# Temperature Dependence of the Electrogenerated Chemiluminescence Efficiency of $Ru(bpz)_3^{2+}$ in Acetonitrile. A Mechanistic Interpretation

## J. González-Velasco

Departamento de Electroquímica, Facultad de Ciencias, Universidad Autônoma de Madrid, 28049 Madrid, Spain (Received: July 28, 1986; In Final Form: November 16, 1987)

The temperature dependence of the electrogenerated chemiluminescence (ECL) efficiency ( $\eta_{ECL}$ ) and the quantum yield  $(\phi_p)$  of Ru(bpz)<sub>3</sub><sup>2+</sup> has been measured. Also the temperature dependence of the luminescence quantum yield  $(\phi_p)$  of the lowest Ru(bpz)<sub>3</sub><sup>2+</sup> d- $\pi^*$  metal-to-ligand charge-transfer (MLCT) excited state was determined. In the low-temperature range (between 5 and 35 °C),  $\eta_{ECL}$  and  $\phi_p$  increase with decreasing temperature, while the ratio  $\eta_{ECL}/A\phi_p$  remains nearly constant. At higher temperatures (between 35 and 75 °C), a sharp decline in the  $\eta_{ECL}/A\phi_p$  ratio is attributed to the disappearance of the  $Ru(bpz)_3^{3+}$  ECL precursor, by reaction with the solvent. Evidence that this reaction takes place is demonstrated by the ECL dependence on pulsing frequency and pulsing limit, as well as by the ECL variation with temperature. Changes in the anodic and cathodic waves recorded in voltammograms as well as an alteration in the absorption spectrum of the original solution induced by repetitive pulsing and by a temperature increase support this supposition. The similarity in the  $\eta_{ECL}$ and  $\phi_n$  values in the low-temperature range is attributed to the efficient formation of the excited state by an electron-transfer reaction between  $Ru(bpz)_3^{3+}$  and  $Ru(bpz)_3^+$  formed during the anodic and cathodic potential pulses, respectively. Unlike for the  $Ru(bpy)_3^{2+}$  case, the ECL efficiency is limited only by the luminescence quantum yield at low temperatures, whereas at higher temperatures  $\eta_{\text{ECL}}$  is limited mainly by a decomposition reaction of the 3+ precursor formed during the anodic pulse and by quenching of the excited state by reaction products or solvent. Changes in the  $\eta_{ECL}/A\phi_p$  ratio with temperature during the anodic and cathodic pulses are attributed to the different stabilities of the 1+ and 3+ precursors.

## Introduction

Electrogenerated chemiluminescence (ECL) has been the object of many studies in recent years owing to the possibility of using it for developing lasers<sup>1</sup> or display devices<sup>2</sup> and because it offers an insight into low electron transfer<sup>3</sup> takes place in homogeneous reactions between precursors. The electrogenerated chemiluminescence can be the result of electron-transfer reactions between oxidation and reduction products of metal chelate ions<sup>4-8</sup> on electrodes. Likewise, reactions between anions and cations resulting from electrooxidation or -reduction of organic substances (like 9,10-diphenylanthracene<sup>9</sup> (DPA) or rubrene<sup>10</sup>) produce ECL. ECL can also be the result of reactions between cation radicals resulting from the electrooxidation of an organic substance and anion radicals obtained from electroreduction of another organic substance.<sup>11</sup> In many of the cited cases, especially in thos reactions involving transition-metal complexes, the efficiencies of homogeneous electron-transfer reactions in producing excited states and light have been determined to be high. For instance, in the case of the 3+ and 1+ forms produced by pulsing between adequate anodic and cathodic potential values in Ru(bpy)<sub>3</sub><sup>2+</sup>, ECL efficiencies ( $\eta_{ECL}$ , defined as number of emitted photons/number of Faradaic electrons) between 3.5% and 6% have been reported,<sup>4</sup> whereas other ECL-producing reactions in which organic systems are involved frequently have  $\eta_{ECL} < 1\%$ .<sup>12</sup> Efforts have been made to develop ECL systems characterized by a high value of  $\eta_{\rm ECL}$ .<sup>4,13</sup> Such high efficiencies for excited-state production and for light emission can supply important data to understand how electron transfer takes place and to explain the mechanism through which the excited state and light are produced. Also, the elucidation

(3) Hoytink, G. J. Discuss. Faraday Soc. 1968, 45, 14.

(6) Tokel-Takworyan, N. E.; Bard, A. J. Chem. Phys. Lett. 1974, 25, 235.
(7) Lytle, F. E.; Hercules, D. M. Photochem. Photobiol. 1971, 13, 123.
(8) González-Velasco, J.; Rubinstein, I.; Crutchley, R. J.; Lever, A. B. P.;

of the ECL production mechanisms can be important in relation to the aforementioned potential applications of ECL. For example, the solvent dependence of  $\eta_{\text{ECL}}$  for rubrene has clarified some questions on ECL mechanisms.<sup>14,15</sup> Also, the magnetic field effect on  $\eta_{\text{ECL}}$  helped distinguish between S-route and T-route ECL systems.<sup>16</sup> Another way of clarifying details on the ECL emission mechanism is to measure the temperature dependence of  $\eta_{\rm ECL}$ . Thus, the temperature dependence of  $\eta_{\text{ECL}}$  was recently determined for systems like 9,10-diphenylanthracene (DPA),9 Ru(bpy)<sub>3</sub><sup>2+</sup>,<sup>17,18</sup> or rubrene.<sup>19</sup> In the last case, the observed temperature dependence of  $\eta_{\rm FCI}$  was concluded to arise from a decrease in the rate of triplet quenching at lower temperatures.

