

Electrogenerated Chemiluminescence. 35. Temperature Dependence of the ECL Efficiency of $\text{Ru}(\text{bpy})_3^{2+}$ in Acetonitrile and Evidence for Very High Excited State Yields from Electron Transfer Reactions

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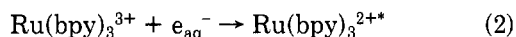
The temperature dependence of the ECL emission yield, ϕ_{ECL} , of $\text{Ru}(\text{bpy})_3^{2+}$ in acetonitrile has been determined and was found to correlate closely with the luminescence quantum yield, ϕ_e , of the lowest $\text{Ru}(\text{bpy})_3^{2+}$ $d\pi^*$ metal-to-ligand charge transfer (MLCT) excited state. Evidence is presented that at low temperatures ($< -30^\circ\text{C}$) the ECL emission yield becomes equal to the luminescence quantum yield implying an efficiency for excited state formation in the electron transfer reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{Ru}(\text{bpy})_3^{2+}$ of near 100%. High efficiencies for excited state formation are rationalized on the basis of the excited state spectroscopic properties of $\text{Ru}(\text{bpy})_3^{2+}$ and the resulting implications to electron transfer theory and the ECL mechanism are discussed.

Introduction

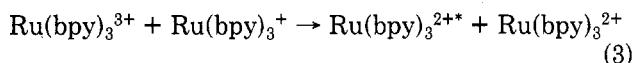
Chemiluminescence resulting from electron transfer reactions involving transition metal chelate ions can be produced in a variety of ways and has been the subject of several investigations.^{1-5,8-11} For example, the $\text{Ru}(\text{bpy})_3^{2+}$ $d\pi^*$ metal-to-ligand charge transfer (MLCT) excited state can be produced via reduction of $\text{Ru}(\text{bpy})_3^{3+}$ by suitable reducing agents such as hydrazine or hydroxide ion¹



by solvated electrons in pulse radiolysis experiments^{2,3}



and by other transition metal complex ions^{4,5}



The $\text{Ru}(\text{bpy})_3^{2+}$ excited state may also be produced by oxidation of $\text{Ru}(\text{bpy})_3^+$ via suitable oxidizing agents such as the 10-methylphenothiazine (MP) radical cation.⁵



When light emission occurs from the reaction of ions generated at an electrode surface the phenomenon is referred to as electrogenerated chemiluminescence (ECL).^{6,7} Chemiluminescence has been observed in the form of ECL emission from other Ru(II) chelates as well, incorporating, for example, 1,10-phenanthroline⁵ and 4,7-diphenyl-1,10-phenanthroline⁸ as ligands; from Re(I)⁹ and Os(II)¹⁰ diimine complexes; and from Pt(II) and Pd(II) metalloporphyrins.¹¹

The efficiencies of homogeneous electron transfer reactions involving transition metal complexes (as represented by eq 1-4) in producing excited states and light can be high. For example, in pulse radiolysis experiments in aqueous solutions 38% of the solvated electrons consumed produce the $\text{Ru}(\text{bpy})_3^{2+}$ triplet MLCT state^{2,3} and another 55% produce high energy product(s) which may occur through a $\text{Ru}(\text{bpy})_3^{2+}$ intermediate excited state.³ In addition ECL efficiencies, ϕ_{ECL} , between 3.5 and 6.0% have been reported for the reaction represented by eq 3.⁵ Compared to the luminescence quantum yield, ϕ_e , of 0.042 ± 0.002 for $\text{Ru}(\text{bpy})_3^{2+}$ in water at 25°C ,¹² the reported

values of ϕ_{ECL} imply efficiencies for the formation of excited states in the ion annihilation reaction of near 100%. Such a value is unusually high for an ECL reaction and values typically $< 50\%$, and more frequently $< 1\%$, have been reported for organic systems.⁶

High efficiencies for excited state production and emission in ECL and other chemiluminescence systems have important implications in terms of electron transfer theory, mechanism for excited state and light production, and the utilization of chemiluminescence systems for practical purposes. For example, it has generally been assumed on the basis of the Marcus theory for electron transfer¹³ that the highest energetically accessible product state will be the one most efficiently populated in an ECL reaction.⁶ This assumption leads to the conclusion that in a system in which the emitting state is populated directly, as opposed to indirectly through triplet-triplet annihilation or energy transfer, the ECL efficiency should in principle be limited only by the luminescence quantum yield. $\text{Ru}(\text{bpy})_3^{2+}$ is the only known ECL system, however, in which this prediction has apparently been realized. The reasons for low yields of excited state formation and emission in organic systems are still a subject of debate and could be related to energy wastage problems such as excited state quenching and ion decomposition, and to a fundamental failure of electron transfer theory to predict the relative importance of reaction pathways leading to several different product states. A thorough examination of the $\text{Ru}(\text{bpy})_3^{2+}$ system could contribute to an understanding of this problem. In addition any information which contributes to the elucidation of factors affecting excited state and emission yields in chemiluminescence processes is relevant to the practical utilization of such processes, for example, in electronic display devices¹⁴ and lasers.¹⁵

To determine more accurately both the magnitude of the efficiencies for excited state production and the trend of values of ϕ_{ECL} with ϕ_e we have carried out a study of the ECL and emission spectroscopy of $\text{Ru}(\text{bpy})_3^{2+}$ in acetonitrile as a function of temperature. A temperature study was chosen on the basis of the known variation in the luminescence quantum yield of $\text{Ru}(\text{bpy})_3^{2+}$ with this parameter¹² and because there is a general lack of knowledge concerning the effect of temperature on ECL efficiencies.¹⁶

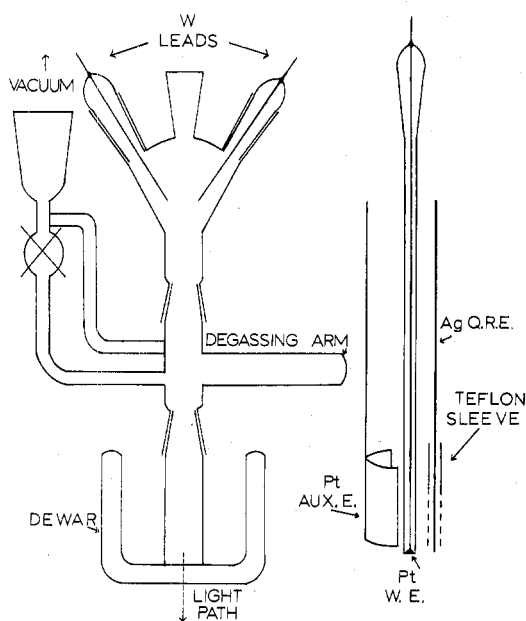


Figure 1. Variable temperature ECL and electrochemical cell.

