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Ultrasonic Modification of Light Emission from Electrochemiluminescence Processes

Christopher Malins,[†,‡] Robert Vandeloise,[†] David Walton,[§] and Emile Vander Donckt*,[†]

Service de Chimie Organique Physique, Faculté des Sciences, Université Libre de Bruxelles,
C. P. 160/08. Av. F. D. Roosevelt 50, 1050 Brussels, Belgium, and School of Natural and
Environmental Sciences, University of Coventry, Priory St. Coventry CV1 5FB, U.K.

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The influence of ultrasonic irradiation on the electrochemiluminescence evolved from the electrochemical oxidation reaction of tris(2,2′-bipyridyl)ruthenium(II) chloride [$Ru(bpy)_3Cl_2$] or tris(1,10-phenanthroline)ruthenium (II)chloride [$Ru(phen)_3Cl_2$] in aqueous oxalate has been examined. Under the conditions described here, insonation resulted in an increase in the luminescence yield of over 100%, in a highly reproducible manner. These effects were found to result from ultrasonic irradiation and can be understood with reference to the changes in mass transport of reactants through the bulk solution and modification of the electrode Nernst diffusion layer that have been observed by other workers. A relationship between the light intensity and the square of the cell current was observed under various ultrasound powers, and it was found that this is consistent with the kinetic scheme proposed by Bard *et al.* for the electrooxidation reaction under silent conditions. This indicates that the reaction mechanism under insonation is consistent with that proposed for the silent reaction. The electrochemiluminescence spectrum under insonation was measured with greater precision than previously and was shown to be identical to that under silent conditions. Luminescence quenching by oxygen, problematic in earlier reports, was measured under insonation and also with greater precision than previously in the silent system. The Stern−Volmer relationship was obeyed under both sets of conditions, and oxygen quenching phenomena appear to be unaffected by insonation of the system.

Introduction

The application of ultrasound to electrochemical processes (sonoelectrochemistry) is an area of research that is currently attracting an increasing amount of interest due to a number of advantages that this technique possesses over conventional electrochemical methods.[1−3] The use of ultrasound in electrochemistry is emerging as a way both of augmenting traditional techniques to improve the efficiency of well-studied electrode processes and, in certain cases, to facilitate new electrochemical reaction pathways.[4] Recent applications involve the improvement of light output from well-studied electrochemiluminescence (ECL) reactions[5,6] and the diminution of passivating electrode films[7,8] that often form as a consequence of electrode processes.

Cavitational collapse[9] and microstreaming phenomenon near the electrode have the effect of simultaneously increasing the active surface area of the electrode[7] and preventing the formation of passivating films. Ultrasound provides a source of agitation to the whole system, increasing the mass transport across the electrode double layer, which is no longer simply limited by diffusion.[10] Ultrasonic degassing helps to reduce the aggregation of gas bubbles at the electrode surface,[11] leaving a larger active surface area. This is particularly relevant when working in aqueous media, where solvent electrolysis results in gaseous products.

In this study we present a quantitative account of a series of related experiments on the electrooxidation of $Ru(bpy)_3Cl_2$ or $Ru(phen)_3Cl_2$ in aqueous oxalate.[12−15] In these reactions the excited state of the ruthenium complex is produced at the working electrode and relaxes with the emission of red/orange light ($\lambda_{max} = 610$ and 590 nm, respectively). There has been some discrepancy in literature reports of this ECL system, both with and without ultrasound. Here we provide a thorough account of physicochemical parameters in both silent and insonated systems.

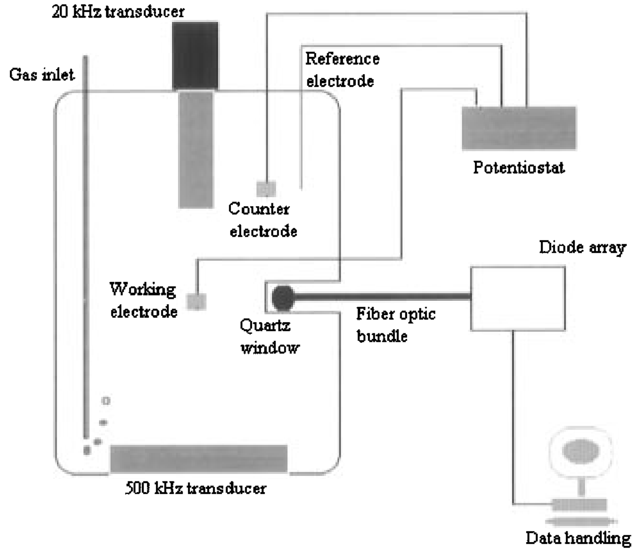

Figure 1. Schematic representation of the sonoelectrochemistry cell.

