Mechanisms of Chemiluminescent Electron-Transfer Reactions. V. Absolute Measurements of Rubrene Luminescence in Benzonitrile and *N*,*N*-Dimethylformamide

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Abstract: Absolute intensity–time measurements and total quantum output data have been obtained for the chemiluminescent rubrene anion–cation annihilation in benzonitrile and *N*,*N*-dimethylformamide (DMF). The reactants were generated in triple-potential-step experiments, and the data were analyzed by recently published procedures. The results suggest that luminescence arises exclusively from the direct generation of the rubrene triplet in the redox reaction and that the emitting singlet is produced by triplet–triplet annihilation. The emission probability of charge transfer is about 10^{-3} for benzonitrile solutions and about 5×10^{-4} for solutions in DMF. No systematic variations of these probabilities with concentration were observed. On the basis of this triplet mechanism, the triplet yield of charge transfer was estimated at 10–30%. The results further suggest that 50–100% of the triplets participate in annihilation, that radical ion quenching is unimportant, and that the low-emission yield results largely from inefficiencies in triplet–triplet annihilation, rather than from efficient triplet quenching. Unusual dependences of the efficiency parameter, α, and the quenching parameter, β, on the ion generation sequence were also observed for benzonitrile solutions Both effects may arise from oxidation products of water which are possibly produced in the anodic step.

The mechanism by which the electron-transfer reaction between the rubrene (5,6,11,12-tetraphenylnaphthacene) anion and cation radicals yields its characteristic chemiluminescence has long been an intriguing question. The luminescence spectrum is nearly identical with that of rubrene fluorescence; hence the first-excited singlet state of rubrene has been identified as the emitter.[1,2] This particular system has been especially interesting because the precision of the reaction enthalpy calculation is not high enough to permit one to say whether or not the emitting state is directly accessible to the electron transfer.[3,4] Thus the mechanistic mystery is whether the electrogenerated chemiluminescence (ecl) arises *via* direct emitter production by electron transfer (the S route), *via* an indirect pathway involving the annihilation of triplets produced in the redox reaction (the T route). or *via* a combination of both mechanisms (the ST route). Moreover, the latter two paths are complicated by doubt as to whether rubrene is even able to undergo triplet–triplet annihilation.[3]

Feldberg's analysis of intensity–time behavior for triple-potential-step generation of luminescence[5,6] and our recent extensions of it[7] have suggested means by which one can use an added triplet quencher to distinguish between the mechanisms. Experiments in the form suggested have not been reported because suitable quenchers of the rubrene triplet are generally too reactive toward the ions or toward the electrode used to generate them. However, Visco and Chandross[3] and Chang, Hercules, and Roe[2] did study intensity–time behavior for the rubrene anion–cation reaction in benzonitrile. The latter group observed Feldberg slopes that were strongly dependent on the forward step time, and they rationalized this behavior by invoking radical ion quenching steps in the T route. But in directly comparable experiments, Visco and Chandross observed Feldberg slopes very near the -1.48 limit and independent of forward step time. Any one of the three routes to emission is viable on the basis of their work. The discrepancy between these two reports has not been resolved in the literature; hence one must discount somewhat the suggestion that reported intensity–time analysis supports the T route.

Nevertheless, the idea that a triplet pathway contributes significantly to emission in this system has been boosted accountably by the recent experiments of Bard and his coworkers. In particular, Maloy and Bard measured an emission efficiency (photons emitted per electron-transfer event) for rubrene luminescence generated at a rotating platinum ring-disk electrode which was comparable to those observed for markedly energy-deficient systems under similar conditions.[8,9] This efficiency was an order of magnitude smaller than that measured for the DPA anion–cation reaction, and Maloy and Bard have commented that the pathway involving easily quenched triplet intermediates is consistent with these results. More recently, Faulkner, Tachikawa, and Bard have suggested that their observation of a magnetic field enhancement of rubrene chemiluminescence may indicate a triplet pathway to be an important route (if not only one) to emission.[4]

We have applied our techniques for the measurement of emission efficiencies and for the analysis of luminescence decay curves to the triple-potential-step generation of rubrene chemiluminescence from benzonitrile and *N*,*N*-dimethylformamide solutions. We wish to report here our results, which suggest that

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(1) D. M. Hercules, R. C. Lansbury, and D. K. Roe, *J. Amer. Chem. Soc.*, **88**, 4578 (1966).

(2) J. Chang, D. M. Hercules, and D. K. Roe, *Electrochim. Acta*, **13**, 1197 (1968).

(3) R. E. Visco and E. A. Chandross, *ibid.*, **13**, 1187 (1968).

(4) L. R. Faulkner, H. Tachikawa, and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 691 (1972).

(5) S. W, Feldberg, *ibid.*, **88**, 390 (1966).

(6) S. W. Feldberg, *J. Phys. Chem.*, 70, 3928 (1966).

(7) R. Bezman and L. R. Faulkner, *J. Amer. Chem. Soc.*, 94, 3699 (1972).