Experimental Section

Materials. Matheson Coleman and Bell Spectroquality acetonitrile was dried and degassed by three transfers from dry phosphorus pentoxide under vacuum. Alternatively, acetonitrile was purified by refluxing 24 h under dry nitrogen over calcium hydride (3 g/L), then distilling and collecting the center 50% fraction again under dry nitrogen. The solvent was then transferred under vacuum after two freeze-pump-thaw cycles ($<10^{-5}$ torr) into a collection flask containing predried (24 h at 400 °C) Fischer Type 4A molecular sieves. Spectroscopic and electrochemical results were not dependent upon the method of solvent purification. Tetra-*n*-butylammonium perchlorate (TBAP) purchased from Southwestern Analytical Chemical Co. was recrystallized three times from a 1:1 ethanol-water solvent mixture, then dried thoroughly under high vacuum at 85–100 °C for 48 h. $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ was prepared by metathesis with excess NaClO_4 in water from $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ purchased from G. F. Smith Chemical Co. The resulting material was purified by four recrystallizations from ethanol-water, then dried under high vacuum for 48 h.

Equipment. Cyclic voltammetry and ECL measurements were carried out in the controlled potential mode using a Princeton Applied Research (PAR) Model 173 potentiostat and Model 175 universal programmer. The output of the PAR Model 176 current follower was either recorded directly using a Houston Instrument Model 2000 X-Y recorder or monitored and subsequently recorded using a Nicolet Model 1090 A digital oscilloscope.

The electrochemical cell employed for the variable temperature ECL and cyclic voltammetry experiments is shown in Figure 1. The cell consists of three sections the first of which allows the insertion and parallel positioning of the working (Pt disk sealed in uranium glass; area, 0.064 cm^2), auxiliary (Pt foil, 2.9×1.0 cm; total area, 5.8 cm^2), and reference (silver wire) electrodes in the sample compartment. The second section consists of a 10-mL graduated degassing arm and high vacuum stopcock with associated joints allowing complete cell assembly, connection to a vacuum line, and vacuum tight isolation from the atmosphere. The third section consists of a 5-mL sample compartment integrally sealed into a double-walled evacuated Pyrex Dewar (100-mL capacity) which was silvered to minimize light loss through scattering. Direct

spectroscopic observation of the Pt disk electrode could be made through the two flat sections of Pyrex glass at the bottom of the Dewar. Within the sample compartment the auxiliary foil electrode was folded in a cylindrical arrangement around the working electrode with the silver wire quasi-reference electrode (QRE) being positioned between the Pt foil and disk as close to the disk as possible. The silver wire was sheathed in a perforated Teflon tube which prevented contact with the Pt foil but allowed contact with the solution. The resulting geometry promoted an even current distribution over the surface of the Pt disk and minimized the uncompensated solution resistance between the working and reference electrodes. The use of a large area Pt foil ensured that most of the counter electrode current was non-Faradaic, i.e., was involved in double layer charging.

Solutions were prepared by transferring 5 mL of the solvent under vacuum at -30 °C into the degassing arm containing the supporting electrolyte and transition metal complex which had been predried for 12 h at $<10^{-5}$ torr. After two freeze-pump-thaw cycles the solution was then transferred directly to the sample compartment. The cell was constructed and sufficient care was used so that direct contact of the ECL solution with grease (Dow Corning High Vacuum silicone lubricant) was avoided. Temperature variation and stabilization were accomplished either by using a methanol-dry ice mixture or by using the temperature control apparatus described below. The accuracy and precision of temperature control and measurement (using alcohol and mercury thermometers) is estimated to be ± 1.0 °C for -10 °C $\leq T \leq 40$ °C and ± 1.5 – 2.0 °C for $T < -10$ °C and $T > 40$ °C. Thermal equilibration of the electrochemical solution took approximately 15 min and was determined by monitoring the peak currents of successive cyclic voltammograms as a function of time.

Relative ECL intensity measurements were performed using an EG and G Model 550-1 radiometer/photometer equipped with a Model 550-2 multiprobe detector (1.0 cm^2 silicon photovoltaic detector) which exhibited a flat response between 450 and 1000 nm (A/W/cm^2) when used with a "flat" radiometric filter attachment. Integration of the ECL intensity over finite periods of time was accomplished using the Model 550-3 pulse integrator and the combined detection system response was found to be linear over the three decades of sensitivity used in these experiments. Variable temperature photoexcited luminescence measurements were made using an Aminco-Bowman spectrofluorometer equipped with a variable temperature cell holder and RCA 931-A and 4832 photomultiplier tube detectors.

Temperature variation and control were accomplished using a thermally insulated constant temperature bath (Labline, Inc., Chicago, Ill.) equipped with heating coils, fluid circulation pump, and temperature controller. Subambient temperatures were attained using an FTS Systems (Stone Ridge, N.Y.) Model LC-100 liquid cooler cryostat equipped with a Model TCH-1 proportional temperature controller and auxiliary heater. The constant temperature bath fluid pump circulated methanol or water through the cell holder of the Aminco-Bowman spectrofluorometer or through a copper coil heat exchanger in the Dewar of the ECL cell.

