Electrogenerated Chemiluminescence

XXXVI. The Production of Steady Direct Current ECL in Thin Layer and Flow Cells

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ABSTRACT

Studies of the ECL of rubrene in thin layer cells containing two gold electrodes separated by 20-500 μm and viewed parallel to the electrode surface are reported. The agreement between calculated and experimental currents and intensities was good and operating lifetimes of 30 min to 4 hr were observed. Flow cells in which solution is recirculated through two mesh electrodes into a mixing chamber where electron transfer and emission occurs are also described. Higher light intensities were obtainable with the flow cells, which appear to be a more favorable configuration for application to ECL devices.

Electrogenerated chemiluminescence (ECL), in which an electron transfer reaction of electrogenerated species produces an electronically excited state (1-2), has been proposed for several types of electrochemical devices, including displays (3), lasers (4-7), and up-conversion devices (8-9). The practical applications of ECL to such devices have been largely hindered by lifetime problems. For directly pumped ECL lasers, which have been discussed but never reduced to practice, two other problems exist. For most ECL cells the reaction zone thickness, which is governed by the dis-

tance the reactants can interdiffuse before reaction, is too narrow to utilize because of optical constraints in laser design. Moreover the current densities achieved with ECL cells have been judged insufficient to generate the needed level of excited states, even with fairly efficient ECL systems (5).

One possible configuration of an ECL laser device involves a thin layer cell in which the solution is confined between closely spaced generating electrodes. A previous study of this cell configuration utilizing transparent tin oxide electrodes spaced a fixed distance (50 μm) (3) apart, with the ECL observed through the electrode, demonstrated the feasibility of this type of cell. To utilize such a cell for a laser in a

waveguide mode, interelectrode spacings of 500-1000 nm are required. We report here experiments with a thin layer cell employing solid electrodes and an adjustable gap, with ECL viewed end-on (*i.e.*, parallel to the electrode surfaces) and an investigation of the effect of interelectrode spacing on ECL intensity, risetime, and lifetime.

An approach to obtaining a wider ECL zone and the required higher current densities (*i.e.*, reactant fluxes) for a laser involves the use of a flow cell arrangement in which the precursor species are brought to the electrodes by convection (as well as diffusion) and the reactants flow together to cause ECL. The construction of flow ECL flow cells is difficult, because the high purity requirements of the solutions and the necessary pretreatment procedures preclude the use of large solution volumes and many solution pumping arrangements. To date the only flow cells reported have been those utilizing the rotating ring-disk electrode (10); this configuration is not useful for the desired applications. We report here the construction of an all-glass recirculating flow cell in which the solution containing the electroactive species is circulated through oppositely polarized Pt mesh electrodes where the reactant radical ions are generated. The solution streams are then mixed in the area just beyond the electrodes and the resulting emission intensity studied as a function of interelectrode voltage and solution flow velocity. The operation, current densities, and lifetime of such a cell is described.

Experimental

Chemicals.—Rubrene, obtained from Aldrich Chemical Company, was recrystallized from hot xylene (under subdued red light) with cold methanol. The orange-red crystals obtained were dried under vacuum at 10^{-5} Torr for 24 hr. Tetra-n-butylammonium perchlorate (TBAP) (polarographic grade, obtained from Southwestern Analytical Chemical Company) was recrystallized from ethanol and dried under vacuum at 100°C. The solvent system used for all thin layer experiments was benzonitrile (BZN) and benzene (BZ). BZN (reagent grade, purchased from Eastman Organic Chemicals) was purified by a previously reported procedure (11) and then distilled from calcium hydride under vacuum. BZ (spectrograde, obtained from Mallinckrodt Chemical Company) was purified as previously reported (12) and then vacuum distilled on to a sodium mirror, permitted to stand for 2 hr, and then distilled into a flask containing Woelm Alumina (Research Organic/Inorganic Chemical Company, Sun Valley, California). Both BZN and BZ were then dried in a Vacuum Atmospheres Corporation (Hawthorne, California) glove box. 1,2-Dimethoxyethane (DME) (Eastman Chemical Company) was vacuum distilled several times from lithium aluminum hydride and then into a clean flask. AN was purified as previously reported (8). Both the AN and DME were stored on a vacuum line and distilled directly into the electrochemical cell.