In this work, we present data of  $\eta_{ECL}$  and its temperature dependence for the  $Ru(bpz)_3^{2+}$ -acetonitrile system. At low temperatures the similarity in the behavior of this metal chelate and  $Ru(bpy)_3^{2+17,18}$  is due to electron transfer between the 3+ and 1+ forms of  $Ru(bpy)_3^{2+}$ , which is highly efficient at populating the triplet emitting state. Therefore, in this temperature range the emission quantum yield,  $\phi_p$ , of the charge transfer plays a decisive role in determining  $\eta_{ECL}$ , whereas at higher temperatures the  $\eta_{\text{ECL}}$  dependence of the metal chelate is very different from that of  $Ru(bpy)_3^{2+}$ . This difference has been interpreted as the consequence of a decomposition reaction of the 3+ precursor in which solvent molecules play an important role. Electrochemical<sup>20</sup> and spectrophotometric results also support this interpretation. The decreased efficiency of excited-state formation with temperature underlies the low yields in excited-state formation and emission in many ECL organic systems. In such cases, it was supposed that the low  $\eta_{\rm ECL}$  values obtained were the consequence of excited-state quenching or ion decomposition. This supposition seems to be also valid for interpreting the results of  $Ru(bpz)_3^{2+}$ ECL temperature dependence.

This study confirms the results obtained in a previous, prelim-inary study of the ECL emitted by  $Ru(bpz)_3^{2+.8}$  It was concluded that ECL was produced as a consequence of two different reactions: (a) the 3+/1+ electron-transfer annihilation reaction giving rise to a direct population of the triplet manifold; (b) a reaction

- (14) Pighin, A. Can. J. Chem. 1973, 51, 3467.
  (15) Tachikawa, H.; Bard, A. J. Chem. Phys. Lett. 1974, 26, 246.
  (16) Faulkner, L. R.; Tachikawa, H.; Bard, A. J. J. Am. Chem. Soc. 1972,
- 94, 691.
- (17) Wallace, N. L.; Bard, A. J. J. Phys. Chem. 1979, 83, 1350.
- Itoh, K.; Honda, K. Chem. Lett. 1979, 99.
   Itoh, K.; Sukigara, M.; Honda, K. J. Electroanal. Chem. Interfacial
- Electrochem. 1980, 110, 277.
- (20) González-Velasco, J., unpublished results.

<sup>(1)</sup> Measures, R. M. Appl. Opt. 1974, 13, 1121. 1975, 14, 909. Heller, A.; Jernigan, J. L. Ibid. 1977, 16, 61.

<sup>(2)</sup> Laser, D.; Bard, A. J. J. Electrochem. Soc. 1975, 122, 632.

<sup>(4)</sup> Tokel-Takworyan, N. E.; Hemingway, R. E.; Bard, A. J. J. Am. Chem. Soc. 1973, 95, 6582.

<sup>(5)</sup> Luong, J. C.; Nadjo, L.; Wrighton, M. S. J. Am. Chem. Soc. 1978, 100, 5790.

 <sup>(9)</sup> Itoh, K.; Sukigara, M.; Honda, K. Electrochim. Acta 1979, 24, 1195.

Pighin, A.; Conway, B. E. J. Electrochem. Soc. 1975, 122, 619.
 Michael, P. R.; Faulkner, L. R. J. Am. Chem. Soc. 1977, 99, 7754. (12) Faulkner, L. R. MTP Int. Rev. Sci.: Phys. Chem., Ser. Two 1976,

<sup>(13)</sup> Schwartz, P. M.; Blakeley, R. A.; Robinson, B. B. J. Phys. Chem. 1972, 76, 1868.



Figure 1. Temperature dependence of the emission spectrum of a  $10^{-5}$ M solution of  $\operatorname{Ru}(bpz)_3^{2+}$  in acetonitrile;  $\lambda_{excit} = 435 \text{ nm}, \lambda_{emission}(max)$ = 585 nm = constant.

of the 3+ species with solvent or impurities to produce the Ru- $(bpz)_3^{2+}$  excited state.

## **Experimental Section**

 $Ru(bpz)_{3}^{2+}$  was obtained in the form of the  $PF_{6}^{-}$  salt according to literature procedures<sup>21,22</sup> and was used after recrystallization from an acetonitrile solution. Spectroquality grade acetonitrile was purified by a previously described method.<sup>23</sup> Also, the acetonitrile was distilled in the presence of H<sub>2</sub>Ca and under an N<sub>2</sub> atmosphere. After being degassed by freeze-pump-thaw cycles  $(<10^{-5}$  Torr), the resulting acetonitrile did not show any electrochemical activity on a Pt electrode (except the formation of a double layer charging current) between -2.58 and +2.58 V measured versus an Ag wire quasireference electrode. Tetra-nbutylammonium hexafluorophosphate (TBAFP) was prepared by a reaction of NH<sub>4</sub>PF<sub>6</sub> (Ozard-Mahoney) and tetra-n-butylammonium perchlorate (Aldrich). The resulting precipitate was used as a supporting electrolyte after washing with water and recrystallizing it from an ethanol solution. A Rhodamine B solution (Sigma, p.a.) was used as a standard material for determining luminescence quantum yield. As a standard for the ECL efficiency, a  $1 \times 10^{-3}$  M Ru(bpy)<sub>3</sub><sup>2+</sup> perchlorate solution was prepared from the dichloride (Aldrich) by metathesis with excess NaClO<sub>4</sub> in water, and the efficiency values obtained were compared with those previously reported.<sup>3</sup>