Relative Luminescence Quantum Yields. The luminescence quantum yield of $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ as a function of temperature, $\phi_e(T)$, was measured relative to the quantum yield at 25 °C, ϕ_e^0 , in accordance with the following general expression.^{17,18}

$$\phi_e(T) = \phi_e^0 \frac{\int_0^\infty F_T(\bar{\nu}) d\bar{\nu}}{\int_0^\infty F_0(\bar{\nu}) d\bar{\nu}} \frac{(1 - 10^{-A_0}) n_T^2}{(1 - 10^{-A_T}) n_0^2} \quad (5)$$

in which F is the corrected emission spectrum in terms of relative quanta (s/wave number)⁻¹, A is the absorbance of the emitting solution at the excitation wavelength, n is the refractive index of the solution, and $\bar{\nu}$ is the light energy in cm⁻¹. The equation assumes a constant frequency, bandpass, and intensity for the excitation radiation. With small values of A and temperature independent molar absorptivity coefficients, the light absorption ratio reduces to C_0/C_T , where C is the concentration of the emitting species, which in turn can be replaced by D_0/D_T where D is the solution density. If the spectral distribution of the emission is temperature independent, the integrated corrected emission spectrum ratio can be replaced by I_T/I_0 where I is the emission intensity measured at a single wavelength and constant bandpass. Values of I were taken at the emission maximum of Ru(bpy)₃²⁺ luminescence spectra which was located at 604 nm at 73 °C and 608 nm at -40 °C (uncorrected spectra, RCA 4832 photomultiplier tube detector). The spectral distribution of Ru(bpy)₃²⁺ changed only slightly over this temperature range (<3%) as monitored by full and half-widths at half-maximum measured from the emission maximum wavelength. Relative quantum yields measured using excitation wavelengths of 380, 430, and 464 nm agreed within 5%. The absorption maximum wavelength varied by less than ±2 nm as determined by excitation spectra over the 115 °C temperature range studied. Values of density as a function of temperature were obtained from standard tabulations¹⁹ and refractive index values were estimated using Eyckman's equation.²⁰ The concentration and refractive index correction factors generated from these values were found to be accurate to within 2% at the extreme limits of the temperature range employed in this study by measuring the relative quantum yield of 9,10-diphenylanthracene (DPA)²¹ in acetonitrile in a separate control experiment. Samples were prepared using dry degassed acetonitrile in round Pyrex (i.d., 1.14 cm; volume, 2.5 mL) tubes as the variable temperature emission cells. After preparation in a drybox (Vacuum Atmospheres Model HE-43-2 equipped with a Model MO 40-1 Dri-Train inert gas purifier) solutions further underwent three high vacuum freeze-pump-thaw degassing cycles before final sealing with a torch.

The quantum yield of Ru(bpy)₃(ClO₄)₂ in degassed acetonitrile was measured relative to that of Ru(bpy)₃(ClO₄)₂ in degassed, deionized water. Equation 5 was again employed by using the simplifications resulting from noting that the spectral distribution of Ru(bpy)₃²⁺ emission was not a function of solvent and by using aqueous and acetonitrile solutions of the complex having the same absorbance (<3% variation). Samples were irradiated at 450 nm ($\lambda_{\text{max,H}_2\text{O}}$, 453 nm; ϵ , $1.46 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$; $\lambda_{\text{max,CH}_3\text{CN}}$, 450 nm; ϵ , $1.42 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and absorption spectra were measured for the same degassed solutions used for emission spectroscopy. The aqueous solution was degassed using prepurified nitrogen (Big 3 Industries, Inc.) and acetonitrile solutions were prepared in the drybox by using dry, degassed solvent. Square, quartz optical cells were used. The quantum yield of Ru(bpy)₃(ClO₄)₂ in water at 25 °C was assumed to be the same as aqueous Ru(bpy)₃Cl₂ which was taken as 0.042 ± 0.002 .¹²

Relative ECL Emission Efficiencies. Values of ϕ_{ECL} , the electrogenerated chemiluminescence efficiency or yield, are

defined exactly in accordance with the following expression:¹⁴

$$\phi_{\text{ECL}} = \frac{\int_0^{t'} I dt}{\int_0^{t'} i_{c,a} dt} = \frac{\int_0^{t'} I dt}{Q_{c,a}} \quad (6)$$

in which the total ECL intensity, I (einstein/s), integrated over a finite period of time t' is divided by the integrated cathodic or anodic current, i_c or i_a , respectively (Faraday/s), over the same time period which is equal to the total anodic or cathodic charge, Q_a and Q_c , respectively. The ECL efficiency as defined in eq 6 is equivalent to the number of photons produced per radical ion annihilation event (eq 4). The relative ECL intensity was measured as the integrated silicon photocell detector response, J , to which the absolute value of $\int_0^{t'} I dt$ is proportional. The value of the ECL efficiency as a function of temperature, $\phi_{\text{ECL}}(T)$, was then measured relative to the value of $J/Q_{c,a}$ at 25 °C, which is proportional to $\phi_{\text{ECL}}^0 (B(J^0/Q_{c,a}^0) = \phi_{\text{ECL}}^0)$.

$$\phi_{\text{ECL}}(T) = \phi_{\text{ECL}}^0 \frac{J(T) Q_{c,a}^0}{Q_{c,a}(T) J^0} \quad (7)$$

The value of the proportionality constant B relating the measured integrated photodetector response to the total ECL intensity was based on previous absolute ϕ_{ECL} measurements made in this laboratory. As previously noted the spectral distribution of Ru(bpy)₃²⁺ emission was virtually constant over the temperature range monitored eliminating the necessity to correct the measured photodetector response due to variations in the detector sensitivity as a function of wavelength.