Apparatus.—The electrochemical cells used are shown in Fig. 1 and 2. The adjustable thin layer cell contained two gold disk electrodes and a platinum quasi-reference electrode. The disk electrodes were constructed by silver soldering a 4 mm diameter, 1 mm thick gold disk to the head of a 2 mm brass bolt. The disk was then machined into a conical shape with the face of the cone perpendicular to the bolt. The electrode could be wrapped with Teflon tape and pressure fit into a Teflon holder. The adjustable holder employed a modified Teflon needle valve (Fischer-Porter Company). The arms of the cell were aligned to ensure that the electrodes were parallel when in position. The electrode separation was determined by measuring the distance between the external electrode contacts with a 4-5 in. micrometer (J. T. Slocomb Company) and normalizing this to the distance mea-
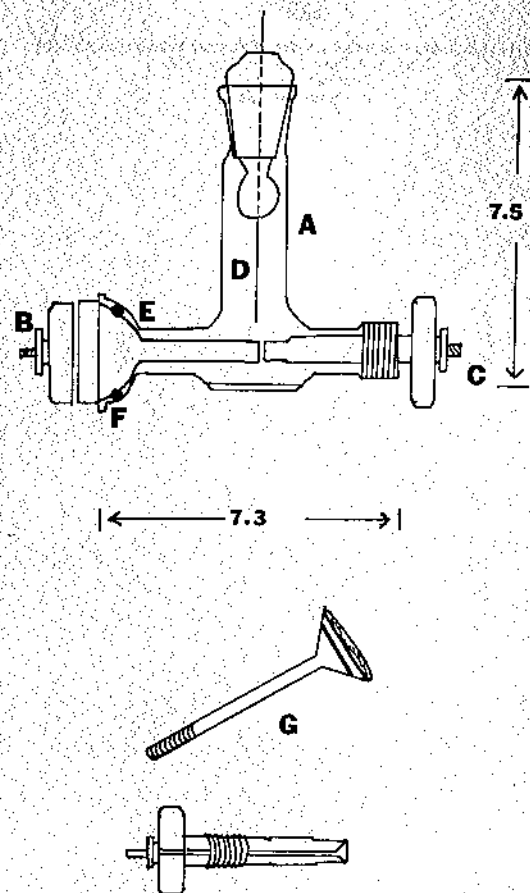

Fig. 1. Thin layer cell. (A) Cell body, (B) stationary disk electrode, (C) adjustable disk electrode, (D) platinum quasi-reference electrode, (E) Teflon O-ring, (F) 18-9 female socket, (G) gold disk (4 mm) soldered onto brass bolt, machined to fit Teflon holder.
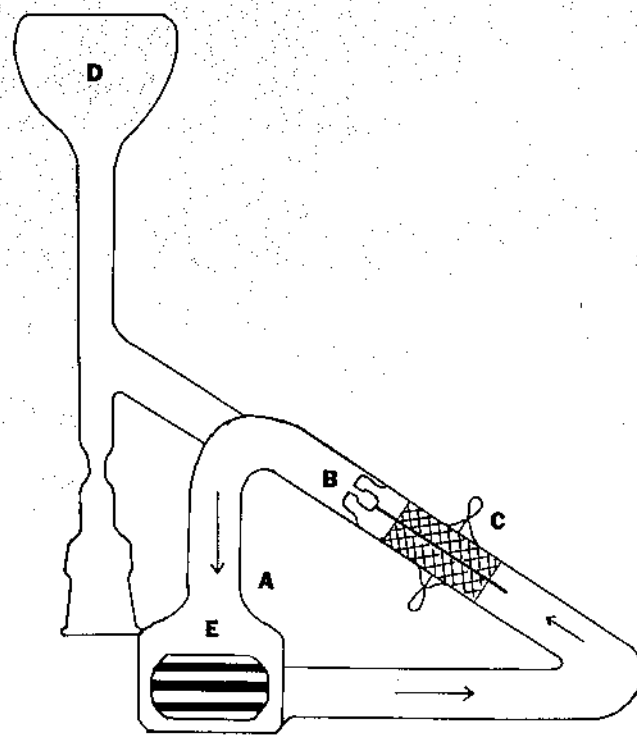

Fig. 2. Pump cell. (A) Cell body with pump, (B) reaction chamber, (C) platinum gauze electrodes with all platinum leads, (D) side arm, and (E) pump with stirring disk.

sured when the separation was zero. All wire and disk electrodes were mechanically polished prior to use with a 0.3 μm polishing alumina (Precision Scientific Company). A Bausch and Lomb dissecting microscope was used to observe the position of the reaction zone and the emission between the electrodes. The flow cell was designed to permit the use of vacuum techniques for solution preparation as well as continuous circulation of the solution. An integral part of the cell is the pump which was made by sealing a Teflon stirring disk (Markson Science Incorporated, Del Mar, California) into a glass cylinder whose dimensions permitted constrained rotation of the stirrer. The solution enters the pump normal to the plane of rotation of the stirrer and exits off-axis and parallel to this plane. The solution is then electrolyzed by two platinum mesh electrodes which are separated by a coarse frit. These two separate streams containing the radical ions then mix efficiently to produce the emission in a confined area (Fig. 3).