A Princeton Applied Research (PAR) Model 173 potentiostat and a PAR Model 175 universal programmer were used for potentiodynamic and phtentiostatic pulse experiments. A Houston Instruments Model 2000 x-y recorder was used.

The ECL measurements were carried out in a three-compartment working cell with a capacity of 3 mL. The working electrode compartment was equipped with an optically flat Pyrex glass window (area  $\sim 2 \text{ cm}^2$ ), parallel to which the working Pt electrode  $(0.06 \text{-cm}^2 \text{ area})$  was located. The distance between the working electrode and the window was  $\sim 3 \text{ mm}$ . A  $\sim 6 \text{ cm}^2 \text{ Pt}$ foil counter electrode was used. A silver wire was used as a quasireference electrode.

The ECL measurements were made by putting the sealed working cell in a light-tight box, painted with black nonreflective paint. The emitted light was monitored with a Hamamatsu TV Corp. R928 photomultiplier tube. The emission spectra were obtained with an Aminco Bowman spectrophotofluorometer



Figure 2. Variation of the luminescence quantum yield ( $\phi_p$ ) of a 10<sup>-5</sup> M  $Ru(bpz)_3^{2+}$  solution in acetonitrile as a function of temperature.



Figure 3. Variation of the ECL efficiency calculated from light and current-time transients (eq 1) recorded during the cathodic pulses;  $|(\eta_{ECL})_c|$  in 10<sup>-5</sup> M Ru(bpz)<sub>3</sub><sup>+</sup> in acetonitrile as a function of temperatures;  $\nu = 1$  Hz.

(SPF). The cell compartment was thermostatically controlled, allowing the temperature-dependent emission spectrum to be recorded. A Cary Model 14 UV-vis spectrophotometer was used for recording the absorption spectra of  $Ru(bpy)_3^{2+}$  and  $Ru(bpz)_3^{2+}$ .

## Results

Figure 1 shows the temperature dependence of the emission spectrum of a  $10^{-5}$  M solution of  $Ru(bpz)_3^{2+}$  in acetonitrile. The emission maximum decreases continuously from 9 to 75 °C without a change in the emission wavelength. In the measurement of luminescence quantum yield it was assumed that the spectral distribution in the fluorescence spectrum does not show any dependence on temperature during the time of the measurement. Therefore, it is possible to replace the integrated corrected emission spectrum ratio<sup>24</sup> by  $I_T/I_0$ , where  $I_T$  represents the emission intensity measured at 585 nm (Figure 1) and temperature T, and  $I_0$  represents the emission intensity at the same wavelength, at the same bandwidth, and at a reference temperature.<sup>17</sup> The excitation wavelength corresponded with the  $\lambda$  maximum in the absorption spectrum, i.e., 435 nm. The ECL and  $\phi_p$  data and the absorption and emission spectra did not show significant changes during at least 4 h after solution preparation. At longer times and especially after an increase in temperature, a change in solution color from orange to deep red was observed, and also the voltammogram taken in this case showed the presence of two additional peaks.8 The value of the phosphorescence quantum yield of Ru(bpz),<sup>2+</sup> was determined with Rhodamine B as a standard material (for Rhodamine B,  $\phi_p = 0.61$  in ethanol at room temperature<sup>25</sup>). The temperature dependence of the luminescence quantum yield for  $Ru(bpz)_3^{2+}$  is represented in Figure 2. The curve shape is similar to that reported for  $Ru(bpy)_3^{2+.17}$  However, the values of  $\phi_p$  at every temperature were smaller than those observed for Ru- $(bpy)_3^{2+}$ . In the temperature range studied,  $\phi_p$  changed from 0.069 at 9 °C to 0.04 at 75 °C, whereas the values obtained for Ru-

 <sup>(21)</sup> Crutchley, R. J.; Lever, A. B. P. J. Am. Chem. Soc. 1980, 102, 7128.
 (22) Crutchley, R. J.; Lever, A. B. P. Inorg. Chem. 1982, 21, 2276.

<sup>(23)</sup> Walter, M.; Ramalay, L. Anal. Chem. 1973, 45, 165.

<sup>(24)</sup> Demas, J. N.; Crosby, G. A. J. Am. Chem. Soc. 1970, 92, 7262. (25) Viktorova, E. N.; Hofman, I. A. Zh. Fiz. Khim. 1965, 39, 2643.