ECL was generated employing a cyclic double potential step waveform in which the potential limits were set to ensure diffusion-controlled oxidation and reduction of Ru(bpy)₃²⁺ with a minimum of interference from more highly reduced species. The total anodic and cathodic charge measured using a PAR Model 179 digital coulometer during a finite time period of the cyclic double potential step experiment consisted of Faradaic and double layer charging components. The double layer charging component was measured using an extrapolation procedure. Values of Q_a and Q_c were first measured at the diffusion-controlled potential limits for the Faradaic reactions, then the anodic potential limit was moved 300 mV negative to the foot of the oxidation wave and the cathodic potential limit was moved 300 mV positive to the foot of the reduction wave and the charge measurements were repeated. Values for the background (double layer) anodic and cathodic charge as a function of applied potential were then measured by setting the cathodic and anodic potential limits 200 mV positive and negative, respectively, in discrete steps measuring Q_a and Q_c after each change in potential and eventually covering a total potential range of about 2.5 V. Plots of Q_a and Q_c were linear vs. $E^{3/2}$ or $\Delta E^{3/2}$ and were extrapolated to the diffusion-controlled potential limits of the ECL experiment in order to determine the double layer charging contribution to the total measured anodic and cathodic charge. The plots of Q vs. $E^{3/2}$ were shown to be linear over the entire potential range of the ECL experiment in a control experiment using 0.1 M TBAP in acetonitrile as the blank solution. The anodic and cathodic components of the extrapolated double layer and final corrected Faradaic contributions to the total charge determined by the procedure described above allways agreed to within 3%, as expected for an ECL system

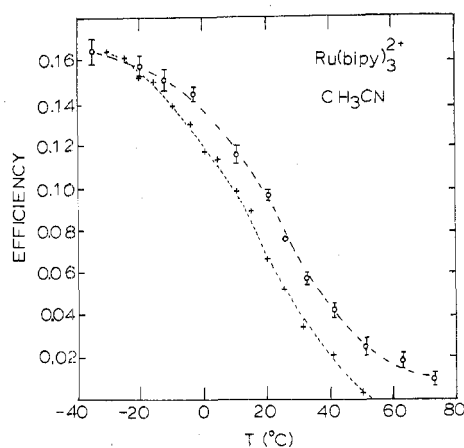


Figure 2. Variation of the ECL efficiency, ϕ_{ECL} , of 1.0×10^{-3} M $\text{Ru}(\text{bpy})_3^{2+}$ in acetonitrile containing 0.1 M TBAP using a pulse width of 500 ms corresponding to a cyclic double potential step frequency of 1 Hz (+), and the luminescence quantum yield, ϕ_e , of 5.8×10^{-6} M $\text{Ru}(\text{bpy})_3^{2+}$ in acetonitrile (O) as a function of temperature. The error bars reflect the experimental error in the relative measurements which is the same for both data sets; the error for the absolute ϕ_e values is $\pm 15\%$; see text for discussion of error in absolute values of ϕ_{ECL} .

in which the reduced and oxidized species participating in the ion annihilation reaction are generated from the same parent precursor species.

Results

The temperature dependence of the luminescence quantum yield of $\text{Ru}(\text{bpy})_3^{2+}$ in acetonitrile is shown in Figure 2 along with the ECL data for purposes of direct comparison. The quantity ϕ_e is seen to be strongly temperature dependent, and within the solvent limited temperature range of approximately 75 to -40°C assumes values ranging from 0.009 to 0.16. The relative quantum yield data were very reproducible and no noticeable photo- or thermal decomposition of $\text{Ru}(\text{bpy})_3^{2+}$ took place at the higher temperatures in acetonitrile within the time duration of the experiment (1–4 h) as determined by emission spectroscopy. As previously noted,¹² however, significant photodecomposition of $\text{Ru}(\text{bpy})_3^{2+}$ at temperatures $>80^\circ\text{C}$ was observed in water. The accuracy of the procedure used to determine the quantum yield temperature dependence was demonstrated by reproducing data previously obtained for $\text{Ru}(\text{bpy})_3^{2+}$ in water from 10 to 80°C .¹² Relative values of ϕ_e in acetonitrile in the presence of 0.1 M TBAP measured at several temperatures were the same within experimental error ($\leq 3\%$) as values measured in the absence of TBAP.

In general ϕ_e exhibited a stronger temperature dependence in acetonitrile than in water and absolute values were higher in acetonitrile at temperatures $\leq 40^\circ\text{C}$ and lower at temperatures $>40^\circ\text{C}$ ($\phi_{e,\text{CH}_3\text{CN}}/\phi_{e,\text{H}_2\text{O}} = 2.5$ at 10°C and 0.53 at 70°C). Absolute quantum yields in acetonitrile were obtained by normalizing the relative results to $\phi_e = 0.075 (\pm 15\%)$ at 25°C which in turn was the value obtained relative to that of $\text{Ru}(\text{bpy})_3^{2+}$ in water at the same temperature.

The ECL emission spectrum obtained from alternately generating the $\text{Ru}(\text{bpy})_3^+$ and $\text{Ru}(\text{bpy})_3^{3+}$ ions at the Pt disk working electrode surface employing a cyclic double potential step waveform was identical with the phosphorescence emission spectrum observed from photoexcited $\text{Ru}(\text{bpy})_3^{2+}$. The correlation of the emission and ECL spectra demonstrated that the $\text{Ru}(\text{bpy})_3^{2+}$ excited triplet state was produced either directly or indirectly in the ECL process and has previously been noted by several investigators.^{1,4,5,10}

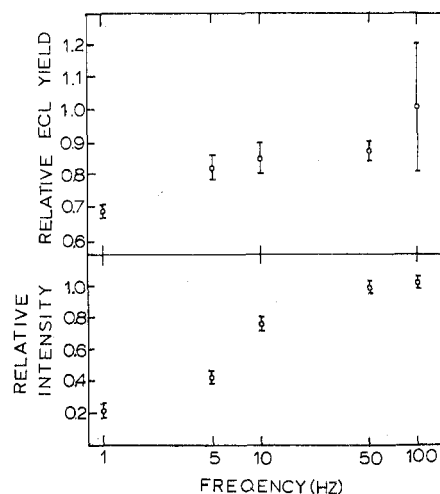


Figure 3. Variation in the relative ECL efficiency, ϕ_{ECL} , (top) and the relative ECL intensity, I_{ECL} , (bottom) for 1.0×10^{-3} M $\text{Ru}(\text{bpy})_3^{2+}$ in acetonitrile containing 0.1 M TBAP as a function of the cyclic double potential step frequency at 23°C .

