

Electrogenerated Chemiluminescence from the Tris(2,2'-bipyridine)ruthenium(II) System. An Example of S-Route Behavior

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The chemiluminescence resulting from reactions of the oxidized and reduced forms of tris(2,2'-bipyridine)-ruthenium(II) has been studied by the sequential step technique. Investigations have been carried out in both acetonitrile and in DMF. Severe electrodeposition phenomena obscured the chemistry of interest in acetonitrile, so most work was done in DMF. Emphasis was placed on a scheme involving initial electrogeneration of the three-electron reduction product $\text{Ru}(\text{bpy})_3^-$, and then production of the one-electron oxidation product $\text{Ru}(\text{bpy})_3^{3+}$ at the working electrode. Homogeneous reactions during the first step degrade $\text{Ru}(\text{bpy})_3^-$ into $\text{Ru}(\text{bpy})_3^{3+}$, which is primarily the species producing chemiluminescence by reaction with $\text{Ru}(\text{bpy})_3^{3+}$. At temperatures below -20°C in DMF, the behavior of the system in individual transients and in families of transients was in accord with expectations for light production by direct population of the emitting state in charge transfer.

For several years, workers in the area of electrogenerated chemiluminescence (ecl) have labored to explain the mechanisms of light production by high-energy electron-transfer reactions. Through a variety of experiments, which have been reviewed extensively,¹⁻⁷ a set of schemes has been developed. In general, an electron-transfer reaction that is sufficiently energetic to produce the emitting state of a product (usually, but not always, a singlet) is expected to do so directly. This "S route" to emission in such "energy-sufficient" systems is therefore quite straightforward. On the other hand, many systems are known in which the electron transfer is insufficiently energetic to leave a product in the observed emitting state. These "energy-deficient" cases are usually regarded as proceeding to emission by producing triplet intermediates in electron transfer, and then generating the emitters by triplet-triplet annihilation (T route).

The principal kinetic tool for studying ecl, i.e., the sequential step technique for producing light transients,^{3,5,6,9-11} has repeatedly given results that are not consistent with this picture.^{6,12-17} Thus, there is strong evidence that the kinetic features of most systems are more complicated than is generally believed.

In this experimental method, one generates the oxidant and reductant from precursors at a small planar electrode in quiescent solution. In the first step (of duration t_p), the first reagent is produced and diffuses into the solution. At $t = t_p$, the potential of the electrode is switched to a value where the second reagent is produced. It then diffuses into the solution, where it reacts with the first reagent at a total rate (N , mol/s) that declines with time as the first species is consumed. The reaction rate can be predicted from the laws of diffusion.^{8,11} A light transient results from the time dependence of the redox reaction rate N and the kinetics of light-producing processes.

For an S-route system, the linkage between the total light intensity (I , einsteins/s) and N is very simple,¹⁶ viz.

$$I = \phi_r \phi_s N \quad (1)$$

where ϕ_s is the probability that a redox event will produce an emitter and ϕ_r is the quantum yield for emission from that species. Usually, the emitter is a singlet and the emission is fluorescence. The product $\phi_r \phi_s$ should be independent of time because ϕ_s is a branching ratio for an elementary process, and the excited state lifetime is gen-

erally too short to be quenched by components in the system having time-dependent concentrations.¹⁶ Thus the intensity ought to be proportional to N , and the transient should follow a readily predictable shape. Such behavior has almost never been seen among energy-sufficient systems, where it ought to be routine. Some early studies of the homomolecular ion annihilations of rubrene and 9,10-diphenylanthracene¹²⁻¹⁴ gave results that inconsistently suggested S-route behavior on the basis of the shapes of the long-time tails of the light transients. More recently, the short-time region has been stressed as an intrinsically more reliable kinetic indicator,^{4,6,10,11,16} and we have shown that in that region the light intensity should be linear with $(t_r/t_p)^{-1/2}$, where t_r is time measured into the second step from its start.¹¹ Kawai et al.¹⁸ have reported single transients adhering to this prediction in the an-thrylamine charge-transfer systems; but they did not attempt to verify the predicted variations in the slopes and intercepts of the linear plots with step time, nor did they test for the expected invariance in behavior with the sequence of reactant generation.