 $(bpy)_{3}^{2+17}$  were approximately 0.115 at 10 °C and 0.01 at 75 °C. Figure 3 shows the temperature dependence of the ECL quantum efficiency ( $\eta_{ECL}$ ) of an acetonitrile solution of Ru(bpz)<sub>3</sub><sup>2+</sup>.  $I_{ECL}$  was obtained by integrating the light transients recorded after the cathodic pulse. The pulsing frequency was 1 Hz between +1.85 V measured versus an Ag quasireversible electrode (AgQRE) and -0.85 V<sub>AgQRE</sub>. The absolute values of  $\eta_{ECL}$  for the Ru(bpz)<sub>3</sub><sup>2+</sup>-acetonitrile system were obtained by using the reported absolute value<sup>17,26</sup> for Ru(bpy)<sub>3</sub><sup>2+</sup> as a standard ( $\eta_{ECL}$  for Ru(bpy)<sub>3</sub><sup>2+</sup> in the same working cell, it was possible to refer the ECL intensities obtained with Ru(bpz)<sub>3</sub><sup>2+</sup> to the aforementioned value, simply by reproducing the same experimental conditions for both dyes.

Calculations of  $\eta_{ECL}$  values were made by taking into account the  $\eta_{ECL}$  definition:

ECL = 
$$\frac{\int_{0}^{t'} I \, dt}{\int_{0}^{t'} i_{c,a} \, dt} = \frac{\int_{0}^{t'} I \, dt}{Q_{c,a}}$$
 (1)

where I (einstein/s) represents the total ECL intensity integrated over a finite period of time t'. Integration of the cathodic or anodic current,  $i_c$  or  $i_a$  respectively (faraday/s), over the same period of time gives the total cathodic or anodic charge,  $Q_c$  or  $Q_a$ , respectively. The  $\eta_{\text{ECL}}$  values represent the number of photons produced in each radical ion annihilation event (i.e., per time in which the 1+ and 3+ forms of the chelate produced during the cathodic and anodic pulses, respectively, react with each other). Therefore, the light-intensity curves recorded after each potentiostatic pulse were integrated and referred to the value obtained for the integrated area in the ECL transients recorded for the Ru- $(bpy)_3^{2+}$ -acetonitrile system, under the same experimental conditions (cell, electrodes, geometry, and distance between optical window and photomultiplier). The values of  $Q_{c,a}$  were obtained from the current-time transients recorded after application of the potential steps from a potential value at which there is not a Faradaic reaction, to a potential value at which the ECL is produced. The actual value of  $Q_{c,a}$  is obtained by subtracting the integrated double layer charge. This value was deduced from current transients recorded after pulsing the potential between two values at which no Faradaic reaction takes place. After integration of the current-time transients recorded, a plot of  $Q_{dl}$ versus E was made, and  $Q_{dl}$  values at the potential at which Faradaic current was obtained were deduced from extrapolations.

The  $\eta_{\text{ECL}}$  values obtained after pulsing in the cathodic direction varied between 0.058 at 5 °C and ~2 × 10<sup>-3</sup> at 70 °C. The  $\eta_{\text{ECL}}$ temperature dependence in Ru(bpz)<sub>3</sub><sup>2+</sup> is similar to  $\phi_p$  temperature dependence in the same system (Figure 2). The  $\eta_{\text{ECL}}$  values at every temperature are smaller than those of  $\phi_p$ , and these differences become more accentuated at higher temperatures. Likewise, the  $\eta_{\text{ECL}}$  values obtained for the Ru(bpz)<sub>3</sub><sup>2+</sup> system were smaller than those calculated for Ru(bpy)<sub>3</sub><sup>2+.17</sup>

Figure 4 shows how the ECL intensity, measured in arbitrary units and recorded after the anodic and cathodic pulses, changes with varying cathodic pulsing limits, for a pulsing frequency of 0.5 Hz, maintaining a constant anodic pulsing limit of +1.90  $V_{AgQRE}$  at T = 25 °C. Whereas  $I_{ECL_e}$  remains approximately constant, a continuous increase in  $I_{ECL_a}$  is obtained the more cathodic the pulsing limit. The ratio between both intensities  $I_{ECL_a}/I_{ECL_c}$  grows with growing cathodic pulsing limit. Figure 5 shows plots of  $I_{ECL_e}$ ,  $I_{ECL_a}$ , and  $I_{ECL_a}/I_{ECL_e}$  versus the

Figure 5 shows plots of  $I_{ECL_e}$ ,  $I_{ECL_a}$ , and  $I_{ECL_e}/I_{ECL_c}$  versus the logarithm of pulsing frequency.  $I_{ECL_a}$  increases almost linearly with log  $\nu$ , whereas  $I_{ECL_e}$  shows an exponential growth with log  $\nu$ . The ratio  $I_{ECL_a}/I_{ECL_c}$  diminishes almost linearly with log  $\nu$ .

## Discussion

Figures 2 and 3 show the similarity between the temperature dependencies of  $\eta_{\text{ECL}}$  and  $\phi_p$  for the  $\text{Ru(bpz)}_3^{2+}$ -acetonitrile system. A sharp decrease of  $\eta_{\text{ECL}}$  and  $\phi_p$  with T is observed, which



**Figure 4.** Variations of  $I_{\rm ECL_a}$ ,  $I_{\rm ECL_c}$  and the ratio  $I_{\rm ECL_a}/I_{\rm ECL_c}$  measured in arbitrary units as a function of the cathodic potential pulsing limit;  $\nu = 0.5$  Hz, T = 25 °C,  $10^{-5}$  M Ru(bpz)<sub>3</sub><sup>2+</sup> in acetonitrile. Potentials were measured versus an Ag quasireversible electrode. The anodic pulsing limit was maintained at +1.9 V<sub>AgORE</sub>.