Experimental Section

Electrolyses were carried out at +1.2 V (*vs* Ag) in a dedicated cell (see Figure 1) of total volume 500 mL, using a EG & G Princeton Model 323 scanning potentiostat with platinum flag electrodes (25 mm^2) and a silver wire reference electrode. Ultrasound was applied at 20 kHz using a Undatim Ultrasonics horn fitted with a titanium tip of area 3 cm^2, or 1.5 cm^2 where

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[*] To whom correspondence should be addressed.

[†] Université Libre de Bruxelles.

[‡] Current address: Biomedical and Environmental Sensor Technology Centre, Dublin City University, Dublin 9, Ireland.

[§] University of Coventry.

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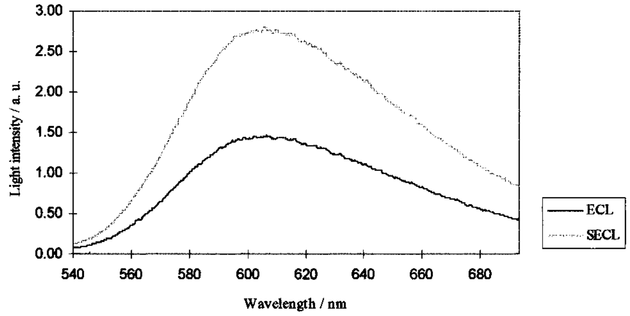

Figure 2. Light intensity against wavelength for the electrooxidation of a 200 μM solution of $Ru(bpy)_3Cl_2$ under insonation (SECL, 20 kHz, 50 W cm^{-2}) and in silent conditions (ECL) in aqueous oxalate.

stated. Ultrasound at 500 kHz was applied using an Undatim Ultrasonics generator and piezoelectric transducer of area 10 cm^2. Calorimetric calibration[10] was carried out to quantify the power outputs of the 20 kHz ultrasonic generator (calibration of the 500 kHz transducer using this method proved inadequate and so the electrical input power is given) with this experimental arrangement, and therefore, within the assumptions implicit in this treatment, all power ratings given in the text are that part of the ultrasound that is converted to thermal energy. All solutions were saturated with nitrogen gas (99.999%, L'Oxhydrique) except where stated, prior to and during experimentation. Light emanating from the working electrode was collected with a glass fiber-optic bundle ($\Phi = 3.2$ mm) and examined using a Hamamatsu C4560 diode array spectrometer and light amplification unit with dedicated software. Light intensities were obtained after an integration time of 2.5 s, which is small in comparison to insonation time. The working electrode was positioned 30 mm away from the ultrasonic source perpendicular to the ultrasonic horn tip and 5 mm away from the end of the fiber-optic bundle. The electrode was prepared prior to each experiment by first polishing with diamond paste (Diamant Boart, 20−40 μm reducing to 0.5−3 μm particle size) and then by exposure to ultrasound (20 kHz, 50 W cm^{-2}) in deionized water for a period of 5 min at a distance of 30 mm, with the surface of the electrode positioned parallel to the surface of the transducer. $Ru(bpy)_3Cl_2$, $Ru(phen)_3Cl_2$, and sodium oxalate were obtained from Aldrich Chemicals Ltd. and used without further purification. Solutions of the ruthenium complexes were made in deionized water with a large excess of sodium oxalate (0.01 M). Thermostatic control of the system maintained a bulk solution temperature of 15 ± 2 °C throughout experimentation. A Hewlett Packard 8452A diode array spectrophotometer with dedicated software was employed for absorption spectroscopy, and a Shimadzu RF-500 PC spectrofluorophotometer with dedicated software was used for luminescence studies. Solutions were saturated with a range of standard gases (L'Oxhydrique; 1 ± 0.05%, 5 ± 0.05% O_2 in N_2, 99.998% O_2, 99.999% N_2) and air, prior to luminescence analysis.