In the absence of a paradigm showing predictable be-

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havior with respect to all experimental variables, one cannot be sure whether the deviations from nonideality manifest defects in the experimental approach, significant misconceptions about the fundamental chemistry, or both. Our goal in this paper and in the companion by Luttmner and Bard¹⁹ is to establish the reaction between $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^{3+}$ (where bpy is 2,2'-bipyridine) as a reasonably well-behaved S-route case under certain conditions.

We have selected this reaction for its simplicity. Emission arises by phosphorescence from a $d-\pi^*$ metal-ligand charge-transfer triplet of $\text{Ru}(\text{bpy})_3^{2+}$, which is the only excited state with an appreciable lifetime.²⁰⁻²² Bard and co-workers,^{22,23} who first studied the ecl, postulated the direct population of the emitter in electron transfer. In independent studies, Wallace and Bard²⁴ and Itoh and Honda²⁵ conducted investigations of the temperature dependence of the ecl efficiency (photons emitted per redox event) and found that, at temperatures below -30°C , the ecl emission yield approached the photoluminescence quantum efficiency, thereby implying 100% efficiency for production of the $d-\pi^*$ triplet in electron transfer. Since that triplet is the emitter and shows no tendency to undergo triplet-triplet annihilation,¹⁷ one can reasonably expect pure S-route kinetics. Even though the key state is a triplet here, we preserve the term "S route" as a descriptor of the kinetics that control the light transient. This reaction seems simpler than energy-sufficient ion annihilations of aromatics, which can produce both singlet and triplet products, and therefore can have parallel S and T pathways to emission.

Experimental Section

Chemicals. $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ was supplied by G. F. Smith Chemical Co. $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ was prepared from it by metathesis with excess NaClO_4 in H_2O . It was then recrystallized three times from an H_2O -EtOH mixture (4:1), and then dried for 48 h at 60°C under vacuum.

Tetra-*n*-butylammonium fluoroborate (TBAF_4) was used as the supporting electrolyte. It was obtained from Southwestern Analytical Chemicals (Electrometric grade), recrystallized three times from a mixture of ethyl acetate-pentane (5:1), and then dried at 95°C under vacuum for 48 h. The electrolyte was stored in a desiccator over CaSO_4 .

Spectroquality acetonitrile was obtained from Matheson Coleman and Bell. The procedure for removal of impurities has previously been described.¹⁶

N,N-Dimethylformamide (DMF), 99%, was obtained from Aldrich. The procedure for removal of amine decomposition products and H_2O has been described in detail.¹⁴

Electrochemical Cell and Sample Preparation. The electrochemical cell used in this work has been described in detail elsewhere.¹⁶ With some small modification, it resembles that of Bezman.¹⁴ The cell consists of a platinum disk working electrode (3.09 mm^2) with a platinum wire quasi-reference electrode (QRE) wound around a glass sheath into which the working electrode is mounted. In order to minimize uncompensated resistance effects we placed the tip of the QRE 2-3 mm from the working

electrode. The counter electrode is also a platinum wire, and is widely separated from the working electrode.

Before each solution was prepared, the working electrode was polished on an Ecomet I polisher/grinder from Buehler Ltd. An aluminum polishing disk covered with a nylon cloth was used with a 100:1 dilution of $0.05\text{-}\mu\text{m}$ alumina powder (Fisher) as abrasive to perform the final polishing procedure. The electrode was thoroughly cleaned with acetone, petroleum ether, and absolute EtOH and placed into the cell body. The cell was then put under high vacuum overnight.

Solution preparation procedures have been described previously.^{14,16} No less than four freeze-pump-thaw cycles were used to remove oxygen from the solution.

Instrumentation. The light produced from a triple potential step experiment was transmitted through a $1/8$ -in. i.d. fiber-optic light guide (American Optical Corporation) to a photomultiplier tube (Hamamatsu R777-01). The light guide was held firmly in position and directed toward the working electrode surface.

The photocurrent output was fed to an i/E converter, which drove a voltage scaler on the computer interface. A Data General Nova 820 minicomputer controlled both reactant ion generation and acquisition of light transients. With the exception of minor modifications of software, the remaining details of the interface and instrumentation are the same as reported previously.^{16,26}

The transients were produced in the usual triple-step mode, for which the initial potential was always 0 V vs. QRE, where $\text{Ru}(\text{bpy})_3^{2+}$ was not electroactive. The two ecl reactants were then produced sequentially in steps of equal length, t_s , after which the electrode was returned to 0 V vs. QRE. Uncompensated resistance was compensated by positive feedback at the 80% level.