(8) J. T. Maloy, Ph.D. Thesis, The University of Texas at Austin, 1970.

(9) J. T. Maloy and A. J. Bard, *J. Amer. Chem. Soc.*, **93**, 5968 (1971).

luminescence arises *via* the T route. An extended Feldberg analysis, based on the assumption that the T route is responsible for emission, has provided estimates of the triplet yield of this reaction and has revealed mechanistic subtleties heretofore unrecognized.

Experimental Section

The rubrene used in this work was obtained from the Aldrich Chemical Co. No extraneous fluorescence or absorption bands were present in solutions made from this material, and no alteration in its optical or electrochemical behavior accompanied its recrystallization from benzene, so it was employed as received. The benzonitrile used as a solvent in about half of the work was spectroquality material produced by Matheson Coleman and Bell; it, too, was used without further purification. The source, extensive purification procedure, and special handling precautions pertaining to the use of *N,N*-dimethylformamide (DMF) as an alternate solvent have been recently elaborated.[10] Polarographic grade tetra-*n*-butylammonium perchlorate (TBAP), supplied by Southwestern Analytical Chemicals, served as the supporting electrolyte in all work. It was not further purified, except for drying by a procedure described previously.[10]

The procedures used for the preparation of solutions and for the measurement of electrochemical and luminescence parameters have been described in detail in an accompanying paper.[10] The design, construction, and calibration of the electrochemical apparatus and the instrument used for absolute measurements of total luminescence have been elaborated quite extensively in other publications;[11,12] hence they will not be recounted here. All such measurements were conducted at 25°.

Corrected fluorescence spectra were obtained using an Aminco-Bowman spectrophotofluorometer *via* the methods and data of Chen.[13]

Results

Except for the experiments executed to assess the stability of the rubrene cation radical, all the luminescence measurements described below were carried out on single pulses of light resulting from sequential reactant generation at a planar electrode by a triple-potential-step program. The nature of this experimental method and the techniques for measurement and data analysis have been described extensively in previous papers.[7,10] Following our established custom, the duration of each generating step has been designated t_f, and the initial and final potentials were chosen to be 0.0 V *vs.* a Pt-wire quasi-reference electrode (qre), which itself was about 0.4 V *vs.* an aqueous sce.

DMF Solutions. Several cyclic voltammograms of each solution were recorded to determine the potential ranges in which rubrene was oxidized and reduced and to assess, whenever possible, the stabilities of the ions that were formed. It was found that the peak potentials drifted anodically *vs.* the qre by about 50 mV during the 3-hr period of each set of experiments. Fully 80% of the drift occurred within 15 min of the first cyclic-voltammetric measurement. This behavior, which has been observed in all systems we have studied, is probably due to the gradual relief of small stresses in the qre metal;[14] however, the effect was not troublesome because the drift rate quickly slowed to an almost imperceptible value. Nevertheless, prior to each group of triple-step experiments, a new cyclic voltammogram was recorded, so that accumulated reference potential changes could be compensated. The cyclic voltammograms also showed that the value of $\Delta E_p = E_p(R/R\cdot^+) - E_p(R/R\cdot^-)$ increased with concentration. Here $E_p(R/R\cdot^+)$ and $E_p(R/R\cdot^-)$ are the peak potentials for oxidation of rubrene to the cation radical and reduction to the anion radical, respectively, and the observed behavior of ΔE_p apparently implies that the cell includes an appreciable uncompensated resistance. Extrapolation of a plot of ΔE_p to infinite dilution yielded a difference of 2.36 V, a figure which agrees well with previously reported results.[3]

The ratio of anodic to cathodic peak currents for rubrene reduction was 1.00 ± 0.02 (sweep rate, 0.2 V/sec), as evaluated by the method of Nicholson.[15] Thus, on the 1-sec time scale used for most triple-potential-step experiments, the anion radical was completely stable. It was impossible, because of the proximate background reaction, to make reliable analogous measurements for the rubrene cation radical.

We have already noted the importance of employing large overpotentials for reactant generation as a means for minimizing the effects of uncompensated resistance on the triple-step experiments, and, on the basis of previous observations,[10] the potential used for the generation of the rubrene anion was 250 mV more negative than $E_p(R/R\cdot^-)$. The use of an equivalently large overpotential for cation generation was not possible; hence an optimum value was selected by means of the following procedure. A series of triple-step experiments was performed in which the rubrene anion was generated in a 1.00-sec forward step and the anodic step potential was varied. The light output was observed to pass through a maximum as the anodic overpotential (relative to $E_p(R/R\cdot^+)$) was increased. The initial rise is apparently due to the effect of uncompensated resistance and the decline in output at high overpotential results from increased participation of background oxidation products. The overpotential at which maximum luminescence was observed for a given system (usually about 180 mV) was selected for subsequent measurements with that system.