All electrochemical experiments were conducted with a combination of a PAR Model 175 universal programmer and a PAR Model 173 potentiostat (Princeton Applied Research Corporation, Princeton, New Jersey). Photometric measurements were conducted with the cell inside of a dark box, using an EG & G Radiometer/Photometer (Model 550-1). The cell current and light intensity were monitored simultaneously on a Moseley Model 7100B dual pen recorder. The rotation rate of the magnetic stirring bar was measured with a Type K53K-AB Strobotac (General Radio Corporation, Concord, Massachusetts).

Procedure

A solution consisting of 4 mM rubrene (R), 0.05M TBAP in a 1:1 mixture of BZN/BZ was used for all thin layer experiments. Although the thin layer cell was air tight, it could not be placed under high vacuum. Thus the solution was prepared in a separate vessel, freeze-pump-thawed several times and returned to the dry box. The cell was then filled, removed from the dry box and reproducibly positioned
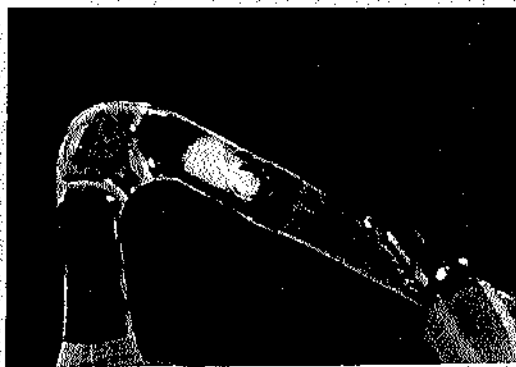
Fig. 3. Flow cell in operation. (A) Reaction chamber, (B) entire pump cell.

above the radiometer inside the dark box. The thin layer experiment consisted of first using cyclic voltammetry to characterize the solution and insure system purity. ECL was generated in the two electrode mode by applying a potential, ΔE, between the electrodes $[\Delta E \cong E_{pa} (R^{\overset{+}{\cdot}}/R) - E_{pc} (R^{\overset{-}{\cdot}}/R) + iR_s]$ (where E_{pa} and E_{pc} are the cyclic voltammetric peak potentials for the anodic and cathodic waves, i is the current, and R_s is the cell resistance). The equal areas of the electrodes yields equal current densities at anode and cathode and the chosen ΔE value prevents formation of the very reactive dication or dianion species. Because the process involved is diffusion controlled, the cell current, ECL intensity and diffusion time can be studied as a function of the distance separating the electrodes. These experiments were carried out and results compared to the theoretically expected values.

Flow cell experiments were conducted using 4 mM rubrene and 0.1M TBAP in AN/BZ solutions. The flow cell was equipped with a side arm where the solution was prepared, freeze-pump-thawed and then gravity transferred to the cell itself. The solution could then be circulated through the cell and the potential difference (ΔE) applied to the two electrodes.