The apparatus for conducting low-temperature studies was constructed along the lines suggested by Grypa and Maloy.²⁷ It consisted of a Matheson Gas Products No. 8-580 regulator, a 2-L dewar flask, copper tubing ($1/8$ in. i.d.), and a cooling cryostat for the cell, which was a double-walled evacuated Pyrex dewar. The cryostat was fitted with a Teflon top machined to fit the electrochemical cell, a thermometer, and an inlet for cold N_2 gas. The gas was refrigerated by leading it from a tank through the copper tubing, which was formed into coils immersed in liquid nitrogen. Temperature control was accomplished by regulating the N_2 flow rate with a needle valve. The cooling process was allowed at least 30 min before measurements were begun to allow for temperature stabilization in the cryostat.

The entire assembly was enclosed in a light-tight box, and the light guide which carried the decay signal to the photomultiplier was held in fixed geometry at a viewing port in the bottom of the cooling cryostat. It directly faced the working electrode. The cell was held in the cryostat in a fixed geometry throughout the course of an experimental day.

Results and Discussion

Electrochemistry and Experimental Design. Initial experiments were performed in acetonitrile, where both cyclic voltammetry and chronocoulometry revealed severe problems with filming of the electrode. In voltammetry, the effect usually appeared as distortions in the shape and height of the second reduction peak, in relation to those

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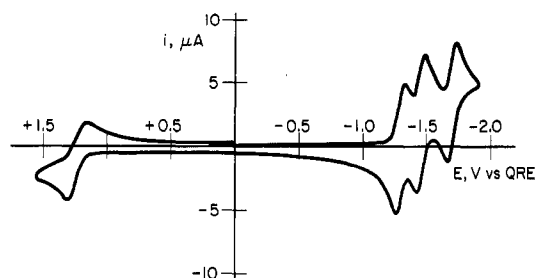


Figure 1. Cyclic voltammogram of 1 mM $\text{Ru}(\text{bpy})_3^{2+}$ in DMF at -25°C . The supporting electrolyte was 0.1 M TBABF_4 . The scan begins at 0.0 V and first moves negatively.

of the first and third reductions. After such behavior began to be visible in voltammetry, one could also see a gold-colored deposit on the electrode upon its subsequent removal from the cell. This deposition, which we associate with the neutral species $\text{Ru}(\text{bpy})_3^0$, seemed to be especially severe on freshly polished electrodes. The relative effects on voltammetry were much greater at low concentrations (0.1 mM) of $\text{Ru}(\text{bpy})_3^{2+}$ than at higher values, and this aspect suggests to us that the deposition problem is usually present in acetonitrile, but can be masked from easy detection. Similar problems with electrodeposition with this and related chelates have been seen by other authors.^{23,28,29} We were unable to obtain straightforward step responses from the ecl process of interest in acetonitrile, and we changed to DMF in hopes of alleviating the obvious solubility problem. Luttmer and Bard¹⁹ seem to have been successful with acetonitrile by using a restricted potential in the reduction phase and, perhaps, a different surface preparation and treatment of the solvent in situ with alumina.

Figure 1 is a cyclic voltammogram of $\text{Ru}(\text{bpy})_3^{2+}$ in DMF at -25°C . There are three reduction peaks situated at -1.33 , -1.49 , and -1.74 V vs. QRE, which are associated with the production of $\text{Ru}(\text{bpy})_3^+$, $\text{Ru}(\text{bpy})_3^0$, and $\text{Ru}(\text{bpy})_3^-$, respectively. A fourth reduction peak, associated with irreversible ligand loss, is at -2.5 V. Good reversible behavior is observed for the first three reductions, the splitting between the anodic and cathodic peaks in each case being 60–70 mV. One oxidation peak appears at 1.31 V vs. QRE. It shows quasi-reversible behavior, with a peak separation of ~ 150 mV. At room temperature this oxidation exhibits more reversible character. No problems with deposition onto the electrode surface were noticeable in DMF, and the solubility of the chelate species generally appeared to be much greater in DMF than in acetonitrile.

Initial ecl experiments featured triple potential step programs that generated as reagents the $\text{Ru}(\text{bpy})_3^+$ and $\text{Ru}(\text{bpy})_3^{3+}$ species, and comparisons were made between the light intensities and the modeled redox rates N . However, as one can see in Figure 1, the first and second reduction peaks are closely spaced, and potential oversteps of 200–250 mV past E_p , which are normally used to establish diffusion-controlled conditions for electroreduction, cannot be employed without simultaneous generation of $\text{Ru}(\text{bpy})_3^0$. If this species is also produced, our model for N will be in error, and a comparison of I with N will not be interpretable.