Chronocoulometric data for generation of the rubrene anion in 1.00-sec potential steps at potentials chosen as outlined above were entirely linear with rubrene concentration and could be fitted to the following least-squares line

$$Q = (11.9 \pm 0.3) + (17.6 \pm 0.3)[\text{rubrene, m}M] \quad (\text{in } \mu\text{C})$$

wherein the precision is expressed as the standard deviation, and Q is the total charge passed in the step.

It has been reported that rubrene cation radicals engage in a chemiluminescent reaction with DMF.[1] To ascertain the interference presented by this reaction, several experiments were performed in which the light output was observed as the working electrode potential was alternated between a value at which the cation was produced and one of several negative values ranging from −1.0 to −1.9 V *vs.* qre. Using even the greatest available photomultiplier sensitivity, no light was observed on either half-cycle unless the negative potential step was cathodic enough to reduce rubrene. Similar experiments in which the positive step potential was varied were also performed, and, because of the en-

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(10) R. Bezman and L. R. Faulkner, *J. Amer. Chem. Soc.*, **94**, 6317 (1972).

(11) R. Bezman and P. S. McKinney, *Anal. Chem.*, **41**, 1560 (1969).

(12) R. Bezman and L. R. Faulkner, *ibid.*, **43**, 1749 (1971).

(13) R. F. Chen, *Anal. Biochem.*, **20**, 339 (1967).

(14) D. J. Fisher, W. L. Belew, and M. T. Kelley in "Polarography 1964," Vol. 2, G. J. Hills, Ed., Interscience, New York, N. Y., 1966, p 1043.

(15) R. S. Nicholson, *Anal. Chem.*, **39**, 1406 (1967).

tirely analogous results, it was concluded that the only observable chemiluminescent process involved the rubrene anion–cation annihilation.

Because electrochemical techniques could not be reliably used to assess the stability of the rubrene cation radical in DMF solutions, a luminescence method originated by Cruser and Bard was employed.[16,17] A number of experiments were performed in which a train of alternating anodic and cathodic potential steps, the potentials of which were selected as outlined above, was applied to the cell. The total light output was integrated and the integral was displayed as a function of time. Step widths ranged from 0.5 to 5.0 sec. The fact that progressively smaller amounts of light were emitted in pulses appearing on steps of like polarity was an indication that the cation was not completely stable. So that the average cation lifetime could be estimated, the ratio of the light output for a cathodic half-cycle to that of the immediately preceding step was calculated for four such pairs at each step time. In accord with the simulation of Cruser and Bard, the ratios for a given step time were equal within 5%, and, by fitting the data for the range of step times to their working curves, the apparent first-order rate constant was found to be $0.2 \pm 0.05\ \text{sec}^{-1}$. Even though the decay mechanism is probably more complicated than pseudo-first-order, the process represents only a minor perturbation, so the 5-sec lifetime indicated by the decay constant probably is not far from the truth. However, reference to the third paper in this series[7] shows that triple-step experiments featuring 1-sec anodic forward steps would require significant corrections to the single-pulse data. Because such procedures are somewhat uncertain, the only results from single-pulse experiments that are reported here were obtained from experiments featuring initial cathodic steps. For the latter case, no corrections for the effect of cation decay were needed for either the emission efficiency measurements or the decay curve analyses.

In the luminescence measurements, however, a correction was required to account for the part of rubrene emission that is not absorbed by the fluorescent screen used in the photometric apparatus (3.0 g/l. rhodamine B, RhB, in ethylene glycol).[12] The RhB solution shows a very sharp cutoff in absorbance at 610 nm and is essentially transparent at longer wavelengths. Because rubrene emission extends slightly into this transparent region, the calibration factor relating photocurrent to the absolute total source emission rate, which was determined with a source whose emission was completely absorbed by the quantum counter, is not directly applicable for the present work. In order to utilize the calibration, one must apply a multiplicative correction, H, to measured photocurrents, so that one obtains the ideal photocurrents that would be observed if all the rubrene emissions were absorbed by the fluorescent screen. Such a correction can be obtained by considering the response of the detection system to incident light of various wavelengths.

In the ideal case mentioned above, the only light falling on the photomultiplier is RhB fluorescence, and the ideal photocurrent is given by

$$i_{\text{ideal}} = \phi_f' G_1 \int_{\substack{\text{rubrene}\\ \text{spectrum}}} I(\lambda)\text{d}\lambda \int_{\substack{\text{RhB}\\ \text{spectrum}}} f(\lambda)\cdot S(\lambda)\text{d}\lambda \quad (1)$$

In this equation, the first integral is the total number of source photons absorbed per unit time by the quantum counter, and $I(\lambda)$ has dimensions of quanta/sec per unit wavelength interval. These absorbed quanta are reemitted by RhB with efficiency ϕ_f', and G_1 is the geometric factor with which the reemitted photons are collected by the phototube. The second integral accounts for the wavelength dependence of the photomultiplier sensitivity, $S(\lambda)$, and the variable $f(\lambda)$ therein is the distribution function describing a normalized RhB spectrum. Since this integral is a constant, it can be abbreviated $S(\lambda_{\text{eq}})$, and one can consider the RhB to behave as a monochromatic light source of wavelength λ_{eq}. The equivalent sensitivity $S(\lambda_{\text{eq}})$ can be calculated according to

$$S(\lambda_{\text{eq}}) = \int I_{\text{RhB}}(\lambda)S(\lambda)\text{d}\lambda \Big/ \int I_{\text{RhB}}(\lambda)\text{d}\lambda \quad (2)$$

where both integrals are carried out over a corrected RhB spectrum.

