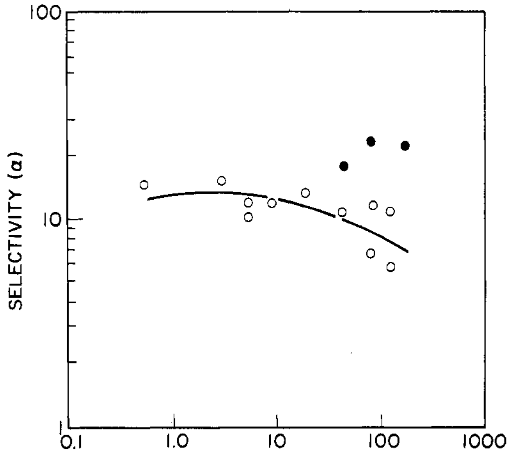

Figure 3. Isotopic selectivities from 2-ns-pulse photolysis of trifluoromethyl bromide. Open circles are for neat trifluoromethylbromide; filled circles are for 5.0 torr of trifluoromethyl bromide + argon. Incident fluence, 2 J cm^{-2}; frequency, 1047 cm^{-1}; temperature, 22 °C.

yield enhancement. In the former the yield must be enhanced during the pulse; in the latter the yield may increase after the pulse. Both explanations are supported by the observation that, when the excitation frequency is removed from the central frequency of the dissociation spectrum, an increase in hexafluoroacetone pressure decreases the observed yield.[9]

Although a precise kinetic explanation for the results presented above may be a matter for some debate, the demonstration that changing the laser pulse length at constant fluence leads to entirely different kinetic dependence is unequivocal. Thus, we have demonstrated significant flux effects of a kind not usually discussed. The low-pressure data ($\leq$0.11 torr) of Table I may be used to demonstrate the importance of intensity effects of a more conventional nature;[12] at constant fluence (1.8 J cm^{-2}) we observed that the dissociation probability for 2-ns pulses is over an order of magnitude greater than that for long-pulse irradiation. This observation could only be amplified or treated in a more quantitative fashion if the temporal profile of the "long" pulse were better defined. Experiments designed to quantify this effect are being considered. We note that two other groups have reported evidence for intensity effects in infrared multiphoton dissociation.[13,14]

Trifluoromethyl Bromide. The experiments reported above have indicated that irradiation by short-pulse CO$_2$ laser pulses at moderate fluences, at pressures where collisions may be neglected during the irradiaiton time, leads to a kinetically simple situation in which dissociation probabilities are determined solely by power broadening and collisional quenching of molecules above the dissociation threshold. Isotopically selective dissociation has been inferred for 2-ns irradiation of CF$_3$H/CF$_3$D mixtures where the isotope shift is large ($\Delta\nu_5$ = 182 cm^{-1}).[5] However, no direct measurements of isotopic selectivity have been made in a situation where the isotope shift is comparable to the power broadening. Such measurements were not possible with the present system for hexafluoroacetone, so trifluoromethyl bromide was used as a test molecule. The ν_1 absorption band of ^{12}CF$_3$Br lies at 1084 cm^{-1}; that for ^{13}CF$_3$Br lies at 1058 cm^{-1}. Figure 3 shows α values observed when CF$_3$Br at natural abundance is irradiated with 2-ns pulses at 1047 cm^{-1} at 2 J cm^{-2}. Isotopically selective dissociation of ^{13}C-bearing molecules is demonstrated. We note that recently workers in other laboratories have found similar results.[15] In agreement with the discussion presented above, there is little effect of pressure on the isotopic selectivity.

Acknowledgment. We thank J. B. Marling for providing us with a preprint of a paper on trifluoromethane photolysis and for communicating results on trifluoromethyl bromide photolysis.

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Electrogenerated Chemiluminescence. 38. Emission Intensity–Time Transients in the Tris(2,2′-bipyridine)ruthenium(II) System

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Ecl transients for potential step experiments on the Bu(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine) system in acetonitrile solutions conform well to the behavior predicted for the case in which the emitting species is produced in the electron-transfer step (i.e., an "energy-sufficient" or "S-route" system). Possible explanations for the deviation of the slope/intercept ratio of the linear ecl intensity vs. $(t_r/t_f)^{-1/2}$ plot (t_f = forward pulse duration, t_r = time during reverse pulse) found for longer pulse lengths and at higher temperatures are examined.