By stepping to the peak potential for production of $\text{Ru}(\text{bpy})_3^+$ in the reduction phase, we were able to obtain behavior that was approximately in accord with S-route

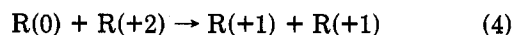
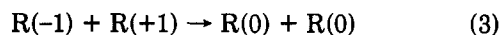
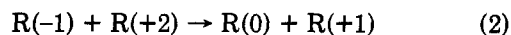
TABLE I: Chronocoulometric Data^a

direction	slope, $\mu\text{C/s}$	intercept, μC
(a) $\text{R}(+2) \rightleftharpoons \text{R}(-1)$		
forward	14.00	0.588
reverse	13.15	0.579
(b) $\text{R}(+2) \rightleftharpoons \text{R}(+3)$		
forward	6.03	0.658
reverse	4.33	0.863

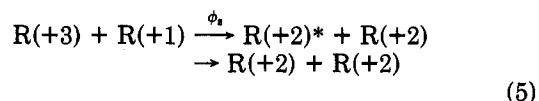
^a Starting potential, 0.0 V vs. QRE. Forward step, 250 mV past peak potential for indicated process. Data are for Anson plots,³⁰ Q vs. $t^{1/2}$ (forward), Q_r vs. θ (reverse). $T = -27^\circ\text{C}$, step width = 100 ms, 200 points at 1-ms intervals.

expectations, but lacked strict linearity in the plots of I vs. $(t_r/t_f)^{-1/2}$ and did not show quantitative trends with varying t_r . We regard the lack of good behavior as a manifestation of the control problems outlined above.

In a different approach to the problem, we employed a triple-step program featuring the production of the $\text{Ru}(\text{bpy})_3^-$ species at the electrode in the forward step, and $\text{Ru}(\text{bpy})_3^{3+}$ in the reverse step. No control problems were expected in this case because the fourth reduction is so widely separated from the third. During the forward step, $\text{Ru}(\text{bpy})_3^-$ diffuses outward from the electrode and encounters a flux of 2+ species, hence the following reactions occur:



where the species are designated by the charges on the complexes. The net result is that virtually all of the electrons injected by reduction go to produce $\text{R}(+1)$ in the diffusion layer (except very near the electrode surface). When the second step begins, and $\text{R}(+3)$ is electrogenerated, the ecl reaction is then the usual one



where ϕ_s is the branching ratio for producing the $d-\pi^*$ triplet $\text{R}(+2)^*$. Only in the earliest moments of the second step, when the homogeneous reaction takes place near the electrode, would $\text{R}(+3)$ be able to react with $\text{R}(-1)$ or $\text{R}(0)$.

In order to suppress the large anodic background seen in DMF at room temperature, we chose to work near -25°C , where the anodic region is fairly clean (Figure 1). Still, double-step chronocoulometry does reveal some background contributions, as evidenced by the comparatively large forward slope (Table I) in the Anson plot³⁰ for oxidation of $\text{R}(+2)$. We do not believe that this discrepancy represents homogeneous decay of $\text{R}(+3)$, since the cyclic voltammetry, on a much longer timescale, manifests no such effect. Moreover, the corresponding reverse Anson slope is essentially exactly one-third of the slopes for $\text{R}(+2) \rightleftharpoons \text{R}(-1)$. All plots showed linear correlation coefficients greater than 0.999.

Theoretical Considerations. The basis of decay curve analysis is a comparison of light intensity I and a modeled redox reaction rate N . Since the rate constants for reactions producing ecl are believed to be very large,^{3-7,31} N is usually regarded as being strictly controlled by the rate at which the reactants diffuse together, at least for $t_f >$

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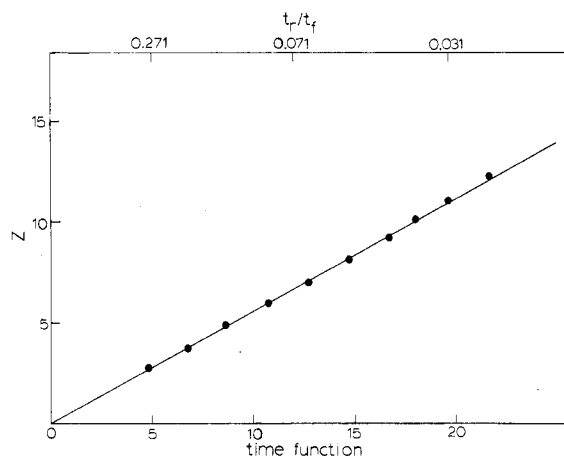
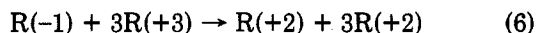