In reality, of course, all wavelengths of the rubrene emission are not absorbed by the quantum counter, and the measured photocurrent is given by

$$i_{\text{real}} = S(\lambda_{\text{eq}})\phi_f' G_1 \int_{\substack{\text{rubrene}\\ \text{spectrum}}}^{610} I(\lambda)\text{d}\lambda + G_2 \int_{\substack{610\\ \text{rubrene}\\ \text{spectrum}}} S(\lambda)\cdot I(\lambda)\text{d}\lambda \quad (3)$$

Here the first integral is carried out over the rubrene spectrum at wavelengths shorter than 610 nm, and the second covers the region at longer wavelengths. The quantity G_2 is the geometric factor relating the number of unabsorbed photons falling on the quantum counter face to those actually striking the photocathode.

The desired multiplicative correction, H, is therefore given by the ratio of i_{ideal} to i_{real}

$$H = \frac{S(\lambda_{\text{eq}}) \int_{\substack{\text{rubrene}\\ \text{spectrum}}} I(\lambda)\text{d}\lambda}{S(\lambda_{\text{eq}}) \int_{\substack{\text{rubrene}\\ \text{spectrum}}}^{610} I(\lambda)\text{d}\lambda + B \int_{\substack{610\\ \text{rubrene}\\ \text{spectrum}}} I(\lambda)S(\lambda)\text{d}\lambda} \quad (4)$$

where B is $G_2/\phi_f' G_1$.

In evaluations of $S(\lambda_{\text{eq}})$ and H, it is important to realize that one does not require absolute values of $I(\lambda)$ and $S(\lambda)$. It is only necessary that the shapes of the curves be reliable. Thus by using a corrected fluorescence spectrum of the RhB solution (in-line viewing, 1.0-cm path length) and the quantum efficiency spectrum of the photocathode supplied by the tube manufacturer, it was possible to obtain λ_{eq} as 635 nm. Integrations were performed on high-quality graph paper by cut-and-weigh methods. In a similar manner, numbers proportional to the integrals needed for the evaluation of (4) were generated using the curves shown in Figure 1. The rubrene spectra were recorded with right-angular illumination of DMF or benzonitrile solutions. In both cases, the solutions were sufficiently concentrated that the short-wavelength reabsorption effects observed

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[16] S. A. Cruser, Ph.D. Thesis, The University of Texas at Austin, 1968.

[17] S. A. Cruser and A. J. Bard, *J. Amer. Chem. Soc.*, 91, 267 (1969).

Table I. Characteristics of Rubrene Ecl from DMF Solutions[a]

C, mM	Feldberg plot[b] Slope	Feldberg plot[b] Intercept		$\phi_{\text{coul}} \times 10^4$	$\phi_{\text{ecl}} \times 10^4$	$\alpha \times 10^3$	$\beta \times 10^3$
0.38	−2.56	−2.18		4.29	4.65	2.92	1.42
0.53	−2.44	−2.08		3.96	4.29	3.22	0.922
0.56	−2.87	−2.03		2.70	2.92	10.5	31.4
0.60	−2.18	−2.08		4.40	4.77	2.81	0.251
0.66	−2.39	−2.07		4.89	5.30	3.30	0.712
0.73	−2.32	−2.09		4.39	4.76	2.78	0.501
0.79	−2.34	−2.16		4.55	4.93	2.58	0.448
0.99	−2.19	−2.10		5.28	5.72	2.78	0.263
Av			Av[c]	4.54 ± 0.32	4.92 ± 0.34	2.91 ± 0.20	

[a] t_f = 1.00 sec. [b] Plot of log ω_i *vs.* $(t_r/t_f)^{1/2}$. See ref 7. [c] Excluding results from the 0.56 mM solution. See text.

in chemiluminescence spectra were essentially duplicated in the recorded fluorescence spectra.

In practice, evaluating H precisely is virtually impossible because B is somewhat uncertain. Nevertheless it is simple to formulate some reasonable expectations about the relative magnitudes of quantities composing B and to obtain thereby an estimate for H. The photons from the integrating sphere that strike the front face of the quantum counter cell have, by the nature of the sphere's operation, directions that are nearly randomly distributed in the hemisphere bounded by the cell face and including the phototube. Of the part of this light that is not absorbed by the quantum counter, a fraction, G_2, will strike the photocathode. However, the light that the quantum counter absorbs is scattered randomly into both hemispheres. Of that scattered toward the phototube, presumably a fraction G_2 is intercepted by the photocathode, and of that scattered back into the sphere, only about 7% returns.[12] Thus it seems reasonable to assume G_1 equal to $0.54G_2$. Since ϕ_f' is very close to unity,[18] B has been taken to be 1.9, and the resulting value for H, 0.70, has been employed for correcting the measured photocurrents.