Results and Discussion

Previous studies concerning the ultrasonic modification of the luminescence of the electrochemically produced excited state of $Ru(bpy)_3Cl_2$ have noted that exposure of the working electrode to ultrasound results in an observable enhancement of the light emitted during the reaction.[5,6] The shape of the electrochemiluminescence spectrum is the same with or without exposure to ultrasound (see Figure 2) and identical to that measured by conventional fluorometry. These spectra are recorded on an automated spectrophotometer with high sensitivity and supersede those reported earlier by one of us,[5] which were obtained on low-gain apparatus with manual wavelength manipulation. Although sonoluminescence is seen to occur in water exposed to ultrasonic irradiation,[16−18] the light levels involved in such processes are very small compared to the emission of the bright red/orange luminescence involved with relaxation of the excited ruthenium complex and are, therefore, as in previous studies, insignificant.

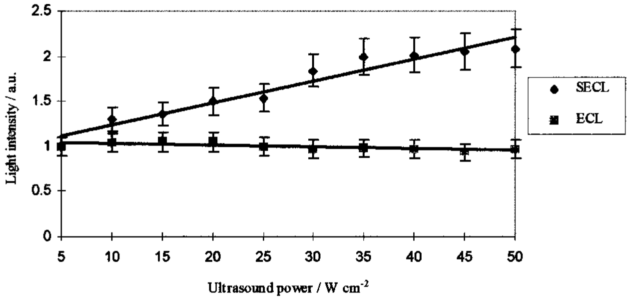

Figure 3. Light intensity against ultrasonic power (20 kHz) for silent (ECL) and insonated (SECL) conditions for a 500 μM aqueous solution of $Ru(bpy)_3Cl_2$.

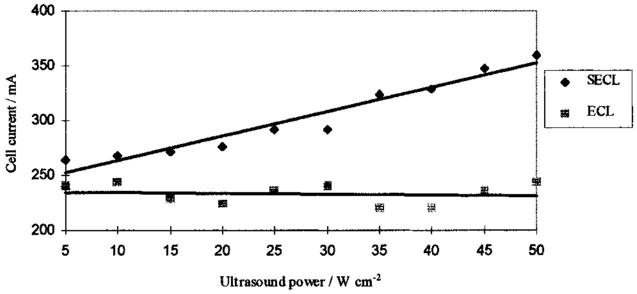

Figure 4. Cell current against ultrasonic power (20 kHz) for silent (ECL) and insonated (SECL) conditions for a 500 μM aqueous solution of $Ru(bpy)_3Cl_2$.

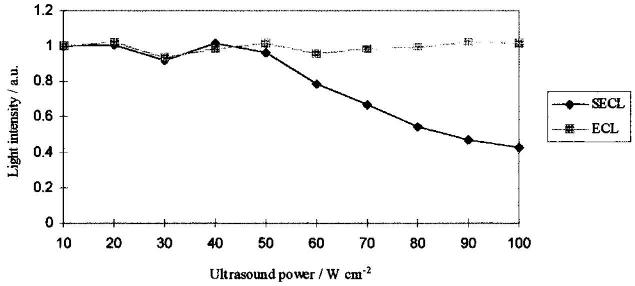

Figure 5. Light intensity against ultrasonic power (20 kHz, titanium tip size 1.5 cm^2) for silent (ECL) and insonated (SECL) conditions for a 500 μM aqueous solution of $Ru(bpy)_3Cl_2$.

Initially, the light emitted at 610 nm from the electrooxidation of a 500 μM solution of $Ru(bpy)_3Cl_2$ was examined under increasing ultrasonic power at a frequency of 20 kHz. The light emission in silent conditions is compared with that found during insonation in Figure 3. As with the other results presented in this study, this plot represents an average value taken from 10 measurements. Repeated measurement revealed the values are reproducible within ±10%. Throughout Figures 3−5 in this communication, the experimental procedure is as follows: insonation for a period of 1 min, giving a point denoted by the mnemonic *SECL*, after which ultrasound was ceased for 1 min and a point denoted by the mnemonic *ECL* was taken in silent conditions, after which insonation was resumed and the next SECL point taken, and so on. From Figure 3 it can be seen that the light emission in silent (ECL) conditions displays only a minor decrease throughout the experiment, whereas the level of light emitted under insonation (SECL) increases in a linear manner with increasing ultrasonic power. Note that every effort has been made to avoid the modification of the surface of the working electrode as a result of prolonged exposure to cavitational collapse. Unless otherwise stated, an insonation time of no more than 1 min was used in this research to minimize this eventuality. The absence of surface modification is ascertained by the measurements taken under silent conditions, which are used as an internal reference. The effect of surface modification that can be promoted by ultrasonic irradiation will be addressed later in this communication.