Results and Discussion

Thin layer cell.—Typical results of thin layer cell experiments are shown in Fig. 4-9. When the voltage step ΔE is applied, current flow begins and quickly attains a steady-state value; the emission commences when the diffusing reactant streams merge after a time controlled by the interelectrode separation (Fig. 4). Experimental values obtained for the steady-state
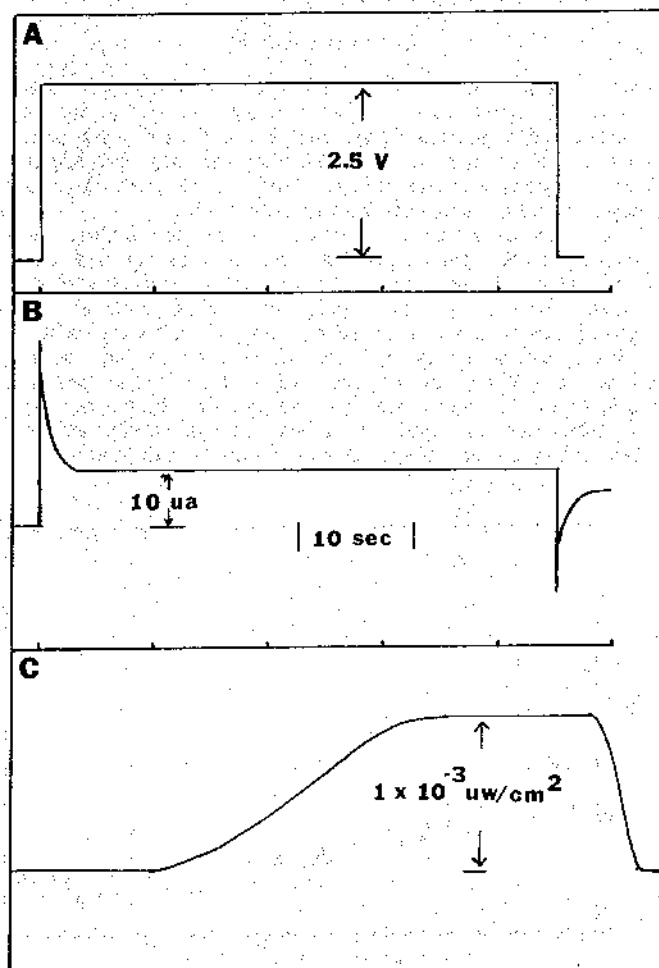

Fig. 4. Typical thin layer experiment. (A) Potential program, (B) current response, (C) resulting ECL intensity. 4 mM rubrene 0.05M TBAP in 1:1 mixture of BZN:BZ, electrode separation = 0.02 cm.

current, i_{ss}, compared to those calculated as a function of electrode separation by Eq. [1] are shown in Fig. 5

$$i_{ss} = nFAD \ (\Delta C/\Delta X) \qquad [1]$$

where n is the number of electrons consumed per molecule in the electrode reaction; F is the Faraday (96,487 C/equiv.); A, the average electrode area (0.141 cm²); D, the diffusion coefficient of rubrene; $\Delta C/\Delta X$, the concentration gradient of radical species at steady state. D for rubrene was determined by chronoamperometry (14) to be 3.1×10^{-6} cm²/sec; this value agrees with that previously found for rubrene in BZN (15) and was used in all theoretical calculations. The i_{ss} values were calculated by assuming that a complete annihilation reaction occurs at the center of the cell so that the rubrene concentration there is equal to its initial value, C (4 mM), while the concentration at each electrode was essentially zero. Thus $\Delta C = C$ for $\Delta X = d/2$ or

$$i_{ss} = 2nFAD \ C/d \qquad [2]$$

The experimental results obtained are in good agreement with those calculated from [2] at electrode separations above 200 μm. At smaller separations the deviation from the theoretical behavior can be rationalized by uncertainties in the determination of the interelectrode distance, d.

The d-c emission that appeared was less intense than that found with 1 Hz alternating pulses in the same solutions but was easily visible. As expected the intensity and time for the appearance of the ECL resulting from d-c electrolysis was a function of the electrode separation. The ECL intensity can be related to cell current by Eq. [3] (16)

$$I_{ss} = \phi_{ECL} \ i_{ss}/nF \qquad [3]$$

where ϕ_{ECL} is the ECL efficiency and I_{ss} the total emission from the cell at steady state. I_{ss} can be calculated from the measured ECL intensity by using a detector of known area and then making the appropriate geometric corrections (for the amount of emission which does not strike the detector).

In this experiment the geometric corrections are based on the fact that the emission is formed in a very thin disk-shaped reaction zone sandwiched between two zones of highly absorbing radical ions which are in turn bounded by the gold disk electrodes. The presence of such high concentrations of radical ions on either side of the reaction zone has several effects on the geometry of the system. First, no corrections need be made for electrode reflectivity effects. Second, a correction must be made for the fraction of

the ECL absorbed by the radical ions. This was estimated to be 97% based on the dimensions of the area between the electrodes. Finally, one must realize that the emission which is not absorbed leaves the reaction zone at a very restricted, slightly diverging, angle. Therefore, the photodiode (area = 1 cm², diam 1.13 cm) was placed 3.6 cm below the cell to insure that the width of the emission was smaller than that of the diode. For this reason the projected image was taken as a ring (radius = 3.6 cm, width = 1.13 cm) and a surface area correction (25.6 cm² : 1 cm²) could be made. No corrections were made for solution absorbance or inner filter effects because the fluorescence efficiency was taken as unity (15) and the photodetector was wavelength independent. The resulting ECL intensity (μW/cm²) was converted to number of photons using Eq. [4] (17)