Figure 2. Experimental (points) and theoretical (line) dimensionless current $Z = -it_f^{1/2}/AD^{1/2}C_P^*$ for the second step in an experiment featuring initial generation of $R(-1)$. The value of $AD^{1/2}C_P^*$ was evaluated experimentally from chronocoulometric data. For this experiment $C_P^* = 1$ mM, $t_f = 5$ s, $T = -25$ °C, and the medium was DMF with 0.1 M TBABF₄.

100 μ s.³¹ With the assumptions of semiinfinite linear diffusion, diffusion-controlled electrogeneration of reagents, and equal diffusion coefficients for all species, the problem becomes amenable to analytical solution.¹¹ We emphasize that one compares an experimental I with a calculated N , thus it is important to have some means for verifying that the basic model of diffusional processes is correct. The most convenient method of doing this is by examination of faradaic current flow during the second step.^{11,16}

For the case at hand, where we generate a three-electron reductant in the forward step, the published expressions for current and reaction rate in step experiments¹¹ do not apply. However, applicable expressions can be derived by assuming that $R(-1)$ generated in the forward step is stable and the production of $R(+3)$ in the second step results in the following net overall process:



The fact that this net process takes place in a series of steps is immaterial to the numeric current-time and redox rate-time functions,⁸ provided that all diffusion coefficients are equal and N is understood to mean moles of electrons transferred per second.

Following an earlier treatment,¹¹ one can then rigorously derive the following expression for the current during the second step

$$-i = \frac{FAD^{1/2}C_P^*}{\pi^{1/2}} \left[\frac{4}{t_r^{1/2}} - \frac{3}{t_f^{1/2}} \right] \quad (7)$$

or, in dimensionless terms

$$Z = \frac{-it_f^{1/2}}{FAD^{1/2}C_P^*} = \frac{1}{\pi^{1/2}} \left[4 \left(\frac{t_r}{t_f} \right)^{-1/2} - 3 \left(1 + \frac{t_r}{t_f} \right)^{-1/2} \right] \quad (8)$$

where C_P^* is the bulk concentration of $R(+2)$ and $t = t_f + t_r$. The other symbols have their usual significance.

Shown in Figure 2 is a plot of the dimensionless experimental current for $t_f = 1$ s and the theoretical Z vs. the time function bracketed in eq 8. Excellent agreement between the predicted and experimental currents is obtained, without adjustable parameters, and it lends confidence in our ability to model homogeneous diffusion processes.

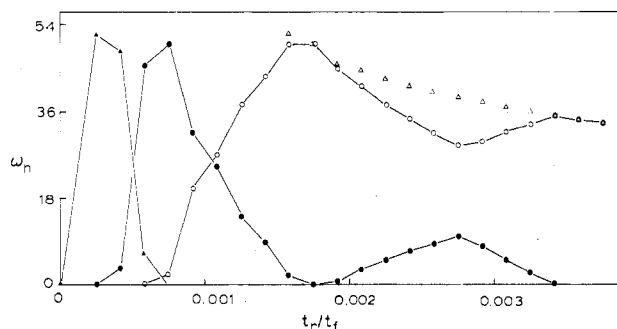


Figure 3. Simulated components of ω_n . In the simulation, there were 6000 iterations per step, and each point here represents one iteration in the second step: filled triangles, ω_3 ; filled circles, ω_2 ; open circles, ω_1 ; open triangles $\omega_n = \omega_1 + \omega_2 + \omega_3$.

Also on the basis of our earlier treatment,¹¹ an expression was derived for the redox reaction rate, N . The linearized result in dimensionless terms is

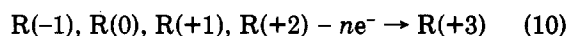
$$\omega_n = a(t_r/t_f)^{-1/2} + b \quad (9)$$

where $\omega_n = Nt_f^{1/2}/AD^{1/2}C_P^*$, $a = 2.15$, and $b = -1.96$. This result applies only to the early part of the light decay ($t_r/t_f \leq 0.2$).