The linear increase in luminescence with increasing power found here was even displayed at very low power outputs, at which no cavitation appeared to be produced by the transducer (the cavitational threshold was observed *ca.* 10 W cm^{-2} with this arrangement, on evidence from the change of audible note of the emitter). Therefore, this effect seems not to be directly associated with cavitational collapse and, from the quasi-consistency of the ECL trace, not associated with electrode surface modifications. This leads us to the conclusion that the luminescence enhancement seen here is a result of the increased mass transport throughout the solution during insonation and the possible effects this has on the electrode Nernst diffusion layer. To confirm this, a plot of the cell current is shown in Figure 4. This shows characteristics similar to that of light intensity shown in Figure 3: a linear increase with ultrasound power applied to the system, although with a distinctly smaller slope, which will be discussed later.

A note of caution has to be sounded over the choice of ultrasound source employed for high-power sonoelectrochemiluminescence studies. The total amount of light incident upon the detector may, in fact, appear to be decreased as a result of the increasing amount of light scattering from high cavitational bubble densities. It was found that, using a horn of tip area 1.5 cm^2 providing ultrasound of a power approaching 100 W cm^{-2}, a large amount of light scattering rendered any increase in the light level unobservable. This is shown in Figure 5, where the increase in cell current with ultrasound power is not mirrored by an increase in light detected. To confirm this a red light emitting diode (LED) was used as the light source ($\lambda_{max} = 630$ nm). It was found that the increase in light detected by the fiber bundle positioned *perpendicular* to the orientation of the LED, which was shielded so that under silent conditions a minimum amount of light was directly incident upon the fiber bundle, was an order of magnitude greater for an ultrasound power of 100 W cm^{-2} (1.5 cm^2 titanium tip) compared to a power output of 50 W cm^{-2} (3 cm^2 titanium tip). This is due to the light scattering resultant from the high cavitational bubble densities. An integration sphere may be employed to compensate for such effects in terms of total light emission, but to avoid such complications it was found that, under these conditions, using a transducer in the power range of 50−70 W cm^{-2} achieves a good balance between the desired effects of ultrasound and undesirable amounts of light scattering.

To quantify the enhancement of electrochemiluminescence under insonation, the ratio given in eq 1 was employed.

$$\Delta = \frac{\mathrm{SECL} - \mathrm{ECL}}{\mathrm{ECL}} \qquad (1)$$

This represents the proportional increase in light independent of luminophore concentration and gives a significant representation of the increase in light as a result of insonation. It was found that there was no variation of this value in changing the luminophore to $Ru(phen)_3Cl_2$ (indeed, all of the results presented here are observed for both luminophore systems), and Table 1 confirmed the independence of Δ for $Ru(bpy)_3Cl_2$ in a range of concentrations. The value of Δ, for the conditions employed here, at an ultrasound power of 50 W cm^{-2} was found to be 1.15 ± 10%: an approximate doubling of light intensity.

TABLE 1: Values of Δ for the Insonation (20 kHz, 50 W cm^{-2}) of Various Concentrations of $Ru(bpy)_3Cl_2$

concentration/μM	Δ
100	1.02
200	1.14
300	1.20
400	1.08
500	1.18

TABLE 2: Luminescence Intensity in Silent and Insonated (20 kHz, 50 W cm^{-2}) Conditions in the Absence and Presence of Luminescence Quencher, for a 400 μM Solution of $Ru(bpy)_3Cl_2$

saturating gas	ECL ± 10%/au	SECL ± 10%/au	Δ
nitrogen	1.33	2.83	1.12
air	0.67	1.39	1.07