$$I \ (photons/sec) = \frac{(total \ watts) \ (6.24 \times 10^{18})}{1239.8/\lambda \ (nm)} \qquad [4]$$

and plotted vs. electrode separation in Fig. 6. A plot of i_{ss} vs. I_{ss} for different values of electrode separation is shown in Fig. 7. Although the data are very scattered the slope of the line (least squares) corresponds to $\phi_{ECL} = 0.013$, which is within the accepted range of reported values for the rubrene system.

The time required [after the application of the voltage (ΔE) to the cell] for the reactants to diffuse together and for ECL to appear can be approximated by Eq. [5] (3)
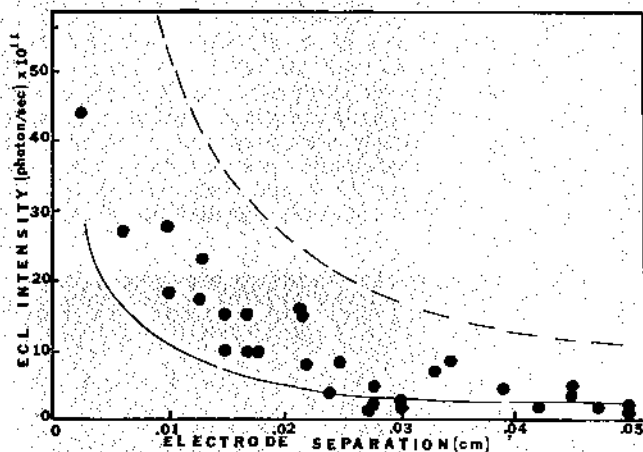

Fig. 6. Plot of ECL intensity vs. electrode separation. ―――, Theory ($\phi_{ECL} = 0.025$); ●, experimental; ――――, theory ($\phi_{ECL} = 0.005$). Solution the same as in Fig. 4.
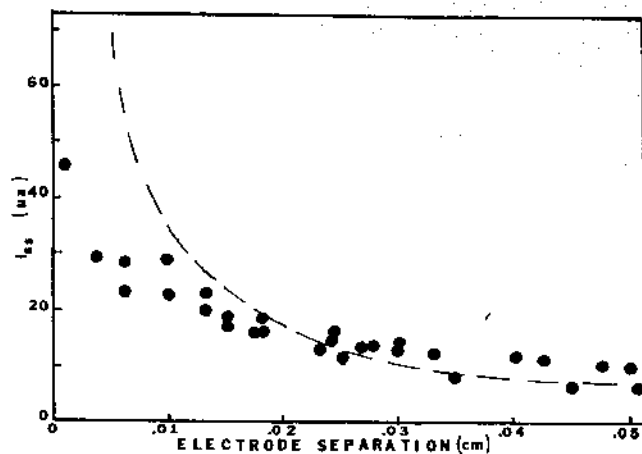

Fig. 5. Plot of steady-state current (i_{ss}) vs. electrode separation. ――――, Theoretical; ●, experimental. Solution the same as in Fig. 4.
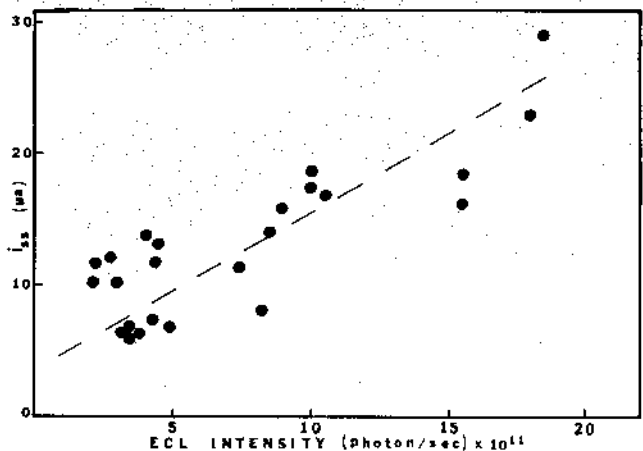

Fig. 7. Plot of steady-state current (i_{ss}) vs. steady state ECL intensity for various values of electrode separation. Solution same as in Fig. 4.

$$t(\text{sec}) = \frac{d^2(\text{cm})}{16\,D} \qquad [5]$$

From this equation and the previously calculated diffusion coefficient, a comparison can be made between the calculated time needed for ECL to appear and the experimental results at different values of d. The results given in Fig. 8 show quite good agreement with the approximate equation. When the thin layer gap was observed under 8× magnification with a simple dissecting microscope, we found that the ECL did not occur in the exact center of the spacing between the electrodes. The reaction zone was clearly closer to the cathode with BZN/BZ as solvent and closer to the anode with DME. This can be explained by the slight instability of the anion or cation in the various solvents.