Although transient techniques and the detailed analysis of current–time curves have been very important in the elucidation of reaction mechanisms in electrochemical investigations, the analogous intensity–time (I–t) transients observed in studies in electrogenerated chemiluminescence (ecl) have been less informative. The usual potential step experiment involves a step for a duration t_f, to a potential where one of the reactants, e.g., the reduced form A$^-\cdot$, is produced at a rate controlled by its diffusion to the electrode. The potential is then stepped to a value where the

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other reactant, e.g., the oxidized form, $D^{+}\cdot$, is produced. The reaction between these species produces an excited state, e.g.

$$A^{-}\cdot + D^{+}\cdot \rightarrow A^{*} + D \quad (1)$$

and the nature of the emission intensity with time should provide information about details of the mechanism. Feldberg[1] first proposed models for the *I*–*t* transients, and later work, especially by Faulkner and his group, led to further refinements and developments of the model.[2-4] However, the experimental results with the least complicated of the ecl systems, the "S-route" system, where the emitting species is produced directly in the electron-transfer reaction 1, have almost always shown considerable deviations from the predicted behavior. This lack of success with presumably simple reactions has led to a reduced confidence in the use of such transients to investigate more complex ecl schemes.

The ecl reaction (eq 2) between $Ru(bpy)_3^{+}$ and $Ru(bpy)_3^{3+}$

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

(where bpy is 2,2′-bipyridine) appears to be an almost ideal one to investigate the transient behavior of an "S-route" system.[5,6] There are no excited states of lower energy than the emitting one formed during the electron-transfer reaction 2, and no energetically available higher emitting states. Moreover, the precursors are both quite stable. Recent work by our group[7] and by Itoh and Honda[8] have independently shown that the yield of excited state in the electron-transfer reaction is very high and approaches unity. Independent studies of the ecl transient in the system under different conditions are reported here and in the companion paper by Glass and Faulkner.[9]

Experimental Section

Chemicals. Tris(2,2′-bipyridyl)ruthenium(II) perchlorate, $Ru(bpy)_3(ClO_4)_2$, was prepared by metathesis of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (G. F. Smith) with excess $NaClO_4$ in H_2O. The crystals were washed with H_2O, recrystallized once from ethanol and twice from acetonitrile (MeCN), and dried under vacuum at 90 °C for 24 h. Tetra-*n*-butylammonium perchlorate (TBAP) was Polarographic Grade from Southwestern Analytical Chemical. The material was dissolved in warm ethanol. After addition of activated carbon and filtration, the material was repeatedly recrystallized from ethanol–water (1:1). A final recrystallization was done from benzene and the crystals were dried at 50 °C for 36 h. Activated neutral alumina (Woelm) was dried under vacuum ($<10^{-5}$ torr) for 72 h at 400 °C. All dry chemicals were stored in air-tight containers in a helium filled glove box (Vacuum Atmospheres) before use.

MeCN was obtained as Spectro Grade (Matheson Coleman and Bell) and was purified by repeated vacuum distillations from P_2O_5 and freeze–pump–thaw cycles to remove dissolved gases. The solvent was then vacuum distilled into a storage flask containing molecular sieves (Linde 4A) which had been activated by heating under high vacuum at 400 °C for 72 h.

Electrochemical Cell and Instrumentation. The electrochemical/ecl cell was of design similar to that used by Wallace and Bard.[7] It incorporated a Pt disk working electrode (area, 0.002 ± 0.0003 cm^2) and a Pt wire quasi-reference electrode located several millimeters from the working electrode surface. The Pt disk was polished with a slurry of 0.2-μm alumina, rinsed with water and then ethanol, and dried $\sim$5 min at 100 °C prior to use. A large Pt foil served as the counter electrode. TBAP and $Ru(bpy)_3(ClO_4)_2$ were weighed and added to the cell in the drybox. In some experiments, activated neutral alumina was also added to the cell ($\sim$1 g/10 mL of MeCN) to remove traces of electrophilic or nucleophilic impurities from the electrolyte.[10] The cell was assembled in the drybox, removed, and evacuated at $\sim 5 \times 10^{-6}$ torr for 5–18 h prior to addition of the solvent. A volume-calibrated side arm on the cell allowed introduction of a suitable amount of solvent by vacuum distillation. A 5-mL sample compartment was internally sealed into a double-walled evacuated Dewar of 100-mL capacity. Temperature variation and stabilization were accomplished by using either a dry ice–methanol mixture or water in the Dewar. After distillation, the cell was removed from the vacuum line, its contents were thoroughly mixed, and the cell was tipped to fill the electrode compartment.