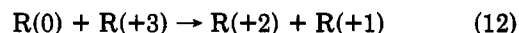
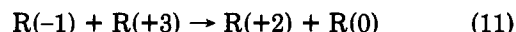
To obtain an approximate picture of the actual mechanistic events making up the overall process (6), we also treated the problem by digital simulation.^{32,33} It was assumed that diffusion-controlled conditions applied at the electrode surface, that all diffusion coefficients were equal, and that during each iteration the limiting reagent for each homogeneous reaction was totally annihilated within each simulation element.

In the forward step, $R(+2)$ was converted to $R(-1)$ at the electrode surface, and homogeneous reactions 2-4 were allowed to occur.

In the reverse step, all reduced forms and the precursor were converted to the oxidized form at the electrode surface:



Simultaneously, diffusion and reaction of $R(+3)$ with the various reduced forms was allowed to occur according to reaction 5 plus the following:



Partial redox reaction rates N_1 , N_2 , and N_3 were defined as moles of electrons transferred per second by steps 11, 12, and 5, so that $N = N_1 + N_2 + N_3$ and $\omega_n = \omega_1 + \omega_2 + \omega_3$. In each iteration of the second step, reactions 5, 11, and 12 were established, then reactions 2-4 were allowed to take place.

Shown in Figure 3 is a plot of the components of ω_n in the very early portion of the second step. This representation is only approximate, as a consequence of the assumptions in the simulation [particularly that of annihilation of the limiting reagent in steps 2-4] and the sequential manner in which reactions were handled, but it provides a picture of the basic chemistry. Note that the only important light-producing reaction is predicted to be that between $R(+3)$ and $R(+1)$ after a very short time into the second step.

The theoretical and simulated ω_n functions agreed rather well over the time domain of interest ($t_r/t_f \leq 0.2$). The

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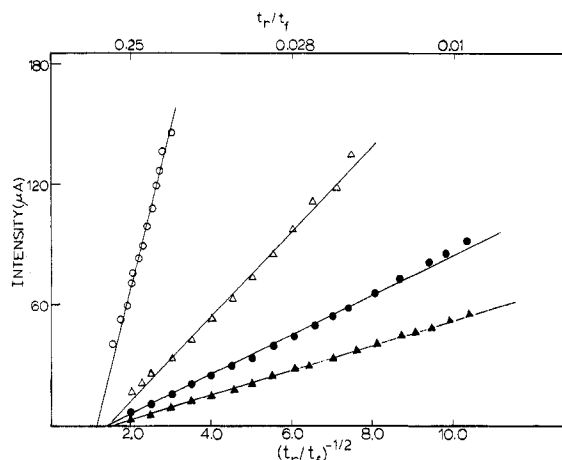


Figure 4. Plots of I vs. $(t_r/t_f)^{-1/2}$ for experiments with 1 mM R(+2) in DMF with 0.1 M TBABF₄ at -27°C . Values of t_f are (clockwise) 0.1, 1, 5, 10 s.

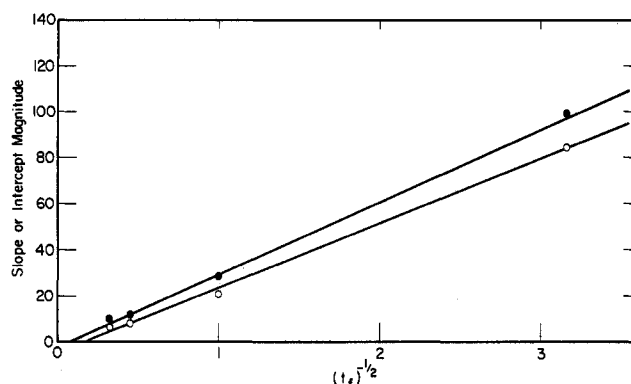


Figure 5. Slopes (open circles) and intercepts (filled circles) of plots in Figure 4 vs. $t_f^{-1/2}$.

maximum relative deviation was less than 6%, and this discrepancy is apparently due to the limitations of the simulation.

Our prediction, then, is that S-route behavior in these experiments would require light transients that show linear plots of intensity vs. $(t_r/t_f)^{-1/2}$ with intercept-to-slope ratios $b/a = -0.91$, regardless of t_f .