TABLE 3: Luminescence Quenching of Aqueous $Ru(bpy)_3Cl_2$ at 610 nm

	pO_2/atm				
	0	0.01	0.05	0.21	1
I°/I	1	1.075	1.113	1.450	3.450

Oxygen is well-known to quench the luminescence of the excited state of $[Ru(bpy)_3]^{2+}$ and of other singlet or triplet excited state species,[19,20] but there has been literature discussion[21] regarding its effect upon the excited state of $[Ru(bpy)_3]^{2+}$. In earlier studies on this system[5,6] the matter was not rigorously addressed. We now do so and find that saturating the luminophore solution with air diminished luminescence both under sonication and in silent conditions. There was no effect on the cell current due to the presence of quencher, which is in agreement with the earlier work by Bard *et al.*[12] under silent conditions. Therefore, normal luminescence quenching is responsible for this decrease in light, and thus the excited species is produced at the working electrode at the same rate regardless of the presence of quencher. For a 400 μM solution of $Ru(bpy)_3Cl_2$ it can be seen in Table 2 that Δ remains constant, even in the presence of quencher, whereas the absolute light intensities are diminished in the presence of air, which is characteristic of a typical luminescence quenching effect. Normalizing the level of luminescence in the presence of quencher to that of conditions in the absence of quencher was then considered.

The relationship between emitted light intensity and quenching constant in solution is described by the Stern−Volmer relation[20] (eq 2).

$$I°/I = 1 + K_{SV}pO_2 \qquad (2)$$

Where $I°/I$ is the ratio of the luminescence intensities in the absence and the presence of the quencher, K_{SV} is the Stern−Volmer constant, and pO_2 is the partial pressure of oxygen in the aqueous phase. From a plot of $I°/I$ against pO_2 at λ_{max} for $Ru(bpy)_3Cl_2$, for the data given in Table 3, and assuming equilibrium conditions between the gas and liquid phases, a linear relationship is found to exist, with $K_{SV} = 2.45$ atm^{-1} (the gradient of the plot). The difference in $I°/I$ when moving from air ($pO_2 = 0.21$ atm) to nitrogen ($pO_2 = 0$ atm) was found to be a factor of 2. Therefore, multiplying the light intensity obtained from this solution in the presence of air by this factor will reveal the light intensity in the absence of quencher. The quenching normalization for this solution is given in Table 4 and shows good agreement with the light intensity values obtained in the absence of quenching, given in Table 2. The

TABLE 4: Luminescence Intensities in Silent and Insonated (20 kHz, 50 W cm^{-2}) Conditions, Normalized To Account for the Presence of Luminescence Quencher, for a 400 μM Solution of Ru(bpy)$_3$Cl$_2$

	light intensities/au		
	ECL ± 10%	SECL ± 10%	Δ
air saturated	0.67	1.33	1.07
quenching normalized	1.34	2.58	0.98

TABLE 5: Luminescence Intensity and Cell Current in Silent and Insonated (500 kHz, 100 W) Conditions in the Absence and Presence of Luminescence Quencher, for a 400 μM Solution of Ru(phen)$_3$Cl$_2$

	ECL ± 10%	SECL ± 10%	Δ
light intensity/au	0.68	0.29	−0.57
cell current/mA	104	168	0.61

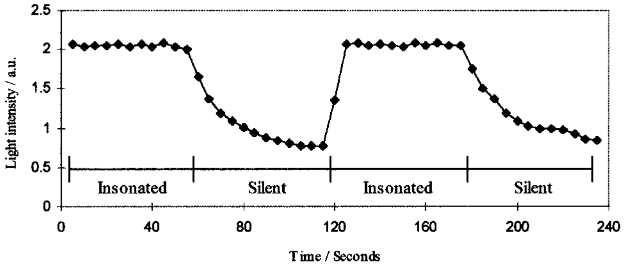

Figure 6. Light intensity against time for the repeated insonation (20 kHz, 50 W cm^{-2}) of a 200 μM solution of Ru(bpy)$_3$Cl$_2$.