The operating lifetime of a single thin layer experimental cell was studied because of the great interest in application of the technique for displays or for use as a laser. The solutions were first subjected to cyclic voltammetry and fluorescence measurements before the experiment was actually begun. An initial cyclic voltammogram is shown in Fig. 9. The experiments were then conducted as described. The cell was permitted to remain on until the light intensity reached its steady-state value (200 sec). The cell was then turned off, and the ECL intensity decayed to zero. The results were very reproducible (within 5%) for repetitive experiments (ca. 30) over a period of 4 hr. When the cell was kept turned on and the experiment was permitted to continue well beyond 200 sec, the light intensity would remain relatively constant for 30 min. After this time the light would decrease at a constant rate until it finally dropped below a detectable level (~5 hr). When another experiment was attempted immediately, no light was detected. If the electrodes were separated, the solution stirred, and the electrodes repositioned with fresh solution from the reservoir in the gap, ECL was obtained but the intensity was about an order of magnitude smaller than the original experiment. Cyclic voltammetry revealed a reducible impurity with this solution, and fluorescence measurements showed a small amount of product that emits a 420 nm. If these experiments are continued, eventually all the electroactive species is consumed. Note also that successful long duration electrolysis in a solution containing 0.05M TBAP was accomplished here, while in a previous study (3) lifetimes of only 3-5 min were found.

Flow cell.—The results of the flow cell experiments showed this technique to be capable of producing stronger and longer lasting emission. In this mass transfer controlled system, the cell current and ECL intensity attained their limiting values very quickly
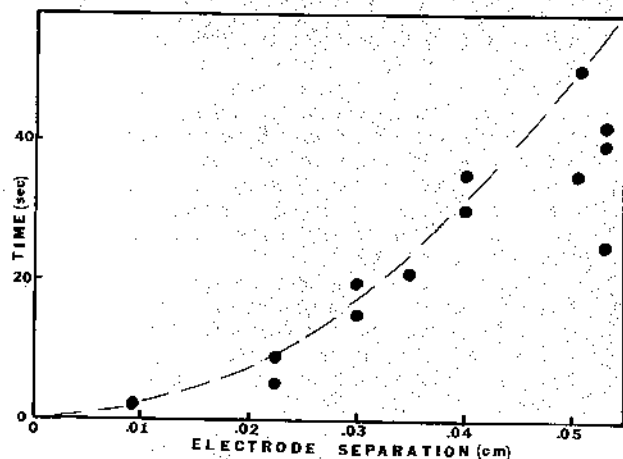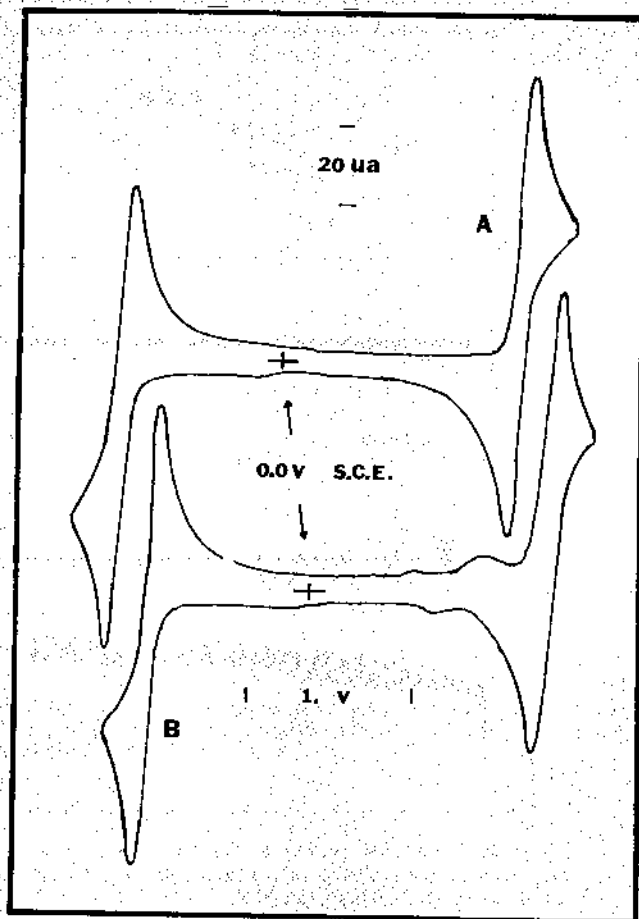

