm{DPA(OH)}^{+} + \mathrm{H_2O} \rightarrow \mathrm{DPA(OH)_2} + \mathrm{H}^+ \quad (13)$$

The formation of $\mathrm{DPA(OH)_2}$ consumed some of the $\mathrm{DPA}^{\bullet+}$ species without DPA regeneration and led to the negative feedback. Despite the competition by reactions 11−13, an ECL signal also appeared. However, the ECL intensity in this system was relatively weak compared to the $\mathrm{C12{-}Ru(bpy)_3}^{2+}$ system.

After the tip penetrated the liquid/liquid interface, the ECL intensity first increased slightly and then decreased rapidly. The small amount of the DPA species trapped in the thin layer of PhCN solution at the tip surface was probably consumed rapidly by reactions 11−13. This was also shown in the rapid decrease of tip current.

We also tried to generate ECL at the interface of a PhCN solution containing $\mathrm{C12{-}Ru(bpy)_3}^{2+}$ or DPA and water containing other coreactants, such as tri-*n*-propylamine or $\mathrm{(NH_4)_2S_2O_8}$. However, these coreactant species were soluble in PhCN, so ECL could be generated homogeneously (as indicated by the strong ECL signal that was observed in these systems when the tip was far from the interface) and heterogeneous ECL processes at the liquid/liquid interface were difficult to establish unambiguously.

The above experiments showed that an ECL reaction could occur at the ITIES of suitable systems. In both cases, the probable reaction for excited state formation (eq 8) is direct electron transfer across the liquid/liquid interface from $\mathrm{CO_2}^{\bullet-}$ to the unoccupied orbital of $\mathrm{C12{-}Ru(bpy)_3}^{3+}$ or $\mathrm{DPA}^{\bullet+}$ to

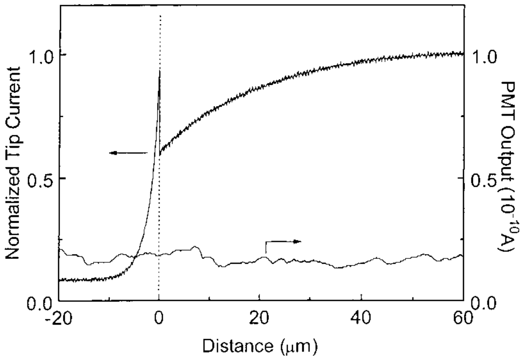

Figure 4. Current−distance and PMT output−distance curves for a 50 μm radius Pt electrode approaching and moving across the PhCN/water interface in the TH (PhCN)/oxalate (aq) system. Tip potential, 1.4 V vs AgQRE. Tip scan rate, 5 μm/s. Positive and negative distances have the same meaning as in Figure 2.

produce the excited state rather than the ground state of the luminescent species. This would constitute inverted region behavior at the ITIES. However, an alternative path is possible, where C12−Ru(bpy)$_3^{2+}$ and DPA could be reduced at the interface.

$$\mathrm{C12{-}Ru(bpy)_3^{2+} + CO_2^{\bullet -} \rightarrow C12{-}Ru(bpy)_3^{+} + CO_2} \quad (14)$$

$$\mathrm{DPA + CO_2^{\bullet -} \rightarrow DPA^{\bullet -} + CO_2} \quad (15)$$

If these reactions occurred, the ECL signals observed in these systems could partially stem from the following annihilation reactions in the PhCN phases:

$$\mathrm{C12{-}Ru(bpy)_3^{3+} + C12{-}Ru(bpy)_3^{+} \rightarrow C12{-}Ru(bpy)_3^{2+}* + C12{-}Ru(bpy)_3^{2+}} \quad (16)$$

$$\mathrm{C12{-}Ru(bpy)_3^{2+*} \rightarrow C12{-}Ru(bpy)_3^{2+}} + h\nu \quad (17)$$

$$\mathrm{DPA^{\bullet +} + DPA^{\bullet -} \rightarrow DPA* + DPA} \quad (18)$$

$$\mathrm{DPA* \rightarrow DPA} + h\nu \quad (19)$$

In these cases, the excited states would be generated via homogeneous reactions and a heterogeneous inverted region reaction would not be established.

TH (PhCN)/Oxalate (aq). Figure 4 shows the tip current approach curve and PMT output for the system 5 mM thianthrene + 0.1 M TBAClO$_4$ (PhCN)//0.1 M Na$_2$C$_2$O$_4$ + 0.1 M NaClO$_4$ (aq). As for the previous system, negative feedback was observed near the interface. However, no emission was detected during the approach process or even after the tip moved across the interface. The reactions between TH$^{\bullet +}$ and C$_2$O$_4^{2-}$ at the interface could be expressed as eqs 6−8 (replacing Ru(bpy)$_3^{3+}$ by TH$^{\bullet +}$). TH$^{\bullet +}$ can also react with H$_2$O as it diffuses to the interface to produce THO as follows:[17]

$$\mathrm{2TH^{\bullet +} \rightarrow TH + TH^{2+}} \quad (20)$$

$$\mathrm{TH^{2+} + H_2O \rightarrow THO + 2H^{+}} \quad (21)$$

After the tip moved across the interface, the tip current decreased dramatically, probably because of the rapid consumption of TH in the thin layer at the tip surface by reaction with water.