Electrode potentials were controlled by a Princeton Applied Research (PAR) Model 173 potentiostat. The desired potential program was generated by a PAR Model 175 programmer. The potentiostat employed a positive feedback circuit that was adjusted by the method of Lauer and Osteryoung[11] compensate for the electrochemical cell resistance. The usual triple-potential-step technique was used to generate ecl transients. Precise control of the potential waveform was checked and verified before and after ecl generation by cyclic voltammetry. Generation of the $Ru(bpy)_3^{0}$ species as an ecl precursor was found to cause irreversible filming of the Pt electrode in related experiments which involved multiple ecl generation cycles. Consequently, the reduction of $Ru(bpy)_3^{2+}$ or $Ru(bpy)_3^{+}$ to $Ru(bpy)_3^{0}$ was avoided in these experiments by careful control of the potential limits. The cathodic limit imposed on the ecl generation potential waveform was restricted to $\sim$90 mV negative of E_{pc} $Ru(bpy)_3^{2+}/Ru(bpy)_3^{+}$ as obtained by cyclic voltammetry.

An RCA 1P28 photomultiplier tube was employed to monitor ecl emission. An RCA CA3140 operational amplifier was used as a photomultiplier anode current follower to allow variable detector gain and fast risetime (4.5 MHz). The analog signal from the operational amplifier was obtained and stored with a Nicolet Model 1090A digital oscilloscope. All ecl experiments were carried out with the cell in a large, light-tight box, whose interior was painted with black nonreflective paint.

Computer Simulation of Ecl Processes. Computer simulation of ecl processes were formulated according to previously established models.[1-4,13] The model used in these studies involved 2000 iterations/step (*L*) and kt_fC = 2000 for the ecl precursor annihilation reaction. The amount of computer time required for a simulation could be shortened considerably by establishing the concentration profile of the initial ecl precursor by numerical cal-

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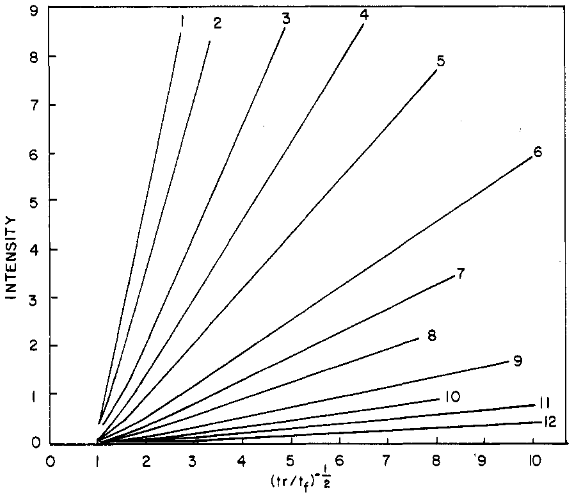

Figure 1. Linearized ecl intensity-time profiles. Precursor generation sequence: $Ru(bpy)_3^+$, then $Ru(bpy)_3^{3+}$. Solution contained 2 mM $Ru(bpy)_3(ClO_4)_2$ and 0.1 M TBAP in MeCN. Al_2O_3 added at ~1 g/10 mL of MeCN. t_f = (1) 1 ms, (2) 2 ms, (3) 5 ms, (4) 10 ms, (5) 20 ms, (6) 50 ms, (7) 100 ms, (8) 200 ms, (9) 500 ms, (10) 1000 ms, (11) 2000 ms, (12) 5000 ms.

culations rather than by digital simulation. For example, generation of ecl precursor B from parent molecule A yields

$$A + e \rightarrow B \tag{3}$$

$$C_A(x,t) = C_A{}^{\mathrm{bulk}}\,\mathrm{erf}\{x/2(D_At)^{1/2}\} \tag{4}$$

$$\mathrm{FCA} = C_A/C_A{}^{\mathrm{bulk}} = \mathrm{erf}\{(j-1)/2(\mathrm{DMA}{*}L)^{1/2}\} \tag{5}$$

$$\mathrm{FCB} = C_B/C_A{}^{\mathrm{bulk}} = \mathrm{erfc}\{(j-1)/2(\mathrm{DMB}{*}L)^{1/2}\} \tag{6}$$

where D_A is the actual diffusion coefficient of species A, DMA and DMB are the simulation diffusion coefficients, x is distance from the electrode, and j is the simulation distance parameter. C_A represents the actual concentration of species A and FCA the fractional concentration. Processes beginning at t_f with generation of the second ecl precursor, including precursor ion annihilation and ecl emission, were then modeled by digital simulation.

