

originate from the $\tau_y(B_{3u})$ sublevel, while the $\tau_z(A_u)$ sublevel should be completely inactive to such vibrations. The measured value of the radiative rate constant ratio for $\tau_y(B_{3u}):\tau_z(A_u)$ to the origin (Table I) is about 4:1. The emission from τ_y shows predominantly out-of-plane polarization as expected and emission from τ_z , the symmetry restricted sublevel, displays a slight in-plane polarization. In fact, the pmdr spectra shown in Figure 1 clearly reveal that some mixed emission is apparent in all transitions since all optical transitions are coupled by all three microwave transitions.

A definitive explanation for the mixed phosphorescence observed in DCB is beyond the scope of data currently available. We have, however, considered various possibilities. Explicit considerations of the crystal field effects focused on the surrounding chlorine atoms, since the reduction of molecular symmetry D_{2h} to C_i site symmetry would occur in all likelihood *via* either chlorine crystal field contributions (*e.g.*, the heavy atom effect) or explicit trap characteristics. An analysis of the DCB crystal structure¹⁵ shows that the sum of weighted ($1/|r|^2$) vectors from each of the 24 nearest chlorine atoms surrounding any DCB molecule yields a resultant vector $0.87\hat{x} + 0.31\hat{y} + 0.38\hat{z}$, relative to the DCB molecular axes. Such a field vector could mix both the in-plane zero-field spin sublevels and the out-of-plane spin sublevel with each in-plane spin state. Obviously, this chlorine-field vector possesses suitable geometry to account for the mixed DCB phosphorescence, but a quantitative assessment of the strength of the external chlorine influence and the trap effects would be necessary before we can venture any definite conclusions. Aside from crystal effects, the relaxation of symmetry restrictions observed in DCB trap phospho-

rescence might also be due to a distortion of the molecule itself. The question of the exact nature of this distortion remains as yet unanswered. The distortion may be caused by a rearrangement of the nuclear skeleton either under the influence of the excited state electronic potential or as an inherent characteristic of the trap. It is noteworthy, however, that the chlorine field gradient in the excited state is substantially lower than in the ground state. As has been discussed¹² this can be due in part to a distortion and in part to increased carbon-chlorine π bonding in the excited state. The average decrease in chlorine field gradients in $\pi\pi^*$ states in those molecules thus far investigated where no distortion is suspected is about 3% (8-chloroquinoline,³⁸ 1,2,4,5-tetrachlorobenzene,³² and 1,4-dichloroquinoxaline³⁹). An average decrease of 3% may well represent the increased π character of the C-Cl bond. DCB, on the other hand, shows an 8% decrease in the chlorine field gradient. Perhaps the additional 5% decrease is due to an out-of-plane chlorine distortion. The pmdr and inversion data do not exclude this possibility. Further experiments are needed to resolve this question adequately.

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(38) M. J. Buckley and C. B. Harris, *Chem. Phys. Lett.*, **5**, 205 (1970).

(39) M. J. Buckley and C. B. Harris, unpublished work.

Theoretical and Practical Considerations for Measurements of the Efficiencies of Chemiluminescent Electron-Transfer Reactions¹

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Abstract: Digital simulation methods and a kinetic analysis have been used to define a concise set of parameters which quantitatively describe the efficiencies of the simplest types of energy-sufficient and energy-deficient chemiluminescent electron-transfer processes. Techniques for data acquisition and analysis are discussed in both theoretical and practical terms for the triple-potential-step generation of luminescence. It is shown that excited state yields of electron transfer are experimentally accessible from the analysis of luminescence decay curves and that total quantum output data can provide a measure of the overall efficiency of chemiluminescence. The effects of reactant instability on these determinations are also considered and rendered accountable.

Although the phenomenon of electrogenerated chemiluminescence (ecl) was first reported about eight years ago,² there have been very few investiga-

tions of the absolute quantum yields of these processes, largely because appropriate instruments have been lacking. Moreover, each report of the absolute output of an ecl process has introduced a new method for

(1) Mechanisms of Chemiluminescent Electron-Transfer Reactions. III. For the previous paper in this series, see D. J. Freed and L. R. Faulkner, *J. Amer. Chem. Soc.*, **93**, 3565 (1971).