TH cannot be reduced by CO$_2^{\bullet -}$ to TH$^{\bullet -}$ because of the large energy required to reduce TH.[18,19] The generation of ECL via annihilation reactions, such as reactions 16−19 in the previous systems, is thus not possible here. The only probable route for ECL would be reactions 6−9 (replacing Ru(bpy)$_3^{3+}$ by TH$^{\bullet +}$). However, in a previous paper,[19] it was shown that the electron transfer between CO$_2^{\bullet -}$ and TH$^{\bullet +}$ was inefficient (for reasons that are not clear). Therefore, a rather low ECL intensity in this system is expected. To increase the ECL intensity, a larger working electrode was tried as the probe.

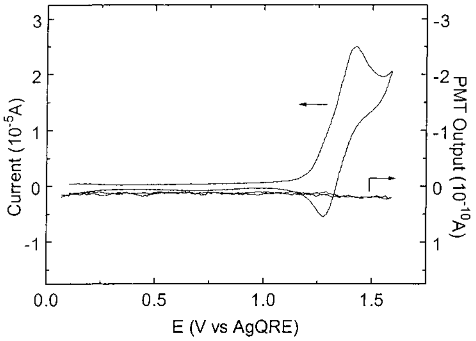

Figure 5. Cyclic voltammogram at a 0.6 mm radius Pt electrode in the organic phase of the TH (PhCN)/oxalate (aq) system far from the interface and the PMT output during the CV. Potential scan rate, 50 mV/s.

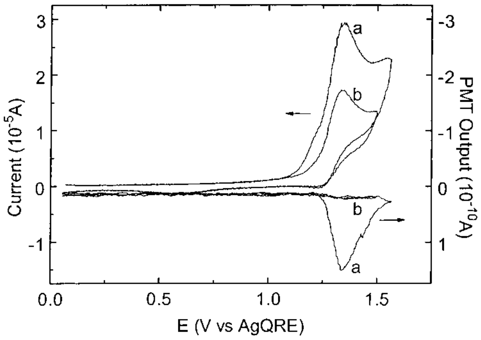

Figure 6. Cyclic voltammograms at a 0.6 mm radius Pt electrode in the TH (PhCN)/oxalate (aq) system after the electrode penetrated the PhCN/water boundary and a thin layer of the organic phase was formed at the electrode surface in the aqueous solution. PMT output was recorded during the CVs. Potential scan rate, 50 mV/s. (a) First cycle; (b) second cycle.

As discussed above, when the electrode penetrated the interface, a very thin layer of the organic solution could be trapped at the electrode surface and more intense ECL could be observed. When a larger Pt electrode (0.6 mm radius) penetrated the PhCN/water interface into the aqueous solution, a thin layer of PhCN could be observed at the electrode surface (a thin red layer of PhCN solution of C12−Ru(bpy)$_3^{2+}$ trapped at the Pt electrode surface could easily be seen). Recently, Shi and Anson[20] employed a similar method for the preparation of thin layers of organic solvents interposed between the surface of graphite electrodes and aqueous electrolytes.

Figure 5 shows the cyclic voltammogram (CV) of a 0.6 mm radius Pt electrode in the organic phase with the electrode far from the interface; the PMT output was also recorded. TH cations were fairly stable, and a reduction peak appeared in the cathodic branch of the CV. A very weak background ECL signal was observed upon the oxidation of TH. After the large Pt electrode moved through the interface, a thin layer of PhCN solution was trapped at its surface. Figure 6 shows the first two cycles of the CV of the thin-layer system. The thin layer at the electrode surface apparently prevented the access of redox species in the aqueous solution to the electrode surface, since no oxidation wave for oxalate was seen. In some cases, when a larger ($a = 1.0$ mm) electrode was used, the thin organic film was apparently incomplete and anodic current attributable to oxalate and water oxidation was observed. In the first cycle, the oxidation current peak shifted slightly to more positive potentials and was slightly higher than that in Figure 5. This probably was caused by the reaction between $TH^{\bullet+}$ and $C_2O_4^{2-}$ at the interface which resulted in the regeneration of TH. In other words, an electrochemical catalytic reaction (EC′) occurred. When a 50 μm radius electrode served as the SECM tip, no positive feedback was observed (Figure 4). Such feedback behavior with different electrode radii has been studied previously.[21] The reduction peak of $TH^{\bullet+}$ in the reverse scan disappeared because of the consumption of the radical cation species by the interfacial reactions. An ECL signal was clearly observed in the potential region where TH was oxidized. During the second cycle, the current for TH oxidation was significantly decreased, probably because of the rapid consumption of TH to produce THO by the reaction between $TH^{\bullet+}$ and H_2O, and the ECL signal became almost undetectable. The products of the reaction between $TH^{\bullet+}$ and water could also have a negative effect on the ECL process. The ~3 s delay for the onset of the ECL signal after the anodic current for TH oxidation commences in Figure 6 probably represents the time required for $TH^{\bullet+}$ to diffuse through the trapped layer to the interface.