Results and Discussion

Experimental Results. According to the analysis of Faulkner,[4] analytical treatment and digital simulation of the ecl transient in potential-step experiments predict dimensionless current-time and ecl precursor annihilation rate relationships of the following forms:

$$\omega_n = a(t_r/t_f)^{-1/2} + b \qquad t_r/t_f < 0.2 \tag{7}$$

$$Z = \pi^{-1/2}\left[2\left(\frac{t_r}{t_f}\right)^{-1/2} - \left(1 + \frac{t_r}{t_f}\right)^{-1/2}\right] \tag{8}$$

where ω_n is the dimensionless rate parameter which is proportional to N, the redox reaction rate; Z is the dimensionless current parameter;[4] and a and b are constants. Although a comparison of the observed ecl intensity with ω_n requires a knowledge of the efficiencies of the ecl processes as well as that of the luminescence detector, one should observe identical intercept/slope (b/a) ratios for ω_n and for I when these functions are plotted vs. $(t_r/t_f)^{-1/2}$. This prediction assumes that I is directly proportional to ω_n, eq 9, i.e., an S-route mechanism,[12] where ϕ_f is the

$$I = \phi_f\phi_s\omega_n \tag{9}$$

fluorescence efficiency and ϕ_s is the yield of emitter in the redox reaction.

As pointed out by Glass and Faulkner,[9] the ecl transient for an energy-sufficient system should satisfy the following criteria: (1) a plot of I vs. $(t_r/t_f)^{-1/2}$ is linear for $t_r/t_f < 0.2$; (2) $(b/a)_{\mathrm{obsd}}$ values are near the theoretical value; (3) equivalent behavior is found when either ecl precursor (i.e., the $Ru(bpy)_3^+$ or $Ru(bpy)_3^{3+}$) is generated first in the potential-step sequence.

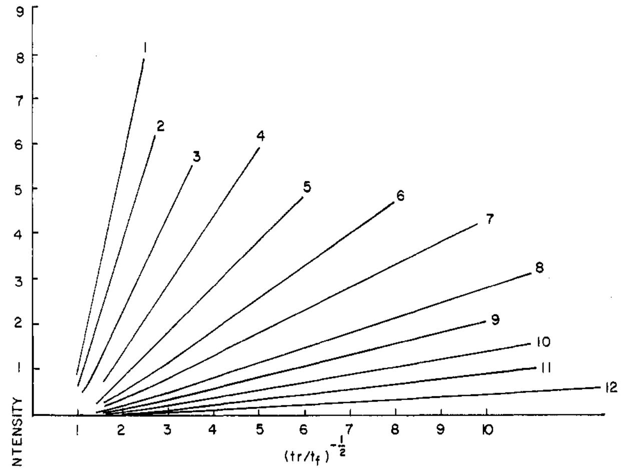

Figure 2. Linearized ecl intensity-time profiles. Precursor generation sequence: $Ru(bpy)_3^{3+}$, then $Ru(bpy)_3^+$. (Other conditions same as Figure 1.)

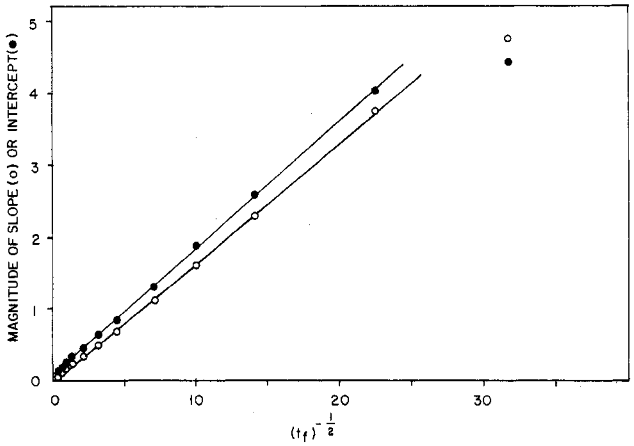

Figure 3. Slopes (+) and intercepts (●) of plots in Figure 1.