**Figure 5.** Plots of  $I_{\text{ECL}_a}$ ,  $I_{\text{ECL}_c}$ , and the  $I_{\text{ECL}_a}/I_{\text{ECL}_c}$  ratio, measured in arbitrary units versus the logarithm of the pulsing frequency in the a 10<sup>-5</sup> M Ru(bpz)<sub>3</sub><sup>2+</sup>-acetonitrile solution; T = 25 °C.

is larger than that reported for the  $Ru(bpy)_3^{2+}$ -acetonitrile system.<sup>17</sup> The differences found between the ECL behavior of both systems have to be explained through the ECL production mechanism. In the  $Ru(bpz)_3^{2+}$ -acetonitrile system, the steps that consume 3+ or 1+ precursors and do not lead to ECL emission must be more rapid and more temperature dependent than the same step for  $Ru(bpy)_3^{2+}$ . This means that the excited  $Ru(bpz)_3^{2+}$ molecules will be more easily transformed through decay processes such as photodecomposition and instability of oxidation and reduction products. Also, quenching of the  $Ru(bpz)_3^{2+*}$  light-emitting state by decomposition products or solvent molecules will be more rapid. The ECL temperature dependence (Figure 2),  $I_{\rm ECL}$  variation with the cathodic potential pulsing limit (Figure 4), and pulsing frequency (Figure 5) agree with these supposititions. Figure 4 shows that, for a constant pulsing frequency ( $\nu$ = 0.042), T = 25 °C, and anodic pulsing limit ( $E = +1.9 V_{AgORE}$ ), a variation of the cathodic pulsing limit over the potential range (-0.2 to -0.8  $V_{AgQRE}$ ) corresponding to the first reduction wave of the complex has little effect on  $E_{\text{ECL}_c}$ , whereas  $I_{\text{ECL}_a}$  grows



Figure 6. Plots of the 2+/3+ waves of a voltammogram recorded for a  $10^{-3}$  M Ru(bpz)<sub>3</sub><sup>2+</sup>-acetonitrile solution and their variation with sweep rate and temperature.

almost linearly with growing cathodic pulsing limit. When  $\nu$  is constant, the same amount of unstable 3+ precursor would be close to the electrode and react with the growing 1+ precursor concentration induced by an increase in the cathodic limit. Thus, the amount of the 3+ form limits the electron-transfer annihilation reaction between 1+ and 3+ precursors, giving rise to a ECL emission independent of the 1+ form present, i.e., independent of the cathodic pulsing limit. When pulsing occurs in the anodic direction, if the 1+ form is stable and a high concentration of 3+ precursor is formed, the ECL depends on the 1+ precursor concentration, which grows with an increasing cathodic limit (Figure 4). Thus, the 3+ form must be unstable, probably due to its high oxidation potential, and decomposes as ligands are displaced by solvent molecules in reactions of following type:

$$Ru(bpz)_{3}^{3+} + 2CH_{3}CN: \rightarrow$$

bipyrazyl + 
$$Ru(bpz)_2(CH_3CN)_2^{34}$$

The pronounced instability of the 3+ form is also shown in Figure 5, in which a plot of  $I_{ECL_a}$  and  $I_{ECL_c}$  versus the logarithm of the pulsing frequency is given (pulsing limits were maintained at +1.9 and -0.8  $V_{AgQRE}$ ). At low pulsing frequencies,  $I_{ECL_a}$  can be up to 15 times higher than  $I_{ECL_c}$ . As the pulsing frequency is increased, the  $I_{ECL_a}/I_{ECL_c}$  ratio approaches 1 and shows an exponential variation with it. During the anodic pulse the 3+ form is produced, which immediately reacts with the 1+ precursor formed during the previous cathodic pulse, giving rise to the  $Ru(bpz)_3^{2+*}$  emitting state and to other substances (see below).

The same proposition would also be valid for the ECL production during the cathodic pulse. However, the fact that ECLan is lower at lower pulsing frequencies means that the longer the time period between pulses, the smaller the concentration of the undecomposed 3+ form, thereby limiting the ECL production during the cathodic pulse. Therefore the results plotted in Figures 4 and 5 are in agreement with the instability of the 3+ form. The rapid decrease of  $\eta_{\text{ECL}}$  with temperature must also be a consequence of such instability. After a time period, which decreases with growing temperature, the original solution undergoes color change, and the corresponding absorption spectrum changes. Also, there is a change in the voltammogram (see Figure 38), in which two additional peaks appear. Other evidence for the decomposition of the 3+ form is given in Figure 6, which shows the variation induced by temperature and sweep-rate changes in the 2+/3+wave.



Figure 7. Plot of the ratio between the anodic and cathodic peak currents in the 2+/3+ wave as a function of temperature;  $10^{-3}$  M Ru(bpz)<sub>3</sub><sup>2+</sup> in acetonitrile; v = 10 mV s<sup>-1</sup>.



**Figure 8.** Plot of the efficiency of excited-state formation  $(\eta_{\text{ECL}}/A\phi_p)_c$  calculated from transients recorded during the cathodic pulse as a function of temperature;  $10^{-5}$  M Ru(bpz)<sub>3</sub><sup>2+</sup> in acetonitrile; pulsing frequency  $\nu = 1$  Hz.