normalized value of Δ is also found to be consistent. This displays the fact that under conditions of exposure to ultrasound at 20 kHz no anomalous quenching behavior is occurring. It is well-known that water sonolysis leads to the formation of H_2O_2 and O_2 via radical processes.[22] However, at 20 kHz, and in the power range used here, it can be stated that the amount of these species produced during experimentation has no effect on light emission levels. Sonication of the system using a 500 kHz transducer (electrical power input rating 100 W) was then performed. Emitters at this frequency have been shown to produce greater amounts of oxygen in aqueous solution[22] as a result of free radical recombination processes than those of lower frequencies. For a solution of Ru(phen)$_3$Cl$_2$ saturated with nitrogen gas it was found that insonation for a period of 1 min produced dramatic effects on light evolution, with only a small change in cell current. This is shown in Table 5. The current rise indicates that the total electrode processes are increased by insonation, but the concomitant luminescence intensity is substantially reduced by luminescence quenching at this higher frequency (Δ = −0.57). Oxygen present in solution can only be removed by continued purging with nitrogen to return the light emission in silent conditions to its original level.

It is known that prolonged exposure to cavitational collapse affects the electrode surface.[7] To illustrate that short time periods of ultrasound exposure have no significant effect on the electrode surface, luminescence during the repeated insonation of a 200 μM solution of Ru(bpy)$_3$Cl$_2$ is shown in Figure 6. Insonating (20 kHz, 50 W cm^{-2}) for a 1 min on/1 min off cycle at constant potential was performed. It can be seen that on cessation of ultrasound the luminescence decays steadily as mass transport effects subside, until silent conditions are reached.

Figure 7 shows electrochemiluminescence under insonation and in silent conditions for a solution of Ru(phen)$_3$Cl$_2$ for a time period of 350 s (*n.b.* each set of measurements taken separately). It can be seen that ECL remains constant throughout this time, although after a period of between 30 and 40 min luminescence decays significantly (this is not shown here). This has been described by other workers to be due to the formation of a passivating film on the working electrode.[23] In contrast, SECL increases with exposure time. This could be due to cavitational collapse increasing the effective surface area of the electrode gradually over a period of several minutes.

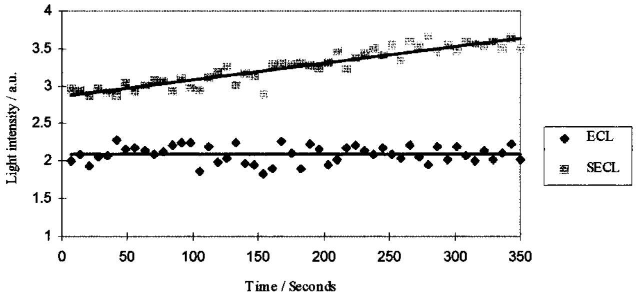

Figure 7. Light intensity against time under silent and insonated (20 kHz, 50 W cm^{-2}) conditions for a 400 μM solution of Ru(phen)$_3$Cl$_2$.

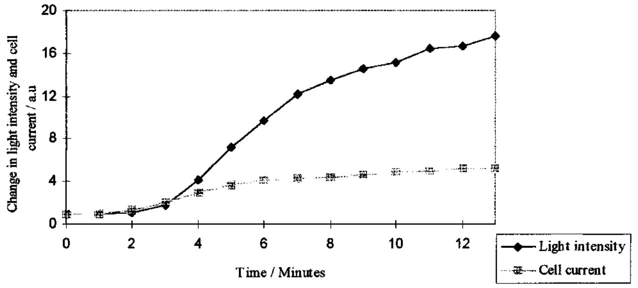

Figure 8. Changes in luminescence (light intensity/initial light intensity) and cell current (cell current/initial cell current) against time for the prolonged insonation (20 kHz, 50 W cm^{-2}) of a 400 μM solution of Ru(phen)$_3$Cl$_2$ using a passivated electrode.

The cleaning effect of ultrasound can be seen by its application to an electrode that has experienced prolonged use in silent conditions and has become passivated as a result. If this is then used under prolonged insonation, there is an increase in both SECL and cell current, as shown for Ru(phen)$_3$Cl$_2$ in Figure 8. The initial increase is due to removal of the passivating surface film from the electrode surface and perhaps also due to an increase in the effective surface area of the electrode by cavitational collapse near that surface. Our attention was drawn to the magnitude of the changes in cell current and light intensity over the time period of this experiment (change in cell current = 4, change in light intensity = 16). It was attempted to correlate these observations with the kinetic scheme proposed by Bard for the silent reaction in aqueous solution[12] shown in Figure 9. The rate equations for step 1, the oxidation at the surface of the electrode represented by the cell current (eq 3), and the rate of light emission in step 6, given in eq 4 are shown here.