(2) (a) R. E. Visco and E. A. Chandross, *ibid.*, **86**, 5350 (1964); (b)

D. M. Hercules, *Science*, **145**, 808 (1964); (c) K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, **87**, 139 (1965).

expressing experimental findings. Aside from complicating comparisons of similar results, this variety of calculation methods has indicated that some clarification is in order regarding the identities and definitions of the parameters that best describe the quantitative aspects of ecl processes.

The first quantum-yield measurements for ecl reactions were performed by Zweig, *et al.*,³ who used as an intensity standard a chemiluminescent reaction whose output had been compared with that of a standard tungsten lamp. The ecl emission was produced by the application of a square-wave alternating voltage to a two-electrode cell and was, therefore, of a transient nature. The results of the experiments were expressed as the ratio of the total light output to the total charge passed through the cell, a method that possesses the significant virtue of simplicity. However, this calculation procedure tends to give inaccurate (probably low) results, because the total charge value contains both faradaic and nonfaradaic components. In a later study using a photometer that was calibrated by an actinometric procedure, Maloy and Bard eliminated the difficulties associated with transient techniques by generating the ecl with a rotating ring-disk electrode assembly.^{4,5} Because steady-state conditions were achieved for both light intensity and cell current, the ratio of the absolute intensity to the disk current could be easily related to the efficiency of the reaction, ϕ_{ecl} , which is the number of photons emitted per electron-transfer event. The use of steady-state conditions simplified the problem of faradaic current determination, but at the expense of a complex experimental apparatus.

Because methods used to analyze data acquired from steady-state and transient methods differ significantly, it seemed worthwhile to examine their individual characteristics in order to see whether one possesses an experimental or theoretical advantage over the other. Most commonly, the transient methods involve the application of a controlled, alternating potential to a small, stationary, noble-metal electrode. The potential control instrumentation for these experiments is simple and commonly available, and the cells can be simple, rugged, and inexpensive. In addition, by appropriate cell design, one can produce conditions that closely approximate semiinfinite linear diffusion. Data analysis is therefore greatly simplified because, first, the Cottrell equation describes the faradaic component of the cell current, and second, because one can easily write digital simulation programs to describe diffusion-kinetic problems. The disadvantage of the transient method is that one must deal with pulses of light and current, the latter of which often contain large nonfaradaic components that must be compensated either in the experiment or in the data analysis. An additional, more subtle complication is that the large initial currents encountered during the potential-step generation of reactants imply that the cell-potentiostat combination must be carefully designed to minimize uncompensated resistance effects, especially when short step times are to be used. How-

ever, instruments for the observation of transient phenomena are, of course, readily available, and various studies have shown that compensation for nonfaradaic currents and for the effects of cell resistance on potential control can be effected. Maloy and Bard's rotating ring-disk electrode system is the only reported apparatus with which ecl has been generated under true steady-state conditions, with the attendant minimization of nonfaradaic currents and uncompensated resistance effects. However, the simultaneous control of the potentials of two electrodes in the same solution is fairly difficult, and vacuum-tight cells for rotating electrodes are complex, delicate, and costly. Complications in data analysis also exist, although Maloy was able to simulate with considerable success the behavior of ecl produced at the rotating ring-disk electrode.⁵ Even so, the programs are somewhat more elaborate and expensive to execute than those involved in the interpretation of transient results.

On the basis of this comparison, it seemed that generation of ecl by transient methods has an important advantage in experimental simplicity and that it would be completely satisfactory for practically all real systems. We have therefore undertaken a series of precise measurements of ecl efficiencies, using transient methods, for several systems of current interest. A precisely calibrated photometer, which was designed and built for this purpose, has recently been described.⁶ To fully utilize its capabilities, several proposed mechanisms for ecl have been reexamined, and a concise set of parameters which are useful for communicating experimental results has been defined. Furthermore, a unified system for the acquisition and analysis of data has been developed to permit actual evaluation of fundamental efficiency parameters for most systems.