An increase in temperature influences the system in the same way as a decrease in sweep rate. At 25 °C and  $v = 100 \text{ mV s}^{-1}$ , the wave is similar to that recorded for a reversible redox couple, whereas at  $T = 70 \text{ }^{\circ}\text{C}$  and the same sweep rate, the cathodic peak is lower than the anodic one. The 3+ form produced during the anodic sweep decomposes, and this decomposition is enhanced by temperature increase. During the cathodic sweep at 70 °C, only a fraction of the 3+ form produced can be reduced to the 2+ form, whereas at 25 °C the decomposition reaction is slower, so that almost the same amount of 3+ form is reduced to 2+ form. At 25 °C and  $v = 10 \text{ mV s}^{-1}$ , the 3+ form produced during the anodic sweep has time to decompose before it can be again reduced to the 2+ form during the cathodic sweep, so that the resulting anodic peak is higher than the cathodic one. Figure 7 clearly shows this temperature effect; it is a plot of the  $i_{pa}/i_{pc}$ , i.e., the ratio between anodic and cathodic peak current in the 2+/3+ wave as a function of T, with constant anodic scan limit and sweep rate. These temperature effects are not detected for the 2+/1+ wave in the same complex.

Efficiency of Excited-State Formation Deduced from  $\eta_{ECL}$ versus T Plots. As in the Ru(bpy)<sub>3</sub><sup>2+</sup> system, <sup>17,18</sup> the values of  $\eta_{ECL}$  and  $\phi_p$  are very similar to each other in the low-temperature range (5–35 °C). Figure 8 shows a plot of the ratio ( $\eta_{ECL}/A\phi_p$ )<sub>c</sub> calculated for the cathodic current and light transients, where A represents a correction factor introduced to compensate for emission losses due to light reflection by the Pt electrode surface. A is essentially 1 for the described experiments.<sup>27</sup> The  $\eta_{ECL}$  values used in Figure 8 are the ECL efficiencies measured during the cathodic pulses and calculated according to eq 1. Between 5 and 35 °C, the ratio of  $\eta_{ECL}$  and  $\phi_p$  shows an average value of around 0.92. This means a high efficiency for excited-state formation and is typical of systems in which the emitting excited state is

<sup>(27)</sup> Lytle, F. E.; Hercules, D. M. J. Am. Chem. Soc. 1969, 91, 253.

SCHEME I

cathodic pulse

$$|Ru(bpz)_3|^{2^+} + e^- = |Ru(bpz)_3|^+$$
 (step 1)

$$\left|\operatorname{Ru}(\operatorname{bpz})_{3}\right|^{2^{*}} - e^{-} \longrightarrow \left|\operatorname{Ru}(\operatorname{bpz})_{3}\right|^{3^{*}} \quad (\text{step 2})$$

annihilation reaction after cathodic and anodic pulse

Ru(bpz)<sup>2+\*</sup> + Ru(bpz)<sub>3</sub><sup>2+</sup> (step 3)

$$Ru(bpz)_{3}^{+} + Ru(bpz)_{3}^{3+} \overset{h}{\underset{k_{2}}{\overset{k_{1}}{\overset{k_{1}}{\overset{k_{2}}}}}{\overset{k_{2}}{\overset{k$$

Ru(bpz)3<sup>2+\*</sup> + Ru(bpz)3<sup>2+</sup> (step 5)

light emission

$$\left|\operatorname{Ru}(\operatorname{bpz})_{3}^{2+*}\right|^{\mathsf{t}} \longrightarrow \operatorname{Ru}(\operatorname{bpz})_{3}^{2+} + h\nu \qquad (\text{step 6})$$

directly produced. In a previous study<sup>8</sup> it was reported that the Ru(bp2)<sub>3</sub><sup>2+</sup>-acetonitrile system behaves as an S-route system where direct population of the emitting state (triplet manifold) occurs upon electron transfer. According to this idea the similarity between the  $\eta_{\rm ECL}$  and  $\phi_p$  values can be understood by analyzing the mechanistic factors influencing the S-route or direct population of the emitting state produced after the electron-transfer annihilation reaction between the 3+ and 1+ forms obtained during anodic and cathodic pulses, respectively.

The reaction sequence shown in Scheme I is proposed (where s = singlet and t = triplet). The potential value for production of the 3+ form (corresponding to a  $t_{2g}{}^5 \pi_L{}^{*0} e_g{}^0$  electronic configuration<sup>28</sup>) was determined as +1.9 V<sub>AgQRE</sub>, whereas the formation of Ru(bpz)<sub>3</sub><sup>+</sup> (corresponding to a  $t_{2g}{}^6 \pi_L{}^{*1} e_g{}^0$  electronic configuration) takes place at -0.8 V<sub>AgQRE</sub>. According to Faulkner et al.<sup>16</sup> the standard enthalpy (in electronvolt) of an ECL redox process is given at constant temperature by

$$-\Delta H^0 = E^0(R'/R'_0^+) - E^0(R/R_0^-) - T\Delta S^0$$
(2)