The results of the intensity–time and total quantum output measurements for the rubrene anion–cation reaction in DMF are summarized in Table I. The quantity C is the rubrene concentration, and the second and third columns display the intercepts and slopes of Feldberg plots of the intensity–time data. The latter parameters were obtained from a least-squares analysis, which indicated their precision to be about ±2%. The total quantum output data are presented as coulombic efficiencies, which are defined according to

$$\phi_{\text{coul}} = (F/Q_f)\int_{t_f}^{\infty} I \, dt$$

The integral in this equation represents the total absolute quantum output of a light pulse, F is the Faraday, and Q_f is the faradaic charge ascribable to reactant generation in the forward step.[7] The final three columns of Table I list more fundamental parameters derived from the measurable data as discussed below.

Although the DMF and benzonitrile solutions were both examined with step times ranging from 0.5 to 5 sec, there was no encounter with nonlinear Feldberg plots or systematic variations in their slopes like those reported by Chang, *et al.*[2] A standard value of t_f = 1.00 sec was therefore adopted for all work reported here.

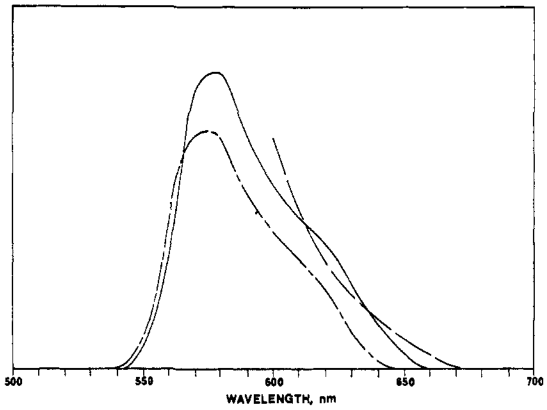

Figure 1. Curves used to obtain the correction for detector response: (– –), relative photocathode quantum efficiency for EMI 9656R photomultiplier; (——), corrected fluorescence spectrum for rubrene in benzonitrile; (–––), corrected fluorescence spectrum for rubrene in DMF. Both fluorescence spectra were obtained with right-angular viewing using 1 mM solutions excited at 420 nm, and both are expressed in intensity units proportional to quanta/nm.

Benzonitrile Solutions. When cyclic voltammograms of each benzonitrile solution of rubrene were recorded, the peak potentials were found to be somewhat more stable than those observed in DMF, and a larger shift in ΔE_p with concentration was noted. The latter effect apparently arises from the lower conductivity of benzonitrile solutions, and at low concentrations ΔE_p approached a limit very close to that observed with our DMF solutions and to that reported by Visco and Chandross for benzonitrile.[3] Since both peaks were well removed from the background limits, it was possible to use potentials for ion generation that were at least 250 mV more extreme than the E_p values, and one could also measure the reverse-to-forward peak current ratio for generation of each ion. At a 0.2-V/sec sweep rate, the ratio in each case was 1.00 ± 0.03; hence both ions were stable on a 1-sec time scale. A further indication of ion stability was that no intensity decay was observed in long-term multicycle experiments.

The chronocoulometric data for rubrene ion generation in benzonitrile at t_f = 1.00 sec were fitted to the following least-squares lines.

Cathodic forward step

$$Q = (7.2 \pm 1.0) + (13.6 \pm 1.0)[\text{rubrene, m}M] \quad (\text{in } \mu\text{C})$$

Anodic forward step

$$-Q = (3.0 \pm 0.3) + (14.8 \pm 0.3)[\text{rubrene, m}M] \quad (\text{in } \mu\text{C})$$

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(18) G. Weber and F. W. J. Teale, *Trans. Faraday Soc.*, 53, 646 (1957).

Table II. Characteristics of Rubrene Ecl from Benzonitrile Solutions[a]