Decay Curves. Shown in Figure 4 are plots of I vs. $(t_r/t_f)^{-1/2}$ for experiments in DMF at -25°C with $t_f = 0.1$ –10 s. The plot for the 100-ms experiment begins at later t_r/t_f because of the intensity maxima to be discussed shortly. Good linear plots apply in all cases, and the least-squares intercept-to-slope ratios are -1.18 , -1.37 , -1.36 , and -1.62 for $t_f = 0.1$, 1, 5, and 10 s, respectively. These numbers are significantly higher in magnitude than the theoretical value of $b/a = -0.91$.

By rearrangement of eq 1 and 9, one finds that both the slopes and the intercepts of the lines in Figure 4 should display direct proportionality with $t_f^{-1/2}$, and the plots in Figure 5 show that the prediction is borne out. The ratio of the slope of line 1 in Figure 5 to that of line 2 should be $-b/a = 0.91$. In reality, the ratio is 1.15.

The overall behavior of the system is concordant with the expectations for S-route light production, in that the expected functional linearities are observed in single transients and among families of transients. The only remaining discrepancy from the behavior predicted by theory is the consistent tendency of the observed intercept-to-slope ratio $(-b/a)_{\text{obsd}}$ to be high. The origin of this effect is not clear, but it seems to be general. Kawai et al.¹⁸ have reported it for the anthrylamine systems, and Luttmer and Bard¹⁹ also observe it in the system of interest

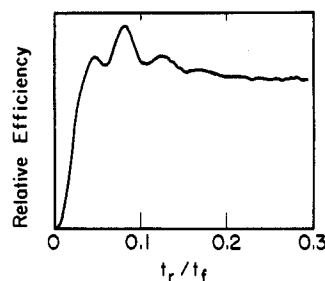


Figure 6. I/ω_n vs. t_r/t_f for $0 \leq t_r/t_f \leq 0.3$. The value of t_f was 0.1 s, and $T = -27^\circ\text{C}$. Data correspond to one transient in Figure 4.

here, despite a totally different experimental attack.³⁴

We consistently see more ideal behavior with shorter t_f (as demonstrated by the sequence cited above) and with lower temperatures. For example, from ratios of slopes of plots equivalent to those of Figure 5, we observed the following trend: T , $(-b/a)_{\text{obsd}}$; ambient, 1.58; -25°C , 1.09; -35°C , 0.96. These data were obtained with 0.2 M TBABF₄, which was twice the value used in experiments described by Figures 4 and 5. No effect of electrolyte concentration was discerned.

There is a temptation to ascribe the high ratios to side reactions, perhaps with the electrolytic products of the faradaic process occurring in parallel with the oxidation of R(+2). The effects of temperature and t_f are concordant with such a view; however, the results given by Luttmer and Bard, involving opposite sequences of reactant generation,¹⁹ generally are not. Other interpretations, such as (a) nonideal potential rise, (b) adsorption of various species, and (c) nondiffusion-controlled electron transfer in solution, should produce trends in $(-b/a)_{\text{obsd}}$ counter to those actually observed. The generality of the behavior suggests that it manifests a fundamental defect in experimental conformity to theoretical model. One possibility is the existence of edge diffusion or convective lateral dispersion of the diffusion layer. The intercepts of plots of I vs. $(t_r/t_f)^{-1/2}$ are themselves manifestations of a finite thickness in the distribution of the first reactant,¹¹ and even slight losses of that species by such processes would tend to depress the intercepts further and raise $-b/a$.

Intensity Maxima. Shown in Figure 6 is a plot of I/ω_n for an experiment with $t_f = 0.1$ s at -25°C . The ordinate is therefore proportional to the instantaneous ecd efficiency $\phi_{\text{ecd}} = \phi_s \phi_f$, and the presence of maxima apparently represent different efficiencies for production of emitting d- π^* triplet. This behavior can be interpreted by an examination of the simulated results presented in Figure 3, which contains independent and time-separated maxima for the reaction of R(+3) with the three reduced forms. Each of these reactions is expected to be light producing, but their energetics are different and can lead to different efficiencies. The free energies, calculated from differences in potentials are as follows for $T = -25^\circ\text{C}$: reactants, $-\Delta G^\circ$, eV; R(+3), R(-1), 3.11; R(+3), R(0), 2.76; R(+3), R(+1) 2.61. The common product R(+2) offers a d- π^* singlet at 2.73 eV, a d- π^* triplet at 2.12 eV, and a set of primarily non-radiative d-d triplet levels near 2.48 eV.²⁴