where  $E^0$ , the standard reduction potentials for the two half-reactions comprising the redox processes, are estimated from the cyclic voltammetric peak potentials. Taking  $T\Delta S^0$  as  $-0.16 \text{ eV}^{16}$ and substituting  $E^0(R'/R'_0^+) = +1.9 \text{ eV}$  and  $E^0(R/R_0^-) = -0.8 \text{ eV}$ , we obtain a value for  $-\Delta H^0$  of 2.86 eV, i.e., the energy that would be necessary for a direct population of the  $d-\pi^*$  excited singlet in  $Ru(bpz)_3^{2+}$  (therefore, the excited state is produced through a metal-to-ligand charge transfer, MLCT). Since this value is close to the singlet-singlet absorption maximum of Ru- $(bpz)_3^{2+}$  ( $\lambda = 435$  nm corresponding to around 2.85 eV), it seems that a direct population of the triplet manifold, whose minimum is situated at 585 nm (2.12 eV) is more likely. Thus, the probability for step 5 (Scheme I) is very small, and the kinetic treatment of the mechanism neglects it as well as intersystem crossing. So, steps 3 and 4 are the only two ways left for the electron-transfer annihilation reaction. Since steps 1 and 2 are considered to be very rapid,<sup>8</sup> step 3 and 4, with the same reactants (the 3+ and 1+ precursors), would be the rate-determining steps. For both reactions, the rate equation would be equally dependent on the concentration of the 3+ and 1+ forms and would differ in the rate constant  $k_t$  and  $k_1$  for steps 3 and 4, respectively. Therefore, the ratio between  $\eta_{\text{ECL}}$  and  $\phi_{\text{p}}$  would have the following form:

$$\left|\frac{\eta_{\rm ECL}}{A\phi_{\rm p}}\right| = \frac{k_{\rm t}}{k_{\rm 1} + k_{\rm t}} \tag{3}$$

Figure 8 shows two temperature ranges in which an almost constant ratio between  $\eta_{ECL}$  and  $\phi_p$  is obtained. The results plotted correspond to  $\eta_{ECL}$  values calculated from light and current transients recorded during the cathodic pulse ( $\nu = 1$  Hz). Between 5 and 35 °C, an average value of 0.92 for the ratio expressed in eq 3 is obtained, so that

$$k_1 = 0.089k_t \text{ (at } T < 35 \text{ °C)}$$
 (4)

The increase in  $\eta_{\text{ECL}}$  with decreasing temperature must be due to an increase in  $\phi_p$ , i.e., an increase in the lifetime of the triplet state in the Ru(bpz)<sub>3</sub><sup>2+</sup> complex. In the range of lower temperatures studied, 8.9% of the 3+ and 1+ forms react by a route different from direct population of the triplet light-emitting state (step 3 in the aforementioned mechanism). This 8.9% loss in  $\eta_{\text{ECL}}$ can be ascribed to electron-transfer annihilation leading to the 2+ form and heat (as represented through step 4 and  $k_1$ ), to quenching of the excited state by impurities, decomposition products, or solvent molecules, and to decomposition of one or both the oxidized and reduced forms.

The electron-transfer annihilation reaction between the 3+ and 1+ forms can be classified as a very exothermic electron-transfer reaction, which, according to the Marcus theory, should take place at negligible rates.<sup>29</sup> This could explain why this reaction accounts for only 8.9% of the whole mechanism, whenever the proposed reaction model is valid. On the other hand, the slight linear decrease of  $\eta_{\rm ECL}/A\phi_p$  with T can be interpreted as the consequence of the decomposition reaction becoming more rapid with growing temperature.

In the range of higher temperatures (Figure 8), the value of the  $\eta_{\text{ECL}}/A\phi_p$  ratio shows a sharp change, so that

$$\left. \frac{\eta_{\text{ECL}}}{A\phi_{\text{p}}} \right|_{T < 35^{\circ}\text{C}} \simeq 0.42 \tag{5}$$

Also, the apparent activation energies of the ECL efficiency measured in both temperature ranges are different  $(28 \text{ kJ mol}^{-1} \text{ at low temperatures versus 40 kJ mol}^{-1}$  in the high-temperature range). This means that a change in the ECL mechanism must take place at higher temperatures. The rate of the decomposition reaction grows and so does the quencher concentration. Therefore, a seventh step must be added to the mechanism, in which the excited triplet state is quenched:

$$\operatorname{Ru}(\operatorname{bpz})_3^{2+*}|^T + Q \xrightarrow{k_Q} Q + \operatorname{Ru}(\operatorname{bpz})_3^{2+} (\operatorname{step} 7)$$

where Q can represent bipyrazyl or acetontrile molecules or any other decomposition product. The activation energy change suggests another mechanism for ECL production. In fact, the ECL intensity-time transient recorded during the anodic pulse shows a steady level of emission, which has been explained as coming from a reaction between the strong oxidant  $Ru(bpz)_3^{3+}$ and solvent, electrolyte, or decomposition products of the complex.<sup>8</sup>

A consideration of step 7 in the reaction scheme changes the kinetic analyses, leading to following expression:

$$\left|\frac{\eta_{\text{ECL}}}{A\phi_{\text{p}}}\right|_{\text{cath}, T<35^{\circ}\text{C}} = \frac{k_{\text{t}}}{k_{1}+k_{\text{t}}+k_{\text{Q}}} \tag{6}$$

From eq 4 results  $k_Q \simeq 1.29k_t$ , i.e., the rate constant for the quenching reaction becomes greater than the rate of the electron-transfer annihilation reaction that produces the excited-triplet-emitting state of the complex. The higher  $k_Q$  value must be due to a growth of the frequency factor for step 7 in the high-temperature range, since the change in activation energy detected must be attributed to a contribution of this step or to a change in the ECL mechanism production.