Techniques of Data Acquisition and Analysis⁷

The generation sequence we have used to produce ecl experimentally is a triple-potential-step program similar to that previously employed by Visco and Chandross⁸ and by Chang, *et al.*⁹ One begins each experiment with the working electrode at its rest potential in an unstirred solution containing only the parent substrates from which the reactant ions are generated. At zero time, a forward step is applied to the electrode in which its potential is changed abruptly to a value in the diffusion-limited region for generation of the first reactant. This step may be either anodic or cathodic, and it lasts for a time t_f . Thereupon the electrode potential is shifted abruptly in a reverse step to a value in the diffusion-limited region for generation of the second reactant. In all our work, this step also lasts for a time t_f , but time measured into the step from its beginning is designated t_r . In the final potential step, the electrode potential is returned to its initial value. Of course, the luminescence appears almost entirely during the second step, and it decays from $t_r = 0$ by an exponential form. During the third step, the electrode boundary conditions are such that both reactants are destroyed there, so very

(3) A. Zweig, A. K. Hoffman, D. L. Maricle, and A. H. Maurer, *J. Amer. Chem. Soc.*, **90**, 261 (1968).

(4) J. T. Maloy and A. J. Bard, *ibid.*, **93**, 5968 (1971).

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

(6) R. Bezman and L. R. Faulkner, *Anal. Chem.*, **43**, 1749 (1971).

(7) A list of important symbols and their definitions is given in the Appendix.

(8) R. E. Visco and E. A. Chandross, *Electrochim. Acta*, **13**, 1187 (1968).

(9) J. Chang, D. M. Hercules, and D. K. Roe, *ibid.*, **13**, 1197 (1968).

little light is produced. Its main experimental use is to prevent reactant buildup in the working solution. One can extract useful information from an analysis of the luminescence decay constants and also from a consideration of the integrated quantum output. Whenever necessary, it has been assumed for the theoretical treatment given below that the electrochemical boundary conditions traditionally associated with diffusion-limited processes apply and that changes in boundary conditions which accompany potential steps are instantaneous.

Analysis of Intensity–Time Curves. The analysis of ecl data is always complicated by the fact that there are at least three viable alternative mechanisms to account for luminescence from those systems for which the chemiluminescence spectrum is identical with the fluorescence of the parent molecule. Generally, however, the direct generation of a product molecule excited state in the electron-transfer reaction is the fundamental mechanistic assumption. The simplest pathway to luminescence is the S route, wherein the emitting first excited singlet state is produced directly in the redox step. There is evidence that this pathway may apply to most systems for which the emitting state is accessible to the electron-transfer reaction (energy-sufficient systems).^{10,11} A more complicated process, the T route, apparently accounts for emission from many energy-deficient reactions.^{1,10–13} This pathway involves the production of triplet states in the redox process, which subsequently undergo triplet–triplet annihilation to yield the emitting singlets. A third possibility, applicable only to energy-sufficient systems, is that both the singlet and the triplet pathways contribute significantly to emission. Although this ST route must be considered as an alternative, there is no evidence that it operates in any real system; hence we will examine here only the expected behavior of systems proceeding either by the S route or the T route.

The techniques of digital simulation of diffusion-kinetic processes were first applied to the ecl phenomenon by Feldberg,^{14,15} who derived the expected intensity–time curves for luminescence produced in a double-step experiment *via* each of the three mechanisms described above. In this very significant work, Feldberg was able to show that intensity–time curves could be linearized, that variations in the slopes of the linear “Feldberg” plots with added triplet quenchers could serve to distinguish between the three mechanisms, and that the plots could yield important quantitative information about ecl. It is, in fact, Feldberg’s work that forms the basis for the decay-curve analysis scheme we present here.

In his first paper, Feldberg essentially treated the S route to luminescence with the special assumption that every homogeneous charge-transfer reaction produces an emitter. In essence, then, his program computed the overall rate of the redox reaction which occurred in the diffusion layer. This reaction rate, N ,

could be linearized with time in an explicit dimensionless representation. For $(t_r/t_f) > 0.1$

$$\log \omega_n = a_n + b_n(t_r/t_f)^{1/2} \quad (1)$$

where a_n and b_n were found to equal 0.71 and -1.45 , respectively. Feldberg then related the overall rate of light emission, I , to N *via* the fluorescence efficiency, ϕ_f ; thus he considered $\omega_i = \phi_f \omega_n$. Although there is evidence that some energy-sufficient ecl reactions do produce emitters without intermediates, this treatment is somewhat unrealistic because it is highly unlikely that they are generated at unit efficiency. However, this contingency can be readily incorporated into the Feldberg treatment by relating ω_i to ω_n through an emission efficiency, $\phi_{ecl} = \phi_f \phi_s$, where ϕ_s is the excited singlet yield of charge transfer. Thus

$$\log(\omega_i/\phi_{ecl}) = \log \omega_n = a_n + b_n(t_r/t_f)^{1/2} \quad (2)$$