$$r_{\mathrm{current}} = r[1] = k_1[\mathrm{RuL_3}^{2+}] \tag{3}$$

$$r_{\mathrm{light}} = r[6] = k_6[\mathrm{RuL_3}^{2+}*] \tag{4}$$

Under steady state conditions

$$r[1] = r[2] = r[3] = r[4] + r[5] \tag{5}$$

We shall assume that the rate $r[5]$ of the bimolecular process between two transient species is slow compared to the rate of the pseudo-unimolecular reactions 2 and 4. This is in agreement with the observation that the ECL efficiency, estimated by comparing the ratio of light intensity to the electrical charge applied to the system, is ~2%.[12] The rates $r[1]$ to $r[5]$ are functions of the spatial coordinates of the electrode surface.

$$\begin{array}{lcll}
RuL_3^{2+} & \xrightarrow{k_1} & RuL_3^{3+} + e^- & [1] \\
RuL_3^{3+} + C_2O_4^{2-} & \xrightarrow{k_2} & RuL_3^{2+} + C_2O_4^- & [2] \\
C_2O_4^- & \xrightarrow{k_3} & CO_2^- + CO_2 & [3] \\
RuL_3^{2+} + CO_2^- & \xrightarrow{k_4} & RuL_3^{+} + CO_2 & [4] \\
RuL_3^{3+} + CO_2^- & \xrightarrow{k_5} & RuL_3^{2+*} + CO_2 & [5] \\
RuL_3^{2+*} & \xrightarrow{k_6} & RuL_3^{2+} + h\upsilon & [6] \\
RuL_3^{2+*} & \xrightarrow{k_7} & RuL_3^{2+} + \text{heat} & [7]
\end{array}$$

Figure 9. Proposed reaction mechanism in aqueous solution under silent conditions.[12]

These rates may differ at various points, although the assumptions necessary for the steady state treatment may be fulfilled in the region in which luminescence occurs. Within these assumptions, the concentrations of the transient species are given by

$$[RuL_3^{2+}*] = \frac{k_5}{k_6 + k_7}[CO_2^-][RuL_3^{3+}] \tag{6}$$

$$[CO_2^-] = \frac{k_3[C_2O_4^-]}{k_4[RuL_3^{2+}]} \tag{7}$$

$$[C_2O_4^-] = \frac{k_2}{k_3}[C_2O_4^{2-}][RuL_3^{3+}] \tag{8}$$

$$[RuL_3^{3+}] = \frac{k_1[RuL_3^{2+}]}{k_2[C_2O_4^{2-}]} \tag{9}$$

Using eqs 7–9, one can rewrite eq 6:

$$[RuL_3^{2+}*] = \frac{k_5}{k_6 + k_7}\frac{k_1^2[RuL_3^{2+}]^2}{k_2k_4[RuL_3^{2+}][C_2O_4^{2-}]} \tag{10}$$

Modifying further using eqs 3 and 4,

$$r_{\text{light}} = \frac{k_5k_6}{k_6 + k_7}\frac{r_{\text{current}}^2}{k_2k_4[RuL_3^{2+}][C_2O_4^{2-}]} \tag{11}$$

Thus

$$r_{\text{light}} = \alpha r_{\text{current}}^2 \tag{12}$$

where α is a constant provided the ruthenium complex and oxalate concentrations are constant.

An alternative route leading to the formation of the excited state of the ruthenium complex has been considered:[5,6,12]

$$[RuL_3^+] + [RuL_3^{3+}] \xrightarrow{k_8} [RuL_3^{2+}*] + [RuL_3^{2+}] \tag{8}$$

This process seems to play a part in the mechanism when acetonitrile is used as the solvent. In water $[RuL_3^+]$ is unstable and decomposes quickly:

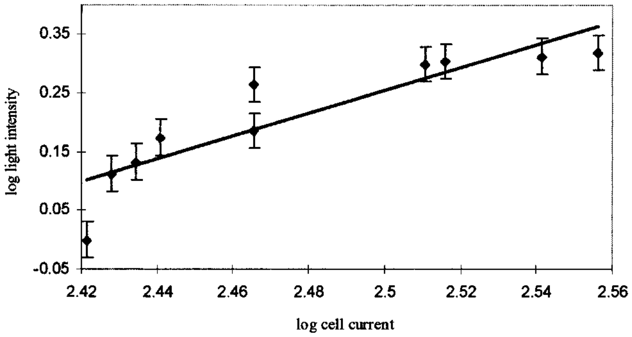

Figure 10. Logarithmic plot of cell current against light intensity for a 500 μM aqueous solution of $Ru(bpy)_3Cl_2$ under insonated conditions (20 kHz) at increasing ultrasound powers.