In conclusion, at high temperatures the decomposition reaction and the decrease in  $\phi_p$  are determinant factors in the ECL emission observed during the cathodic pulse in the Ru(bpz)<sub>3</sub><sup>2+</sup>-acetonitrile-Pt electrode system. As in the case of the Ru(bpy)<sub>3</sub><sup>2+</sup> complex,<sup>17,18</sup> the aforementioned system gives rise to very high excited-state yields at low temperatures, although lower than in Ru(bpy)<sub>3</sub><sup>2+</sup>. Likewise the ECL emission is more unstable, due to more rapid decomposition by solvent molecules of the oxidized form of the complex.

On the ECL Mechanism during the Anodic Pulse. The temperature dependence of the ECL emitted by pulsing to anodic

<sup>(28)</sup> González-Velasco, J., unpublished results.

<sup>(29)</sup> Van Duyne, R. P.; Fischer, S. F. Chem. Phys. 1984, 85, 183.



**Figure 9.** Variation of the ECL efficiency calculated from light and current-time transients (eq 1) recorded during the anodic pulses.  $|(\eta_{ECL})_a|$  as a function of temperature;  $10^{-5}$  M Ru(bpz)<sub>3</sub><sup>2+</sup> in acetonitrile;  $\nu = 1$  Hz.



**Figure 10.** Plot of the efficiency of excited-state formation,  $(\eta_{\text{ECL}}/A\phi_p)_a$  during the anodic pulse as a function of temperature;  $10^{-5}$  M Ru(bpz)<sub>3</sub><sup>2+</sup> in acetonitrile;  $\nu = 1$  Hz.

potential values is different from that obtained by pulsing to cathodic potentials. Figure 9 shows the ECL quantum efficiency  $(\eta_{\text{ECL}})$  values obtained during the anodic pulses as a function of temperature, when v = 1 Hz,  $E_c = -0.8$  V<sub>AgQRE</sub>, and  $E_a = 1.9$  $V_{AgQRE}$ . The  $(\eta_{ECL})_a$  values are smaller than the  $(\eta_{ECL})_c$  values (Figure 2) at each temperature. They change from 0.012 at 9 °C to 0.0028 at 70 °C, but this value is almost constant from 40 °C. As  $\phi$  decreases with temperature, a plot of  $(\eta_{\text{ECL}}/A\phi_p)_a$  versus T (Figure 10) increases almost exponentially. Thus, the efficiency of excited-state formation during the anodic pulse presents an almost constant value of 0.2 in the low-temperature range. This value is smaller than the 0.92 obtained during the cathodic pulse under the same temperature and frequency conditions. The exponential increase of the  $\eta_{\rm ECL}/A\phi_{\rm p}$  ratio obtained at higher temperatures is ascribed to the aforementioned change in ECL emission. The 3+ form reacts with decomposition products of the original complex (for instance, bipyrazyl molecules left free



Figure 11. Jablonski diagram for the  $Ru(bpz)_3^{2+}$  complex.

in a ligand-solvent molecules exchange reaction), which can give rise to an electron injection to the emitting excited triplet state in the not yet decomposed 3+ form. The decomposition reaction is strongly temperature dependent, so that the concentration of products reacting with the 3+ form grows rapidly with temperature.

#### Conclusions

The differences found in the ECL emission features of a Ru-(bpz)<sub>3</sub><sup>2+</sup> solution in acetonitrile during anodic and cathodic pulses can be attributed to a change in the ECL production mechanism connected with a decomposition reaction of the studied complex.

During the cathodic pulse, the 3+ form only reacts with the 1+ form by an electron-transfer annihilation reaction to produce the emitting excited-triplet-emitting state of the complex. This explains the almost ideal behavior shown by the ECL system studied, for which an excited-state production efficiency close to 1 is calculated. This high efficiency can be understood on the basis of the spectroscopic properties of Ru(bpz)<sub>3</sub><sup>2+</sup>, which are summarized in the energy-level diagram shown in Figure 11.<sup>28</sup> The homogeneous electron-transfer annihilation reaction between the 1+ and 3+ forms of the complex is energy sufficient (2.85 versus 2.12 eV), allowing a direct population of the triplet excited state.

At higher temperatures during the anodic pulse, a decomposition reaction of the 3+ form produces bipyrazyl and other decomposition products. These substances are also able to inject electrons in the triplet manifold of the complex, changing the ECL emission mechanism, as the ECL temperature study shows.

Acknowledgment. The support of this research by the DGICyT (Grant PB86-0565) is gratefully acknowledged. An important part of the experimental work concerning this paper was done in the laboratories of Professor Bard at the University of Texas at Austin during a year stay. I thank Professor Bard and co-workers for continuous support and help.

**Registry No.**  $\operatorname{Ru}(\operatorname{bpz})_3^{2+}$ , 75523-96-5;  $\operatorname{Ru}(\operatorname{bpz})_3^{3+}$ , 84303-43-5;  $\operatorname{Ru}(\operatorname{bpz})_3^+$ , 75523-97-6; acetonitrile, 75-05-8.