The appearance of an ECL signal when TH was oxidized in the first cycle clearly suggests the occurrence of the following reactions despite the possibility of reactions 20 and 21:

$$TH^{\bullet+} + CO_2^{\bullet-} \rightarrow TH^* + CO_2 \tag{22}$$

$$TH^* \rightarrow TH + h\nu \tag{23}$$

Because $TH^{\bullet+}$ reacts rapidly with water,[17] it cannot diffuse an appreciable distance into the aqueous phase and a homogeneous ECL reaction with oxalate is unlikely. Thus, the TH (PhCN)/oxalate (aq) system provides more direct evidence for the existence of inverted region behavior of ET reactions across the ITIES with less ambiguity involving prior reduction and homogeneous radical ion annihilation.

Conclusions

Three systems were examined for the heterogeneous energetic ET reactions to produce ECL at the ITIES. Light emission observed in the experiments indicated the formation of excited states. When the radical luminescent species were consumed by reactions with water at the organic/aqueous solution interface, the ECL intensity was weaker. The ECL reactions occurring at the ITIES provide additional experimental evidence for Marcus inverted region ET across a liquid/liquid interface.

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References and Notes

(1) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1956**, *24*, 966 and references therein.

(2) For review of the ECL, see: (a) Faulkner, L. R.; Bard, A. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1977; Vol. 10, p 1. (b) Knight, A. W.; Greenway, G. M. *Analyst* **1994**, *119*, 879.

(3) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 2654.

(4) Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 512.

(5) White, H. S.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6891.

(6) Leland, J. K.; Powell, M. J. *J. Electrochem. Soc.* **1990**, *137*, 3127.

(7) (a) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 1050. (b). Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 4152; (addendum) *J. Phys. Chem.* **1990**, *94*, 7742. (c) Marcus, R. A. *J. Phys. Chem.* **1991**, *95*, 2010; (addendum) *J. Phys. Chem.* **1995**, *99*, 5742.

(8) (a) Girault, H. H.; Schiffrin, D. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1989; Vol. 15, p 1. (b) Benjamin, I. *Chem. Rev.* **1996**, *96*, 1449.

(9) (a) Wei, C.; Bard, A. J.; Mirkin, M. V. *J. Phys. Chem.* **1995**, *99*, 16033. (b) Tsionsky, M.; Bard, A. J.; Mirkin, M. V. *J. Phys. Chem.* **1996**, *100*, 17881. (c) Tsionsky, M.; Bard, A. J.; Mirkin, M. V. *J. Am. Chem. Soc.* **1997**, *119*, 10785. (d) Delville, M.-H.; Tsionsky, M.; Bard, A. J. *Langmuir* **1998**, *14*, 2774.

(10) Barker, A.; Unwin, P.; Zhou, J.; Amemiya, S.; Bard, A. J. Submitted.

(11) Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 4947.

(12) (a) Kwak, J.; Bard, A. J. *Anal. Chem.* **1989**, *61*, 1794. (b) Fan, F.-R.; Bard, A. J. *J. Electrochem. Soc.* **1989**, *136*, 3216.

(13) Rubinstein, I.; Martin, C. R.; Bard, A. J. *Anal. Chem.* **1983**, *55*, 1581.

(14) Cliffel, D. E.; Bard, A. J. *Anal. Chem.* **1998**, *70*, 1993.

(15) (a) Mirkin, M. V.; Bard, A. J. *J. Electrochem. Soc.* **1992**, *139*, 3535. (b) Mirkin, M. V.; Bulhoes, L. O. S.; Bard, A. J. *J. Am. Chem. Soc.* **1993**, *115*, 201.

(16) Sioda, R. E. *J. Phys. Chem.* **1968**, *72*, 2322.

(17) Murata, Y.; Shine H. J. *J. Org. Chem.* **1969**, *34*, 3368.

(18) Keszthelyi, C. P.; Tachikawa, H.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 1522.

(19) Chang, M. M.; Saji, T.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 5399.

(20) Shi, C.; Anson, F. C. *Anal. Chem.* **1998**, *70*, 3114.

(21) Bard, A. J.; Mirkin, M. V.; Unwin, P. R.; Wipf, D. O. *J. Phys. Chem.* **1992**, *96*, 1861.