Typical ecl intensity–time parameter curves obtained for the $Ru(bpy)_3^{2+}$–MeCN system are given in Figures 1 and 2. These are linear at short times [$t_r/t_f < 0.2$] as predicted with a small deviation from linearity observed at longer times in experiments which involved longer ecl pulse widths (i.e., larger t_f values). The behavior was the same for either the $Ru(bpy)_3^+$ species or the $Ru(bpy)_3^{3+}$ species generated first in the ecl producing potential-step sequence. The slope and intercept values obtained from the plots in Figures 1 and 2 are given in Table I. If the diffusion coefficients for the oxidized and the reduced precursor are assumed to be equal, the theoretical value for b/a is −0.95 for this system.[4b] The experimentally obtained magnitude of b/a approached this theoretical value at small values of t_f, but was appreciably larger at longer times. As Figures 3 and 4 illustrate, the magnitude of the slopes and intercepts obtained from the linearized ecl transients vary linearly with $t_f^{-1/2}$ as was also found by Glass and Faulkner.[9] The intercepts showed a much larger deviation from linearity than the slope values do, however.

Experimentally, the ecl intensity and the magnitude of b/a were both found to be functions of temperature, activated alumina treatment, and the history of any particular electrode and solution, as shown by the results in Table II and Figure 5.

TABLE I: Slopes and Intercepts of I-$(t_r/t_f)^{-1/2}$ Plots[a]

t_f, ms	a	$-b$	$-b/a$
A. Precursor Generation Sequence −/+ [$Ru(bpy)_3^+$, Then $Ru(bpy)_3^{3+}$]			
1	4.79	4.46	0.93
2	3.75	4.06	1.08
5	2.30	2.59	1.13
10	1.63	1.89	1.16
20	1.13	1.31	1.16
50	0.67	0.85	1.26
100	0.49	0.64	1.32
200	0.34	0.46	1.34
500	0.21	0.33	1.56
1000	0.14	0.24	1.70
2000	0.094	0.17	1.85
5000	0.053	0.12	2.34
B. Precursor Generation Sequence +/− [$Ru(bpy)_3^{3+}$, Then $Ru(bpy)_3^+$]			
1	4.79	3.88	0.81
2	3.22	2.62	0.81
5	2.16	2.07	0.96
10	1.52	1.67	1.10
20	1.01	1.10	1.17
50	0.71	0.95	1.18
100	0.50	0.69	1.38
200	0.33	0.48	1.46
500	0.24	0.38	1.58
1000	0.17	0.30	1.76
2000	0.11	0.22	2.00
5000	0.061	0.16	2.47

[a] Data from Figures 1 and 2. Solution was 2 mM $Ru(bpy)_3(ClO_4)_2$ and 0.1 M TBAP in MeCN (treated with alumina).

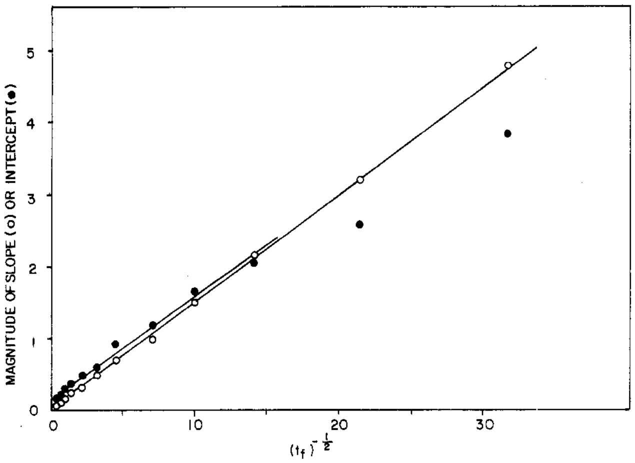

Figure 4. Slopes (+) and intercepts (●) of plots in Figure 2.