C, mM	Feldberg plot[b]					
	Slope	Intercept	$\phi_{coul} \times 10^3$	$\phi_{ecl} \times 10^3$	$\alpha \times 10^3$	$\beta \times 10^3$
			(a) Cathodic Forward Step			
0.59	−2.63	−1.72	0.97	1.05	7.51	4.24
0.62	−2.41	−1.63	1.14	1.23	7.41	1.71
0.77	−2.37	−1.72	1.12	1.21	6.93	1.41
0.80	−2.51	−1.55	1.16	1.26	10.0	2.79
0.98	−2.51	−1.66	1.01	1.09	7.76	2.51
1.04	−2.36	−1.72	1.13	1.22	7.06	1.36
1.13	−2.35	−1.64	1.18	1.28	7.55	1.42
1.25	−2.33	−1.70	1.19	1.29	6.76	1.32
		Av	1.11 ± 0.06	1.20 ± 0.07	7.62 ± 0.63	
			(b) Anodic Forward Step			
0.59	−2.18	−1.98	0.77	0.83	3.69	0.339
0.62	−1.92	−1.94	1.12	1.21	3.72	0.100
0.77	−1.96	−2.01	1.07	1.16	3.56	0.115
0.80	−1.99	−1.97	1.16	1.26	3.62	0.146
0.98	−2.03	−1.93	0.97	1.05	3.86	0.159
1.13	−1.91	−1.90	1.13	1.22	4.00	0.111
1.25	−1.94	−1.99	0.99	1.07	3.61	0.133
		Av	1.03 ± 0.10	1.11 ± 0.11	3.72 ± 0.12	

[a] t_f = 1.00 sec. [b] Plot of log ω_i *vs.* $(t_r/t_f)^{1/2}$. See ref 7.

Because rubrene was the parent compound for each ion, one expects the slopes of these lines to be equal. Within the precision of measurement, the expectation is borne out; hence the average slope was used for subsequent calculations.

It is interesting that, using viscosities from the literature and the data above,[19] one can verify the prediction of the Stokes–Einstein equation that the product of the chronocoulometric slope and the solvent viscosity should be constant from solvent to solvent. The results of the single-pulse luminescence measurements for rubrene solutions in benzonitrile are given in Table II according to the same format used above.

Discussion

As we have noted above, prior evidence has suggested that a triplet pathway is an important contributor to chemiluminescence from the rubrene anion–cation annihilation. This view is strongly reinforced by the results of this work, wherein Feldberg slopes exclusively in the range from −1.9 to −2.9 have been observed. Previous reports have demonstrated that slope magnitudes much greater than the 1.48 lower limit can result, in terms of the usually invoked mechanism, only from the generation of an unstable ion in the forward step or from the participation of a triplet pathway to luminescence.[6,7] The former possibility can be ruled out by the electrochemical evidence; hence the latter is suggested.

However, the earlier reports concerning rubrene chemiluminescence have been somewhat ambiguous in that they have not allowed one to choose confidently between the ST and T routes to emission. Of course Feldberg suggested some years ago that variations in the slopes of the linear intensity–time plots with the degree of triplet quenching could be used to discriminate between the possibilities.[6] In the limit of zero quenching, one expects both routes to give slopes of −1.48. As quenching becomes steadily more important, the ST route is expected to yield a slope magnitude that increases from 1.48, passes through a maximum value, and returns to the 1.48 value as a high-quenching limit. In contrast, the treatment predicts that increased quenching in the T route will lead to monotonically increasing slope magnitudes and that the slope will approach −2.96 as a high-quenching limit.

When one views the data in Tables I and II, one notes that though there is apparently no trend in the luminescence parameters with concentration, a strong correlation exists between ϕ_{coul} and the Feldberg slope magnitude. There is little doubt that there is a tendency for increasing slope magnitudes to accompany decreasing coulombic efficiencies, even though the correlation is not total. It is especially interesting that the highest slope magnitude in each series accompanies the lowest value of ϕ_{coul} and that the largest negative slope, −2.87, is quite close to the high-quenching limit of the T route. Though this trend and the somewhat variable nature of the slope values are both consistent with the expected control of slope magnitude by adventitious triplet quenchers, the observed correlation between slope and luminescence yield is not in accord with that anticipated from the ST route. Obviously the T route fits these observations very well, and that mechanism has been assumed for the subsequent data analysis. We feel that the prior evidence, the results presented here, and the coherence of the following interpretation, which even suggests a reason for the incomplete correlation between Feldberg slope and ϕ_{coul}, comprise an imposing argument that the T route is indeed the luminescent pathway from the rubrene anion–cation reaction.

Using the procedures discussed in an earlier paper, we have analyzed the primary data on this basis, and the results are displayed in the last four columns of Tables I and II. Since the effect of reactant decay is insignificant on the three sets of data considered here, ϕ_{ecl}, which is the probability of emission per electron transfer event, is simply 1.08 ϕ_{coul}. Similarly the efficiency parameter, α, defined as $\phi_{tt}\phi_t\phi_f/(1 - g)$, and the quenching parameter, β, defined as $\phi_f\phi_{tt}f(t)t_f/8k_a(1 -$

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(19) C. K. Mann in "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 2; E. W. Washburn, Ed., "International Critical Tables," McGraw-Hill, New York, N. Y., 1930; C. D. Hodgman, Ed., "Handbook of Chemistry and Physics," 43rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1961.