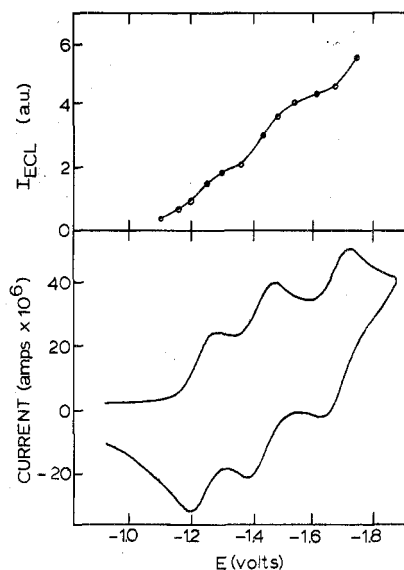


Figure 4. Variation in the relative ECL intensity, I_{ECL} , as a function of the cathodic step potential (top) and the cyclic voltammogram using a scan rate of 200 mV s^{-1} (bottom) of 1.0×10^{-3} M $\text{Ru}(\text{bpy})_3^{2+}$ in acetonitrile containing 0.1 M TBAP at 23°C .

The dependence of the relative ECL intensity and efficiency on pulse frequency is shown in Figure 3. In general the ECL intensity increased with increasing frequency reaching a maximum at approximately 100 Hz and varied by a factor of 5 in the range 1–100 Hz. The ECL efficiency was relatively constant, however, changing by only a factor of 1.3 over the same frequency range. The results may be compared with efficiencies obtained at the rotating ring disk electrode (RRDE) in which a relatively strong dependence was observed on the rotation rate, ω .⁵ The variation in ECL intensity as a function of the cathodic step potential is shown in Figure 4. In the corresponding experiment the anodic step potential was held constant at a value corresponding to the diffusion-controlled production of $\text{Ru}(\text{bpy})_3^{3+}$ while the cathodic potential was stepped at successively more negative values producing in turn $\text{Ru}(\text{bpy})_3^+$, $\text{Ru}(\text{bpy})_3^0$, and $\text{Ru}(\text{bpy})_3^-$. The values of I_{ECL} measured at the cyclic voltammetric peak current potentials for the three reduction waves varied in the ratio 1.00/2.00/3.09 at -1.25 , -1.43 , and -1.67 V vs. Ag QRE, respectively. Similar results have been obtained at the RRDE by Bard et al.⁵

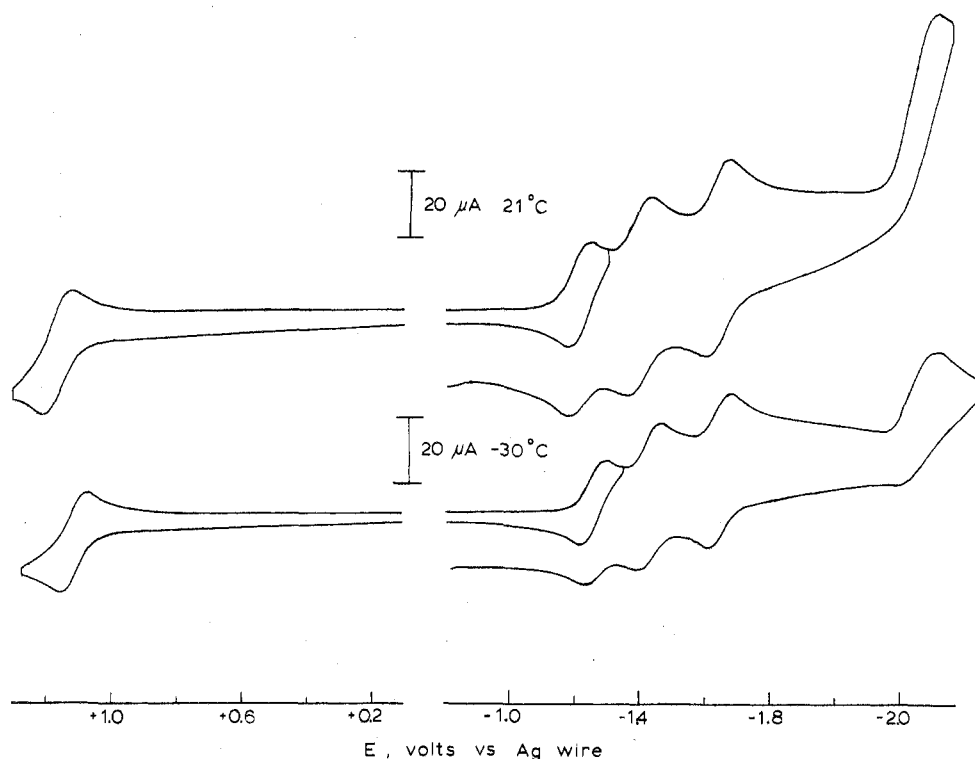


Figure 5. Cyclic voltammograms of 1.0×10^{-3} M $\text{Ru}(\text{bpy})_3^{2+}$ in acetonitrile containing 0.1 M TBAP: at 21 °C using a scan rate of 200 mV s^{-1} (top) and -30 °C using a scan rate of 200 mV s^{-1} (bottom).

Cyclic voltammograms for $\text{Ru}(\text{bpy})_3^{2+}$ in a 0.1 M TBAP acetonitrile solution at 21 and -30 °C are shown in Figure 5. In general anodic and cathodic cyclic voltammetry peak potentials measured using positive feedback iR compensation shifted in a negative direction by 35 mV for an 80 °C decrease in T . The small observed potential shift is attributed predominantly to the temperature dependence of the reference electrode potential and was taken into account in setting the potential limits in the cyclic double potential step ECL experiment. Cyclic voltammetry peak currents, i_p , and anodic-cathodic peak potential separations, ΔE_p , also decreased with decreasing temperature as expected for reversible heterogeneous one electron transfer reactions.²² A decrease in the double layer capacitance and background current and an increase in the uncompensated iR drop between the working and reference electrodes were also observed at lower temperatures.