TABLE II: Effect of Temperature on Ecl Transient[a]

temp, °C	a	b	$-b/a$
First Pulse			
−41	0.82	1.29	1.57
−32	0.86	1.41	1.64
−27.5	0.86	1.46	1.70
−20	0.95	1.61	1.69
−13	0.79	1.66	2.10
−11	0.71	1.41	1.00
−5.5	0.56	1.34	2.39
4	0.64	1.54	2.41
17.5	0.70	1.75	2.50
23.5	0.58	1.65	2.84
36	0.49	2.16	4.41
Fifth Pulse[b]			
−41	1.33	2.07	1.56
−32	1.47	2.36	1.61
−27.5	1.47	2.29	1.56
−20	1.52	2.47	1.63
−13	1.39	2.34	1.68
−11	1.21	2.07	1.71
−5.5	1.13	2.07	1.83
4	1.14	2.22	1.95
17.5	0.98	2.09	2.13
23.5	1.01	2.55	2.52
36	0.81	2.31	2.85

[a] Solution contained 3 mM $Ru(bpy)_3(ClO_4)_2$ and 0.1 M TBAP in MeCN, (no alumina treatments, t_f = 100 ms; precursor generation sequence, −/+. [b] Ecl transient measured after four pulses; pulses $t_f < t_d < 10t_f$.

TABLE III: Slope of Linearized Current Function[a]

t_f, ms	slope, $\mu A\ s^{1/2}$	t_f, ms	slope, $\mu A\ s^{1/2}$
2	1.88	200	1.75
5	1.78	500	1.77
10	1.83	1000	1.78
20	1.75	2000	1.68
50	1.80	mean	1.78
100	1.75	std dev	0.05

[a] 3 mM $Ru(bpy)_3(ClO_4)_2$ and 0.1 M TBAP in MeCN. Precursor generation sequence −/+ [$Ru(bpy)_3^+$ generated first, then $Ru(bpy)_3^{3+}$].

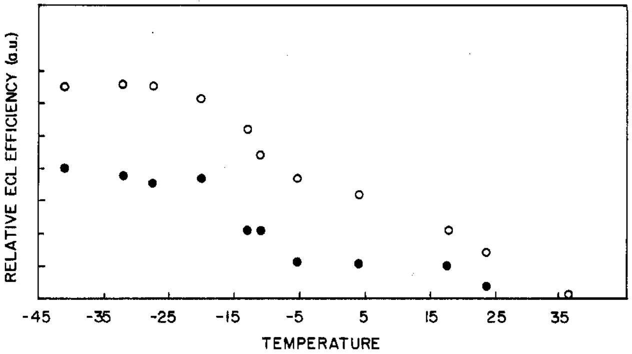

Figure 5. Relative ecl efficiency vs. temperature. Precursor generation sequence: $Ru(bpy)_3^{3+}$, then $Ru(bpy)_3^+$. Solution contained 3 mM $Ru(bpy)_3(ClO_4)_2$ and 0.1 M TBAP in MeCN. No Al_2O_3 added. Single pulse (●) and after fifth (5th) pulse (+). (See test.) t_f = 100 ms.

A plot of ecl efficiency vs. temperature for a typical experiment is given in Figure 5. Although the luminescence quantum yield varies considerably over the temperature interval examined,[7,8] the deviation in ϕ_{ecl} observed here is too large to attribute to changes in luminescence quantum yield alone. Similar results have been reported by Wallace and Bard[7] for the $Ru(bpy)_3^{2+}$–MeCN system. As illustrated by the data in Table II, the intercept/slope ratio decreased and approached the theoretical value as the system temperature decreased. When neutral alumina was added for electrolyte and solvent purification, smaller deviations from the theoretical value of b/a were observed [compare the b/a ratio in Table I (alumina treated) at 100 ms with that in Table II (no treatment) at 23 °C]. In these experiments, some increase in the ecl intensity was often observed after pulsing the ecl cell several times with a delay time, t_d, between cycles of $t_f < t_d < 10t_f$ before recording the ecl transient. Such "pretreatment" also resulted in decreased b/a magnitudes. Freshly prepared ecl cells containing alumina typically showed little or no increase in ecl intensity upon several premeasurement pulses, however. Such behavior reflects possible perturbations in the ecl generation mechanism by parasitic side reactions which may involve either the ionic ecl precursors or excited state products of the ion annihilation reaction.