Fig. 9. Cyclic voltammograms of 4 mM rubrene/0.05M TBAP/BZN/BZ solution; (A) before thin layer experiment, (B) after 4 hr of thin layer experiments. Scan rate (v) = 100 mV/sec. Solution same as in Fig. 4.

after application of the d-c voltage (Fig. 10). Both of these quantities oscillated slightly because of fluctuations in the flow rate of the solution. This effect is also seen in Fig. 11 and 12 which show the dependence of the cell current and ECL intensity on the stirring rate and cell potential. The operating lifetime of this system greatly exceeded that of the thin layer cells. This can be attributed to the larger flux of radical ions and shorter lifetime required for the radical ions before the electron transfer reaction. In a typical experiment the ECL initially occurred solely in the mixing chamber. The emission produced was continuous and could be controlled by the flow rate of the solution. During electrolysis, if the flow rate was stopped for 30 sec and then restarted, light pulses an order of magnitude more intense than the continuous level were obtained. At this point in the experiment the radical ions were very stable. In fact, during a stop flow experiment, the electrolysis could be stopped for several minutes before the pump was restarted and the light pulse obtained was relatively unchanged. After about 2 hr when the ECL began to fail, the emission was observed to stream from one of the electrodes. This can be attributed to a difference in the radical ion stabilities, as observed also in the thin cell experiments. In this case, an instability of one of the species causes an excess of the opposite species after the mixing process. This excess is circulated throughout the whole solution volume, and results in emission at the electrode where the less stable radical ion is formed as the more stable radical ion reaches it. This was verified by producing an excess of the less stable species (using a 3 electrode system). By purposeful generation at an excess of one species the
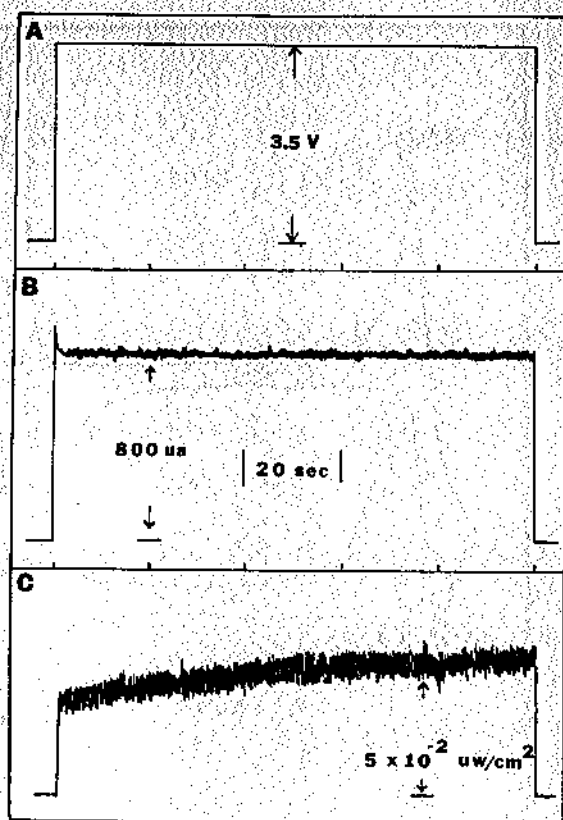

Fig. 8. Effect of electrode separation on time of ECL appearance. ----, Theoretical; ●, experimental. Solution same as in Fig. 4.