A striking effect of temperature on the fourth reduction wave of $\text{Ru}(\text{bpy})_3^{2+}$ is also documented in Figure 5. This wave has previously been attributed to the four electron reduction of the $\text{Ru}(\text{bpy})_3^{2+}$ complex to form the $\text{Ru}(\text{bpy})_3^{2-}$ ion which undergoes rapid chemical decomposition by loss of a bipyridine ligand. Both the free ligand and ruthenium complex products can undergo further electrochemical and chemical reactions and at room temperature the resulting cyclic voltammogram is indicative of an irreversible process (scan rate, ν , $<100 \text{ mV s}^{-1}$) involving the transfer of 2.5–2.7 electrons (as determined from values of $i_p C^{-1} \nu^{-1/2}$). Similar behavior has been observed for the third reduction wave of $\text{Ru}(\text{bpy})_2(\text{CN})_2$.²³ The details of the decomposition mechanism and identity of the final products have not been determined. At -30 °C the fourth reduction wave for $\text{Ru}(\text{bpy})_3^{2+}$ becomes quasi-reversible (1.5–1.7 electrons transferred; $i_{pc}/i_{pa} \approx 0.7$ at ν , 500 mV s^{-1}) demonstrating an increase in the thermal stability of the reduced intermediate complex at low temperatures.

Relative ECL efficiencies plotted as a function of temperature are shown in Figure 2. Since charge was

measured directly, the temperature dependence of the diffusion coefficient and bulk concentration of $\text{Ru}(\text{bpy})_3^{2+}$ was of concern only from the standpoint of concentration dependent reabsorption of ECL emission. However, the electrode was positioned to allow a light path through the solution of ≤ 3 mm, and over the temperature range covered relative changes in the fraction of light reabsorbed as a function of T were insignificant compared to the total fraction of light transmitted. The data shown in Figure 2 were very reproducible between -40 and 35 °C having been obtained in a period of 2 days over the entire temperature range each day using the same solution. The results were reproduced in a separate experiment employing a slightly different ($\sim 10\%$) $\text{Ru}(\text{bpy})_3^{2+}$ concentration, which was approximately 1.0 mM. At $T < 35$ °C no decomposition of the ECL solution as determined by emission spectroscopy could be detected after the equivalent of 4 h of continuous pulsing. After several minutes of continuous pulsing at temperatures above 35 °C, however, significant decreases in the ECL intensity were observed; the rate of decomposition increasing at higher temperatures. Above 60 °C no ECL emission was observed using the silicon photovoltaic detector. After performing ECL experiments at high temperatures, even briefly, subsequent experiments at low temperatures showed greatly reduced ECL intensities (as much or more than a factor of 10) indicating possible surface modification of the Pt working electrode (e.g., product adsorption) which could not be detected by cyclic voltammetry, or bulk decomposition of $\text{Ru}(\text{bpy})_3^{2+}$ through thermally induced side reactions of the electrogenerated ions. As previously noted the $\text{Ru}(\text{bpy})_3^{2+}$ excited triplet state does not decompose at high temperatures in acetonitrile.

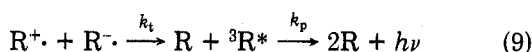
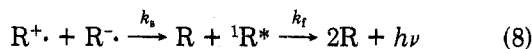
In general the ECL efficiencies of $\text{Ru}(\text{bpy})_3^{2+}$ parallel the emission quantum yield as a function of T . The absolute data in Figure 2 were obtained by setting ϕ_{ECL} equal to 0.050 at 25 °C using an average value determined from the absolute RRDE measurements previously made in this laboratory. The magnitude of the normalized ECL

efficiencies indicates that the minimum efficiency for excited state formation from the ion annihilation reaction, ϕ_{ECL}/ϕ_e , varies from 65% at 25 °C to 100% at -35 °C. Even using 3.5% as the lower limit of ϕ_{ECL} determined in RRDE experiments,⁵ then values of ϕ_{ECL}/ϕ_e still increase from 47% at 25 °C to 71% at -35 °C (ϕ_{ECL} , 11.5% at -35 °C) and are among the highest ECL efficiencies and minimum efficiencies for excited state formation which have been measured.⁶

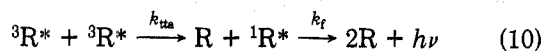
Discussion

The data shown in Figure 2 provide one of the few available quantitative studies correlating the variation in ϕ_{ECL} and the relationship between ϕ_{ECL} and ϕ_e as a function of temperature.¹⁶ The data confirm on a more quantitative level that very high excited state yields can be realized in the Ru(bpy)₃²⁺ ECL system as inferred from a comparison of independent literature ECL efficiency⁵ and luminescence quantum yield¹² results. In addition the trend in values of ϕ_{ECL}/ϕ_e with temperature and the results of the normalization procedure indicate that at low temperatures ϕ_{ECL} becomes nearly equal to ϕ_e corresponding to efficiencies for excited state formation from the ion annihilation reaction of near 100%. Ru(bpy)₃²⁺ is the only ECL system in which high efficiencies for excited state formation are directly reflected in the efficiency of light emission and in this respect is unique compared to organic ECL systems which invariably have low values of ϕ_{ECL}/ϕ_e .⁶ The origins of the unique behavior exhibited by Ru(bpy)₃²⁺ can be ascribed to (1) the mechanistic factors which affect ECL efficiency, and (2) the spectroscopic properties of the Ru(bpy)₃²⁺ complex.