The most energetic reaction, that between R(+3) and R(-1), is sufficiently potent to populate the d- π^* singlet, which crosses with almost unit efficiency to the emitting d- π^* triplet level. This option may lead to high light-producing efficiency. The reaction between the R(+1) and R(+3) is energy-sufficient only to reach the d-d triplet levels and the emitting d- π^* triplet. The fraction of this

(34) We also see it in the rubrene/DMF system at low temperatures. These results will be reported shortly.

reaction yielding d-d triplets will result in predominately nonradiative decay, since the rate constant for this process is very fast. This situation could imply a correspondingly low efficiency of light production. Finally, the reaction between the R(+3) and R(0) is marginal for reaching the d- π^* singlet. The fraction of events leading to the d- π^* singlet will lead to high efficiency for emitter production, but the remainder will deposit the energy into d-d and d- π^* triplets. Thus one might expect an intermediate efficiency for light production. One could plausibly identify the first maximum with ω_3 and the remaining ones with ω_2 , as suggested by Figure 3. However, given the intrinsic limitations of the assumptions underlying Figure 3 and the effects of finite potential risetime, one is not justified in quantitatively interrelating Figures 3 and 6.

It is important to realize that these ideas about yields can only be regarded as a qualitative, but consistent, explanation, since many states of d- π^* and d-d orbital parentage may contribute to the thermally equilibrated excited state distribution.

Criteria for S-Route Behavior. There has long been discussion about the most appropriate means for diagnosing S-route behavior in transient experiments.^{3,4,6,8-14,16,18,19,35} Two schemes have been put forward: (a) the observation of linear Feldberg plots with slopes near -1.45,^{3,4,8,9} and (b) the observation of flat plots of I/ω_n vs. t_r/t_f .³⁵ Criterion a is ambiguous and is subject to severe interference from low-level side reactions,^{9,35} and criterion b tends to fail if there are slight experimental defects such as finite potential risetimes. A more appropriate approach is to stress the expected functional dependences within

families of transients, hence we propose the following criteria for S-route behavior:

(1) Linearity of plots of I vs. $(t_r/t_f)^{-1/2}$ for $t_r/t_f \leq 0.2$.

(2) Plots of the intercepts and slopes of the individual linearized transients that are linear with $t_f^{-1/2}$ and pass through the origin.

(3) A ratio of the slopes of the plots in (2) giving $(-b/a)_{\text{obsd}}$ near the theoretical value.¹¹

(4) Quantitatively equivalent behavior upon reversal of the order of reactant generation.

These criteria capture the essentials of S-route behavior in experimentally realistic terms without overstressing strict quantitative observation of the theoretical $-b/a$ value, which may be subject to errors from a number of fairly minor experimental defects. It is highly unlikely that a system with a large T-route contribution would be able to fulfill these criteria, because the bimolecular triplet annihilation step will generally defeat criteria 1-3,^{9,35,36} and because variations in the triplet lifetime caused by trace electroactive or electrogenerated impurities in the diffusion layer^{14,35} will defeat criterion 4. On the other hand, between our work³⁷ and that of Luttmner and Bard, the system at hand here has fulfilled them all and seems reliable as an S-route model.

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Nuclear Magnetic Resonance of Oriented Fluorobenzene in a Nematic Potassium Laurate Mesophase. Distance Ratios and Order Tensor Elements

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Proton-proton and proton-fluorine distance ratios and elements of the order tensor are obtained from nuclear magnetic resonance spectra of fluorobenzene partially oriented in a potassium laurate lyotropic mesophase. Corrections for harmonic vibrations are applied and it is shown that for proton-proton and proton-fluorine distance ratios corrections are significant. Errors due to weighting in the structural analysis as well as errors due to solvent dependence of the scalar couplings are investigated. These experiments show that the anisotropy in the indirect couplings after vibrations have been considered are negligible. The elements of the order tensor are discussed in terms of the orienting influence of the interface and alkyl chains of the mesophase surfactant.

Introduction

This study is a continuation of our previous work on the orientation and structure of aromatic compounds partially oriented in a potassium laurate mesophase¹⁻¹¹ and includes results for fluorobenzene. The present investigation provides structural results for the hydrogen and fluorine nuclei corrected for harmonic vibrations. Before corrections

proton-proton distance ratios from microwave and nuclear magnetic resonance methods were inconsistent. Originally

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