Since ϕ_{ecl} for an S-route system should be virtually constant with time, the intercept, a_i , and the slope, b_i , of an experimental plot of $\log \omega_i$ *vs.* $(t_r/t_f)^{1/2}$ (a Feldberg plot) can be identified as $a_n + \log \phi_{ecl}$ and b_n , respectively. Obviously, then, the emission efficiency is accessible experimentally *via* the relation $\phi_{ecl} = 10^{(a_i - a_n)}$. However, it is important to recognize here that a_n and b_n are both strong functions of reactant stability and that Feldberg’s numbers, as quoted above, apply only to stable reactants. Means by which unstable reactants can be accommodated are considered in detail below.

In an actual experiment, both intensity–time and total quantum output data may be obtained, but since only one measurable parameter, ϕ_{ecl} , governs the overall luminescence process, one may calculate it independently from either kind of information. Extraction of ϕ_{ecl} from total quantum output is detailed in the next section.

Though ϕ_{ecl} is the experimentally accessible parameter, it is the singlet yield, ϕ_s , that is fundamentally descriptive of charge transfer and is most useful for comparing the results of similar experiments. However, a determination of this parameter requires explicit knowledge of the emitter’s fluorescence efficiency *in situ*. The linear intensity–concentration relationships observed for many ecl systems suggest that ϕ_f is frequently a constant,¹⁶ and in such cases it seems entirely reasonable to estimate its magnitude from values obtained optically. Nevertheless, variations in ϕ_f due to quenching processes are certainly conceivable, and, in such cases, one can assess the importance of the quenching processes by the use of experimental and mathematical techniques developed for the measurement of quenching rates in conventional systems.

In the consideration of the T and ST routes to ecl given below, the basic mechanism shown in Scheme I has been assumed. In this mechanism, R, $^1R^*$, and $^3R^*$ represent ground, first-excited singlet, and lowest triplet state molecules of the substrate from which the ion radicals, $R^{\cdot+}$ and $R^{\cdot-}$, are derived. Substance Q is any quenching species, and $1/\tau$ is considered to be the sum of apparent first-order rate constants for all triplet-deactivating processes except for reactions d–f. In this connection, we take the apparent first-order constant for a bimolecular process to be the product of

(10) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 209 (1969).

(11) L. R. Faulkner, H. Tachikawa, and A. J. Bard, *ibid.*, **91**, 691 (1972).

(12) A. Weller and K. Zachariasse, *J. Chem. Phys.*, **46**, 4984 (1967).

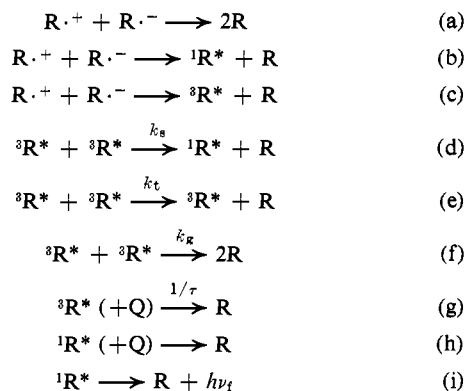
(13) D. J. Freed and L. R. Faulkner, *J. Amer. Chem. Soc.*, **93**, 2097 (1971).

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

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

(16) S. A. Cruser and A. J. Bard, *Anal. Lett.*, **1**, 11 (1967).

Scheme I



the second-order quenching constant and the Q concentration. Reaction i is assumed to compete with all processes of the type h with a fluorescence efficiency ϕ_f . Finally, the electron-transfer reactions a–c are considered to have a sum of rates equal to the diffusion-controlled rate, which is probably very fast indeed for this energetic process involving oppositely charged ions.^{17,18} Even though the mechanism is written for the case in which both reactants are derived from the same parent, extrapolation of the results to the corresponding mechanism for an ecl process involving ions derived from different precursors is quite straightforward. This mechanism is somewhat more general and more realistic than that employed by Feldberg,¹⁵ wherein he neglected (a), (e), and (f) altogether and considered only a special case of process g. One can use this mechanism and Feldberg's treatment to arrive at conclusions similar to his regarding means for discriminating the S, T, and ST routes to luminescence, but, more importantly, if one confines the examination to the T route (process b inoperative), one can refine his analysis to obtain a completely quantitative description of luminescence in terms of experimentally accessible composite parameters.