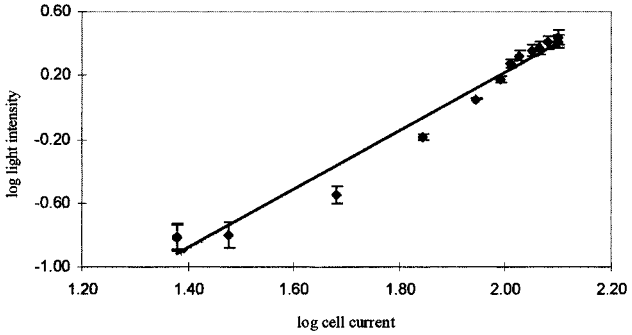

Figure 11. Logarithmic plot of cell current against light intensity for a 400 μM aqueous solution of $Ru(phen)_3Cl_2$ under insonated conditions (20 kHz, 50 W cm^{-2}) for a time of 13 min using a passivated electrode.

$$[RuL_3^+] \xrightarrow{k_9} \text{decomposition products} \tag{9}$$

If step 5 in Figure 9 is replaced by step 8 and step 9 is added to the kinetic scheme, then, making assumptions similar to those previously defined,

$$r[9] \gg r[8]$$

The equation described below is then resultant:

$$r_{\text{light}} = \frac{k_6k_8}{k_6 + k_7}\frac{r_{\text{current}}^2}{k_2k_9[C_2O_4^{2-}]} \tag{13}$$

This again shows that the intensity of light emission should depend on the square of the cell current.

Equations 12 and 13 can then be written in logarithmic form:

$$\log r_{\text{light}} = \log \alpha + 2 \log r_{\text{current}} \tag{14}$$

A logarithmic plot of light intensity against cell current using the data from Figures 3 and 4 is given in Figure 10. The line of best fit displays a gradient of 1.94 (Pearson correlation coefficient = 0.795). The more rapid increase in light evolution compared to cell current on depassivation of the electrode seen in Figure 8 can also be accounted for with reference to the squared dependency found in eq 14. A logarithmic plot of the light intensity and cell current data used to produce Figure 8 is shown in Figure 11. The line of best fit has a gradient of 1.83 (Pearson correlation coefficient = 0.972). Although there appears to be a substantial nonstatistical deviation of the residuals, we believe that the gradients of the plots (1.94 and 1.83) obtained by application of eq 14 to our data (obtained from two independent experiments in quite different conditions) confirm the suitability of the kinetic treatment and indicate that the electrode processes occurring under insonation can be justified by the same mechanism that has been described under silent conditions and, therefore, that the electrochemistry of the system remains unchanged under ultrasound: the modifications of mass transport and the Nernst diffusion layer result in the enhancement of light emission seen here.

Conclusions

The ultrasonic enhancement of light emission from the electrooxidation of $Ru(bpy)_3Cl_2$ and $Ru(bpy)_3Cl_2$ in aqueous oxalate is found to be highly effective, resulting in an increase of typically over 100% under our experimental conditions. This process did not require the presence of cavitational bubbles and can be considered to be a result of mass transport effects combined with associated modification of the electrode Nernst diffusion layer. Within the framework of the experiments performed here, the mechanism proposed by Bard *et al.*[12] for silent conditions is found to be applicable, and the electrochemiluminescence was found to be quenched in the usual manner. The kinetic scheme revealed a squared relationship between the cell current and the electrochemiluminescence light intensity, which to the authors' knowledge is previously unreported. However, modification of the electrode surface due to prolonged exposure to cavitational collapse was found to have a significant effect on the magnitude of emitted light intensity and cell current.

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References and Notes

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