Mechanistic factors which affect ECL efficiency have previously been summarized.^{6,7,24} In general one may distinguish between two extreme cases: (1) the emitting excited state, singlet or triplet, is formed directly in the electron transfer reaction^{5,25,26}



and (2) the emitting excited state is produced indirectly by an energy transfer or upconversion process involving the primary excited state formed in the electron transfer reaction. In organic ECL systems in which only non-emitting triplets are energetically accessible ($-\Delta H^\circ$ for the electron transfer reaction to produce ground state products $< E_s$, the singlet excited state energy)²⁷ the inherently inefficient triplet-triplet annihilation reaction^{6,28,29} leads to the production of emitting singlets



and in ECL systems in which triplet-triplet annihilation is the only emission pathway values of ϕ_{ECL} must always be less than 5% as a theoretical upper limit⁶ and are usually much less than 1%. In principle ECL systems in which the emitting excited state is produced directly are capable of much higher efficiencies and will be limited predominantly by the luminescence quantum yield, if the excited state yield is high and the electrogenerated ions are stable on the ECL time scale.³⁰

The inherently inefficient upconversion reaction to produce emission coupled with the facts that (1) most organic triplets do not emit at room temperature and (2) organic triplets in general have long radiative lifetimes leading to efficient energy wastage through quenching reactions in fluid solution are factors which have been cited

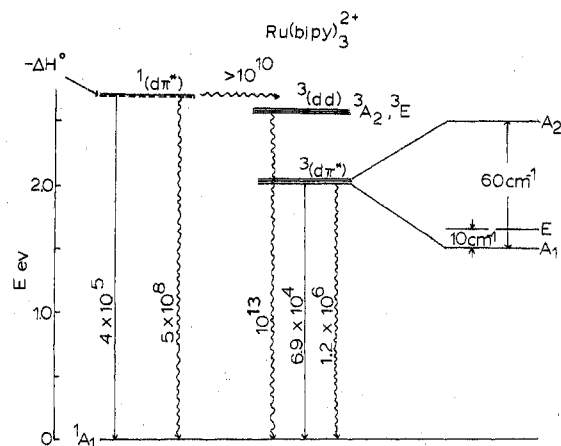


Figure 6. Energy level diagram for Ru(bpy)₃²⁺.

to explain the observed low ECL efficiencies for most ECL systems.^{6,7,24,26} The few primary efficiencies for excited state formation, ϕ_p ,³¹ which have been measured³² also tend to be low. For example, Faulkner has measured values of ϕ_p for triplet formation ranging from 2 to 50%,^{29,33} the interesting exception being the 10-phenylphenothiazine (+)/fluoranthene (-) system for which a relatively high value of 80% was obtained by triplet interception with *trans*-stilbene.³¹ The measured primary excited state yields tend to support the proposition that nonradiative decay through exciplex or excimer formation could also be a significant yield limiting factor in organic systems,³⁴ since the highest values of ϕ_p are measured for large molecules with bulky substituents which can inhibit excited state complex formation through steric hindrance. In addition factors which affect the relative distribution among different accessible product states in the ion annihilation reaction are not well understood on a quantitative level. On the basis of the Marcus theory for adiabatic electron transfer it is frequently assumed that the highest energetically accessible product state is the one most efficiently populated;¹³ however, other factors such as spin statistics and the possibility for nonadiabatic electron transfer³⁵ undoubtedly limit the quantitative reliability of the theory's predictions.⁶

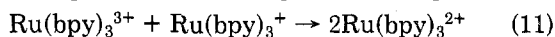
The spectroscopic properties of Ru(bpy)₃²⁺ relevant to ECL can be discerned in the energy level diagram shown in Figure 6. The lowest singlet and triplet dπ* MLCT states (E_s , 2.73 eV,³⁶ E_T , 2.12 eV,^{12,36} as determined from the lowest energy absorption and highest energy emission peaks respectively at 77 K) have previously been described in terms of transfer of a d electron from the central d⁶ ruthenium metal core to a ligand centered π* orbital. Comparison of the intersystem crossing rate constant, $k_{\text{isc}} > 10^{10} \text{ s}^{-1}$, with estimated values of the radiative, $k_r \sim 4 \times 10^5 \text{ s}^{-1}$, and nonradiative, $k_{\text{nr}} \sim 5 \times 10^8 \text{ s}^{-1}$, rate constants of the lowest energy excited singlet MLCT state³⁷ reveals that population of the ¹dπ* state results essentially exclusively in intersystem crossing to the triplet manifold and rapid internal conversion to the lowest ³dπ* MLCT state. Spectroscopic studies confirm the absence of fluorescence emission from the complex.^{37,38} The exceptionally high value of k_{isc} is a result of a general enhancement of singlet-triplet spin forbidden processes by strong spin-orbit coupling^{36,38} which also prohibits the assignment of pure singlet and triplet character to Ru(bpy)₃²⁺ excited states. The lowest ³dπ* state consists of a manifold of three levels of A₁, E, and A₂ symmetry separated by 10 and 50 cm⁻¹, respectively.³⁹ Below 77 K the average radiative and nonradiative rate constants are markedly temperature dependent; however, in the tem-

perature range used in this study only the A_2 level is populated leading to the temperature independent rate constants shown in Figure 6.¹² The well-documented variation of the $\text{Ru}(\text{bpy})_3^{2+}$ emission lifetime and quantum yield with T in the high temperature limit ($>77\text{ K}$)^{12,40} has been attributed to a Boltzmann equilibration between the lowest $^3d\pi^*$ MLCT state and another state (assigned as the 3A_2 or 3E dd state on the basis of photochemical evidence¹²) situated approximately 3600 cm^{-1} higher in energy and having a combined nonradiative decay rate constant of $\sim 10^{13}\text{ s}^{-1}$.¹² The energy level scheme in Figure 6 is a simplified version of the true situation for $\text{Ru}(\text{bpy})_3^{2+}$ since other triplet MLCT states lie between the lowest energy singlet and triplet states.^{12,38} In addition the variation of ϕ_e and τ_e with temperature is subject to significant solvent perturbations leading, for example, to different results in acetonitrile and D_2O ¹² compared to water¹² implying some solvent dependence on the parameters shown in Figure 6.