$g)^2\tau^2C$, are straightforwardly derived from the Feldberg plot parameters *via* the published working curves.[7] In these definitions, ϕ_f is rubrene's fluorescence efficiency, ϕ_t is the triplet yield of charge transfer, C is the bulk concentration of rubrene, τ is the triplet lifetime in the absence of triplet–triplet annihilation, and $f(t)$ is the thickness of the reaction zone rendered in dimensionless units.[7] The quantity k_a is the overall rate constant for triplet–triplet annihilation and is the sum, $k_s + k_g + k_t$, of the individual rate constants for the excited singlet, the ground state, and the triplet channels of annihilation. Finally, ϕ_{tt} is the efficiency of the excited singlet channel, defined kinetically as k_s/k_a, and g is $k_t/2k_a$.

It is a particularly interesting and satisfying aspect of this analysis that the apparently almost random Feldberg parameters yield estimates of α of comparable precision to the measured ϕ_{coul} values and the extracted ϕ_{ecl} data. In contrast, β is quite variable. Certainly such behavior is expected from the T route, because α contains only fundamental properties of basic reactions, whereas β includes a variety of factors, which, for convenience, are combined into τ. Since some of the components of τ will be inherently irreproducible (*e.g.*, certain quenching processes) and since τ appears to the second power, the value of β will obviously not be well defined. The inverse-square dependence of β on τ also implies that, even though small changes in quenching can produce large variations in β, significant changes in ϕ_{ecl} should be associated only with fairly large variations in β. This expectation is largely borne out by the data; however, there is some correlation in the results between increasing α values and enhanced values of β, an effect which is particularly prominent for the 0.56 m*M* solution of Table I. The discussion below will suggest that this effect may not be entirely artificial. The results from this latter solution also furnish an indication that variations in concentration of trace impurities are responsible for the poor precision of the β measurements. Although the supporting electrolyte which was used to prepare all but the 0.56 m*M* solution was vacuum dried immediately before use, the salt employed for the latter had been opened to the atmosphere several times beforehand. In view of the hygroscopicity of TBAP, it seems likely that either water or a product of water was the quencher responsible for variations in β.

Interest in α is inherently high because it contains ϕ_t, which is probably the single most important parameter describing charge transfer. Extracting ϕ_t requires a knowledge of $\phi_f\phi_{tt}/(1 - g)$; hence it is unfortunate that no data describing the kinetic efficiencies of rubrene triplet–triplet annihilation exist. However, one can follow the previous discussion of this point[7] by taking ϕ_{tt} as 0.01–0.02 (representative of the p_c data introduced by Parker)[20–23] and $1 - g$ as 0.63. These values can then be combined with the literature fluorescence efficiency (1.0 for rubrene[24]) to produce estimates of ϕ_t of 0.1, 0.15, and 0.3, respectively, from the α data in Tables I, IIa, and IIb. Obviously a great deal of faith cannot be placed in these numbers as realistic quantitative estimates, but their magnitude is surprisingly high and strongly suggests that the charge-transfer process yields electronic excitation relatively efficiently.

In addition, the results indicate a very high fractional participation of triplets in the annihilation. One can show that this quantity, which we define as the ratio of the number of triplets reacting by annihilation to the total number of triplets, is $2\phi_{ecl}/\alpha(1 - g)$. Under this definition, the fraction can exceed unity to a limit of $(1 - g)^{-1}$, because the triplets which remain from triplet channel annihilation may participate more than once. Even so, the fractions of 0.54, 0.51, and 0.96, which one calculates from the data in Tables I, IIa, and IIb, respectively, are surprisingly high. Compared to the estimated ϕ_t values, these numbers presumably merit considerably more confidence because they involve only an assumption about $(1 - g)$. These interesting conclusions show that the low overall efficiency of even this T-route ecl process is due principally to inefficiencies in the disposition of triplets rather than to a low initial excited state yield.

Perhaps the most intriguing observation that can be made about the efficiency data is that in benzonitrile the nature of the ecl process apparently depends upon the order of reactant generation. Concentration profiles produced in digital simulations of the triple-step experiments show that the rate–time behavior of charge transfer is essentially independent of the order in which the reactants are generated.[7] For systems involving stable ions, a condition shown to hold for rubrene in benzonitrile, the value of ϕ_t must therefore also be independent of the generation sequence if the simple T mechanism applies. Moreover, β and ϕ_{ecl} can change with the generation order only if the level of quenching by a substance other than the radical ions changes considerably with that order. Although the data of Table II indicate that ϕ_{ecl} is apparently independent of the generation sequence, α and β decidedly are not. This effect, which reflects a truly fundamental difference in intensity–time behavior for the two generation modes, must therefore necessarily involve reactions not included in the set used to derive the data analysis scheme. Of course, this fact suggests that reactants other than the radical ions may be involved.

In an examination of the behavior of β, it is instructive to consider the previously cited work of Visco and Chandross,[3] who also studied the intensity–time behavior of luminescence from rubrene in benzonitrile solutions. However, these authors found Feldberg slopes, using either generation sequence, in the vicinity of -1.5. If the T route is accepted on the basis of the earlier discussion as the pathway to rubrene emission, then one must conclude that insignificant quenching of the triplet intermediates occurred in their work. This conclusion implies that the radical ions are not important quenchers in these experiments and that in our work the value of τ is governed by the presence of foreign substances in the reaction zone. Of course this latter idea was suggested above by other features of these results. Interestingly, a comparison between our experimental procedures and those used by Visco and Chandross reveals a possible basis for the contrasting

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(20) C. A. Parker, "Photoluminescence of Solutions," Elsevier, Amsterdam, 1968, and references contained therein.