In all studies of $Ru(bpy)_3^{2+}$–MeCN system, the current showed a linear variation with the time function given by eq 8 and had a zero intercept. Slopes obtained from typical current–time function plots at various values of t_f are given in Table III. Only at very short times during the second potential pulse ($t_r < 1$ mS) was appreciable double-layer charging current observed; this caused a positive deviation from the theoretical current–time function behavior. The good fit of the current–time behavior to that predicted by Faulkner's theory of ecl transients[4] confirms the theoretical model of the diffusional processes and demonstrates that the ionic ecl precursors generated in the triple-potential-step sequence are stable.

Digital Simulations. While the linearity of the I vs. $(t_r/t_f)^{-1/2}$ plots, the independence of behavior on generation sequence, and the tendency toward the theoretical b/a value at short pulse lengths and low temperatures support the ecl transient model for energy-sufficient systems, the deviations found for the b/a value require an explanation. To investigate possible causes of this deviation, we investigated the effects of different perturbing factors on the simple S-route scheme by digital simulation. To ensure that the simulations were sufficiently accurate, the unperturbed S-route case was first simulated and compared to the analytical treatment. In the absence of kinetic perturbations, plots of the simulated redox rate (ω_n) vs. $(t_r/t_f)^{-1/2}$ were linear over the range examined [$0.02 < t_r/t_f < 0.25$] with correlation coefficients equal to unity within 1 part in 10.^{5} The magnitude of the slope and intercept obtained from these simulations agreed with the values of the slope and intercept calculated by using Faulkner's treatment of ecl transients[4] within 7%. Unequal diffusion coefficients of the +1 and +3 species would cause a deviation of the b/a rates.[4b] However, the diffusion coefficient ratio would have to be about 10 to account for the highest b/a values obtained experimentally. Past electrochemical studies show that the diffusion coefficients are almost equal. Moreover, the ecl I–t curves were independent of the direction of the potential step. Thus the deviation cannot be ascribed to this cause.

Side reactions of the precursor species could cause the deviation. However, digital simulations of parasitic kinetic processes revealed that significant increases in the magnitude of b/a only occurred with very large rates for unimolecular ion decay (kt_f = 0.2–100) or disproportionation of precursor (kt_f = 20–200). Such large instabilities were not found in the electrochemical experiments. Moreover, instability of only one of the precursors (e.g., the +1 species) would yield considerably different b/a values depending on the ecl generation sequence, an effect not observed experimentally.

Finally, various excited-state quenching processes were examined by digital simulation techniques. These processes included pseudo-first-order quenching of the excited state (10), quenching by precursor (e.g., radical ions) (11),

$$\mathrm{R^* + Q \rightarrow R + Q} \tag{10}$$

$$\mathrm{R^* + R^{+}\cdot\ (or\ R^{-}\cdot) \rightarrow R^{+}\cdot\ (or\ R^{-}\cdot) + R} \tag{11}$$

and quenching by a small amount of an impurity, Q, (12)

$$\mathrm{R^* + Q \rightarrow R} \tag{12}$$

as processes competing with emmission by the excited state (13). An increase in the magnitude of b/a was observed

$$\mathrm{R^* \rightarrow R} + h\nu \tag{13}$$

only by the quenching reaction 12, and then only at relatively high initial quencher concentrations and unreasonably long radiative lifetimes (τ) for R*. For example, for t_f = 1 s, and [Q] = 10^{-6} M, the b/a ratio would be −1.1 for $k \sim 2 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ only if $\tau \sim 500\ \mu$s. Since the actual τ for $\mathrm{Ru(bpy)_3^{2+}}$ is about three orders of magnitude smaller than this value, it is unlikely that quenching by adventitious impurities can account for the effect.

Conclusions

Most of the criteria outlined by Glass and Faulkner for I–t transients in S-route systems are met with the $\mathrm{Ru(bpy)_3^{2+}}$–MeCN system. The ecl intensity is linear when plotted vs. $(t_r/t_f)^{-1/2}$ with $t_r/t_f < 0.2$ under a variety of experimental conditions. The experimentally measured current–time curves agree well with theory. The only discrepancy between theory and experiment lies in deviations in the b/a values; these appear to arise predominantly from perturbations in the intercept values. As noted by Glass and Faulkner, these deviations may arise from errors from a number of minor experimental defects rather than from theoretical misconceptions about the fundamental electrochemistry. However, they may also reflect effects of quenching or subtle and still-unresolved nuances in the ecl reaction mechanism.

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