In terms of ECL emission properties the energy level diagram in Figure 6 provides a framework for explaining the unique behavior of $\text{Ru}(\text{bpy})_3^{2+}$ (and other transition metal chelates for which the energy level scheme applies in general) compared to organic systems. For example, the high intersystem crossing rate constant ensures that direct population of both the singlet and triplet $d\pi^*$ MLCT states in the ion annihilation reaction results exclusively and efficiently in the formation of the emitting triplet. In addition one may estimate λ for the $\text{Ru}(\text{bpy})_3^{2+}$ ECL reaction at $\geq 0.7\text{ eV}$ ⁴¹ which in comparison with ΔG° places the electron transfer reaction leading to the triplet state close to the "normal" free energy region where Marcus theory calculations are more accurate.¹³ This observation leads to the conclusion that in the $\text{Ru}(\text{bpy})_3^{2+}$ system direct triplet formation is probably the predominant ion annihilation pathway. That triplets can be produced directly and efficiently via electron transfer is demonstrated by the efficient chemiluminescent reaction of $\text{Ru}(\text{bpy})_3^+$ with MP^+ (eq 4) in which ΔH° (-2.1 eV) is not sufficiently energetic to produce $d\pi^*$ singlets but is sufficient to produce $d\pi^*$ triplets.⁵

In addition the short triplet lifetime of $\text{Ru}(\text{bpy})_3^{2+}$ (τ_e , $0.58\text{ }\mu\text{s}$ at $25\text{ }^\circ\text{C}$ in water)¹² greatly reduces light wastage through triplet quenching by impurities, the supporting electrolyte or electrogenerated ions in the ECL reaction zone. The emitting state is also the lowest electronic level in the excited state manifold eliminating the need for an inefficient energy transfer or upconversion step such as triplet-triplet annihilation to produce light. Furthermore the reaction between two large, bulky, and positively charged reactants to produce positively charged products is not conducive to excited state complex formation, and possible energy loss through enhanced nonradiative decay via excimers or exciplexes is not likely. To our knowledge there is no spectroscopic or other evidence in the literature to suggest excited state complex formation between two transition metal complexes possessing chemical and physical properties analogous to the $\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^+$ system.

The observation that at low temperatures the emission quantum yield becomes nearly equal to the ECL efficiency provides unique evidence that ground state production



is not an important pathway in the ECL mechanism of $\text{Ru}(\text{bpy})_3^{2+}$. Very low ($<7\%$) yields for direct ground state production are also reported for the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with solvated electrons.³ Both Marcus and nonadiabatic electron transfer theories predict that extraordinarily

exothermic electron transfer reactions approach comparatively negligible rates.³⁵ Heretofore, evidence in the ECL field has been inconclusive for this prediction since the small efficiencies observed in organic systems could be attributed to many factors, the most obvious being associated with side reactions and production of long-lived nonemitting triplets. The only other evidence has been indirect and includes the measurement of high primary yields of excited triplet state formation in the 10-phenylphenothiazine (+)/fluoranthene (-) reaction³¹ and the analysis of ECL transients for the DPA system.³⁵ It is emphasized that 100% efficiency necessarily implies that $\text{Ru}(\text{bpy})_3^{2+}$ exhibits none of the complicating features implicit with the limitations in efficiency observed for organic systems and as such should provide the best model available for the investigation of many aspects of the ECL phenomenon.

There are several possible explanations for the decrease in the ECL efficiency for $\text{Ru}(\text{bpy})_3^{2+}$ compared to ϕ_e at high temperatures including temperature dependent ion instability and variation in the efficiency with which radical ions react (escape of ions from the ECL reaction zone). Evidence for temperature dependent ion stability has been presented in the cyclic voltammograms depicting the fourth reduction wave of $\text{Ru}(\text{bpy})_3^{2+}$ (Figure 5) and instability on a bulk coulometric time scale has previously been noted for $\text{Ru}(\text{bpy})_3^+$ in acetonitrile.⁵ In addition evidence for noticeable decomposition was observed at high temperatures ($>40\text{ }^\circ\text{C}$) in the form of irreversible ECL intensity decreases which could not be attributed to excited state reactivity on the basis of the luminescence spectroscopy results. Proof that ion stability was the root cause of the observed behavior, however, is lacking. Thermal equilibration with higher electronic states in the ECL reaction leading to enhanced nonradiative decay presumably is not the cause either since this factor should be accounted for in the luminescence quantum yield. Further work will be necessary to specifically identify the root cause of such behavior.

Summary

The data presented in Figure 2 is the first definitive evidence in the ECL literature which shows that ECL efficiencies can be correlated with the luminescence quantum yield of the emitting excited state^{16,42} and that primary yields for excited state formation can be near unity in the ECL reaction involving transition metal chelates. In organic systems due to the many mechanistic factors which limit chemiluminescence and excited state yields and on the basis of the available literature data it is less probable that an analogous correlation could be found. The results of this study and other preliminary studies⁴² may logically be extended to transition metal complexes in general which have excited state properties similar to $\text{Ru}(\text{bpy})_3^{2+}$, to which may be added (1) the stability of electrogenerated ions, at least on the time scale required for diffusion and homogeneous electron transfer, and (2) chemical and physical hindrance to excited state complex formation if such complexes lead to enhanced nonradiative decay.

That ϕ_{ECL} can be correlated with ϕ_e and that both quantities can be affected to approximately the same degree by environmental factors and variations in molecular structure have important implications in terms of the practical utilization of ECL systems; for example, in electronic display devices¹⁴ and lasers.¹⁵ High ECL efficiencies are important in the development of ECL devices in terms of enhancing the current efficiency for light production, producing enough light to meet various

threshold requirements, and in overcoming borderline deficiencies in ECL systems such as ion instability where the rate of bulk ion decomposition on a long time scale can be reduced by generating fewer ions leading to excited states of higher emission efficiency. Further attempts at developing practical ECL systems employing transition metal complexes, especially considering that Ru(bpy)₃²⁺ is one of the most stable ECL systems known,⁵ would appear justified. Investigations are presently continuing to determine the scope of the implications of the results in this study to other transition metal complexes.

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$$\Delta H^\circ = E^\circ(R/R^-) - E^\circ(R^+/R) - T\Delta S^\circ$$
 where $E^\circ(R/R^-)$ and $E^\circ(R^+/R)$ are the standard potentials for the relevant redox reactions (usually estimated by cyclic voltammetry peak potentials) and ΔS° is the standard entropy; see ref 6.
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