Fig. 10. Typical flow experiment. (A) Potential program, (B) current response, (C) resulting ECL intensity. Stirring rate ≅ 500 rpm, 4 mM rubrene/0.1M TBAP/ACN/BZ.
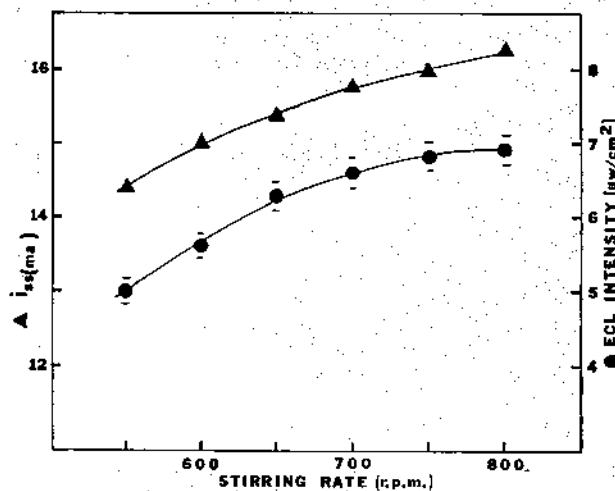

Fig. 11. Flow rate dependence of ECL. No geometric corrections made. Solution same as in Fig. 10.

Fig. 12. Potential dependence of ECL. No geometric correction made. Stirring rate ≅ 600 rpm. Solution same as in Fig. 10.

streaming effect could not only be eliminated but it could be forced to occur at the opposite electrode. Such an ion degradation process tends to cascade and eventually all of the emission appeared at one electrode and not in the mixing chamber. Finally after about 30 hr the ECL ceased.

Fluorescence analysis showed only a trace amount of rubrene remained while revealing a large amount of product emitting at 420 nm. Further extraction shows two crystalline products (yellow and brown) with fluorescent maxima corresponding to 400 and 425 nm. Mass spectroscopic data showed that the products were isomers of dihydrorubrene. This finding is in agreement with that described by Moreu et al. (18) in the synthesis of dihydrorubrene.
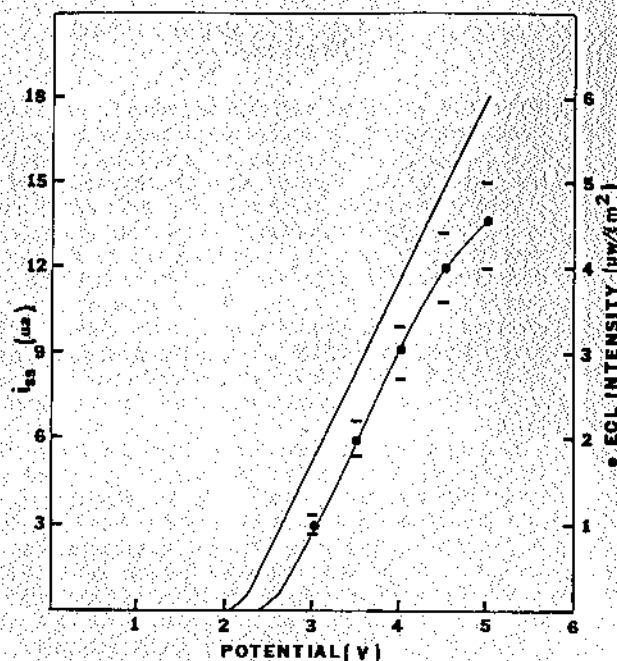
Conclusions

In this paper the feasibility of the development of an ECL device has been studied. Parameters affecting the electrically induced emission have been examined in both diffusion and convective modes. The results show that flow techniques do indeed have advantages over thin layer techniques for the production of continuous ECL. The thin layer mode of ECL formation is seen to be an impractical source of emission for an ECL device. The emission from this diffusion-controlled process is weak and is confined to a very narrow area, sandwiched between two zones of the highly colored radical ions. The lifetime of this d-c emission (5 hr) proved to be much greater than that previously published (3), but still unsatisfactory for any practical application. A major problem with this configuration appears to be the very small volume of solution confined between the electrodes. This volume is very susceptible to impurities which are either initially introduced or electrochemically generated. Detrimental side reactions which occur under these conditions, cause depletion of the electroactive species or formation of species which can effectively quench the ECL. These findings, along with the reaction zone geometry problem, suggest that the thin layer cell will not be useful for laser applications.

A better approach to this problem would be to utilize a flow system for the production of ECL. This method produces stronger emission due to the larger radical ion flux and the shorter radical lifetimes necessary for anion-cation annihilation. Buildup of impurities is minimized, and they are distributed through a much larger volume of solution. By making physical improvements on cell design (e.g., larger electrodes, faster mixing) one could perhaps increase the ECL intensity an order of magnitude but probably not much more than this.

These experiments were performed using one of the better chemical systems known for the production of ECL. Even this system eventually failed. The mechanism for this failure is still not well understood, but at least partially occurs because of degradation of the parent molecule.

Acknowledgment

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