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(23) K. Kikuchi, H. Kokubun, and M. Koizumi, *ibid.*, **44**, 1527 (1971).

(24) L. S. Forster and R. Livingston, *J. Chem. Phys.*, 20, 1315 (1952).

intensity–time data. The latter authors carried out their experiments in an oxygen-free drybox, and under their conditions it is possible that the solvent and supporting electrolyte became uncommonly dry by a long-term equilibration. Though the solutions used in this work were prepared and handled with great care,[10] they were prepared in air and probably contained more water than those of Visco and Chandross. If water gives rise to substances controlling β, it is possible to rationalize all the aspects of its behavior by the following argument.

In experiments featuring a cathodic forward step, the rubrene anion formed first diffuses away from the electrode, and, because it is a powerful reductant, it probably frees the diffusion layer of residual oxygen. However, it is also likely that the reversal step replenishes the supply of oxygen *via* a partial electrodic oxidation of residual water, both because large amplitude positive steps are used and because the phenyl substituents on rubrene prevent its ions from removing water by reaction. Of course, oxygen is known to have an abnormally large diffusion coefficient;[25] hence any oxygen produced at the electrode will diffuse ahead of the rubrene cation. Thus it will probably maintain a steadily high concentration in the reaction zone and will quench some of the triplets formed there.

In experiments featuring the anodic forward step, the electrogenerated oxygen produced in the first step faces a concentration gradient in the second step both toward and away from the electrode. Thus its rapid diffusion rate will tend to disperse it toward the bulk and to move it to destruction in the reaction zone early in the reversal step; hence the concentration at later t_r values will be lower than that applicable to the opposite generation sequence.

This rationale is supported by the results of several pertinent experiments involving DMF solutions of rubrene. The following table displays the Feldberg plot parameters measured for 1.16 m*M* solution of rubrene after it had first been degassed *via* one freeze–pump–thaw cycle and then after it had been deareated by four additional cycles.

Cycle	Slope	Intercept
1	−2.66	−2.55
5	−2.65	−2.53

Obviously the parameters were virtually unaffected by the change in the dissolved oxygen concentration from *ca.* 10^{-5} *M* in the first case to an electrochemically undetectable level in the second. These results certainly support the view that the radical anion effectively eliminates residual oxygen as a factor determining β.

In a second group of experiments, the intensity–time data were collected before and after the water content of a 0.69 m*M* solution of rubrene was increased. The results, summarized as shown below, show that the slope parameter, which is affected primarily by changes in β, increased markedly upon the addition of water.

$[H_2O]$, m*M*	Slope	Intercept
Initial	−2.03	−2.23
Initial + 15	−2.30	−2.43

This kind of explanation for the behavior of β with generation sequence indicates that some of the rubrene anion will be consumed by the electrogenerated oxygen, but the amounts need not be significant and, in any case, are undetectable electrochemically. Another phenomenon must therefore be responsible for the dependence of α on the step sequence, but the nature of that phenomenon is not at all obvious. However, the experiments involving the addition of water and the evidence that a slight correlation exists between α and β suggest that water or a product derived from it may be involved. In any case, we have found these unusual effects of generation sequence to be restricted to the rubrene systems, and it seems likely that they arise because the rubrene ions are rather unimportant as triplet quenchers for these step experiments.

This view, that radical ion quenching does not significantly control the rubrene triplet lifetime, apparently conflicts with the recent suggestion that the inhibition of this process by magnetic fields is responsible for the observed enhancement with increasing field strength of luminescence from the rubrene radical annihilation.[4] However, one can probably reconcile this disagreement by recognizing that the quenching of rubrene triplets by foreign substances, notably oxygen, will often involve changes in total spin angular momentum. In such cases, the angular momentum selection rules elaborated by Merrifield will apply,[26] and one expects field-influenced quenching rates like those observed for radical ion quenching.

The values of ϕ_{ecl} reported here are substantially larger than even the maximum value of 7.4×10^{-5} reported by Maloy and Bard.[8,9] In view of the near agreement between our measurements and theirs for the 9,10-diphenylanthracene–DMF system, the difference between the reports for rubrene is probably real. It may result from a greater participation of quenching processes in their work or from fundamental differences in the nature of the reaction zones attained in the two generation methods. In particular, it seems likely that for comparable overall charge-transfer reaction rates, the volume of the zone will be somewhat larger at the rotating ring-disk electrode. If so, triplet–triplet annihilation will compete less favorably with deactivating processes; hence the steady-state method would be expected to yield a lower estimate of ϕ_{ecl} than the transient techniques.

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