It has been well established *via* digital simulation that the redox reaction occurs in a very small volume of solution at the junction of the two regions containing the reactant ions.¹⁴ In fact, the simulated charge transfer is ordinarily restricted to the two volume elements immediately adjacent to this boundary. In considering whether one can reasonably employ the simulation technique to model processes d–i, one must recognize that the proper treatment of triplet–triplet annihilation, being second order in the triplet concentration, depends heavily on the assignment of the triplet products of charge transfer to a volume element of realistic size. An examination of the probable magnitude of τ , the expected triplet quenching by the radical ions, and other points discussed below suggest that the triplets are contained in a region somewhat smaller than the volume resolution of the simulation. If so, it is plainly arbitrary and unrealistic to assign them to one or two simulation elements. Since one cannot know *a priori* what the proper volume is, the series of reactions d–i cannot be reasonably simulated except at vastly improved resolution and at the accompanying prohibitive cost. Of course the fundamental reason for this situation is that the time resolution ordinarily

employed (1 msec for $t_f = 1$ sec) is far too coarse to deal properly with the kinetic aspects of any reaction in the scheme presented above. Recognizing these limitations, Feldberg abandoned the method in favor of a kinetic treatment that described a reaction zone of volume V_r , throughout which he considered uniform concentrations to apply. The digital simulation was used only to supply the overall rate of electron transfer. It is important to recognize that this rate can be reliably determined by digital simulation because it depends on the (relatively slow) rate of diffusive reactant transport toward the reaction zone. We believe the Feldberg method to be basically sound; hence we have employed it to cover the extended reaction scheme presented above.

The rate of change of the triplet concentration in the volume of solution in which the luminescence occurs is given by the following.

$$dT/dt = L/V_r - 2k_g T^2 - 2k_s T^2 - k_t T^2 - T/\tau \quad (3)$$

Repopulation of the lowest triplet state by intersystem crossing from the first excited singlet is ignored here because much evidence suggests that processes e and f greatly predominate over d (see below). Thus the rate of repopulation must be negligibly small compared to the rate of initial triplet population, L/V_r . Defining $k_a = k_g + k_s + k_t$ and $g = k_t/2k_a$, one can rewrite (3) as

$$dT/dt = L/V_r - 2k_a(1 - g)T^2 - T/\tau \quad (4)$$

from which the steady-state assumption will yield the triplet concentration

$$T = \{4k_a(1 - g)\tau\}^{-1} \times \{-1 + [1 + 8k_a(1 - g)\tau^2 L/V_r]^{1/2}\} \quad (5)$$

Since $L = \phi_t N$ for the present case, one can straightforwardly combine eq 1 and 5; hence one can readily test the magnitude of dT/dt against the terms on the right-hand side of eq 4. Substitution of virtually any realistic combination of parameter values into the resulting relationships reveals that dT/dt is negligibly small at any value of (t_r/t_f) of experimental interest. The steady-state assumption is therefore properly invoked in this instance.

If one defines the excited singlet yield of triplet–triplet annihilation according to $\phi_{tt} = k_s/k_a$, then the overall rate of light emission is given by

$$I = \phi_t \phi_{tt} k_a T^2 V_r \quad (6)$$

$$I = \phi_t \phi_{tt} \left\{ \frac{V_r}{8k_a(1 - g)^2 \tau^2} \right\} \times \left\{ 1 - \left[1 + \frac{8k_a(1 - g)\tau^2 L}{V_r} \right]^{1/2} + \frac{4k_a(1 - g)\tau^2 L}{V_r} \right\} \quad (7)$$

Though Feldberg expressed $V_r = fA(Dt_f)^{1/2}$ (so that f is conveniently the reaction zone thickness on the usual dimensionless simulation space axis),¹⁵ it is perhaps better to recognize a possible time dependence of f explicitly, because the actual reaction volume depends on the (time dependent) sum of the rates of the processes disposing of triplets. Substituting, then, for V_r and L in eq 7 and defining $\alpha = \phi_t \phi_{tt} \phi_f / (1 - g)$ and $\beta = \phi_t \phi_{tt} f(t) t_f / 8k_a(1 - g)^2 \tau^2 C$, one obtains

$$\omega_i = \beta [1 - (1 + \alpha \omega_n / \beta)^{1/2}] + 0.5 \alpha \omega_n \quad (8)$$

(17) P. J. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

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

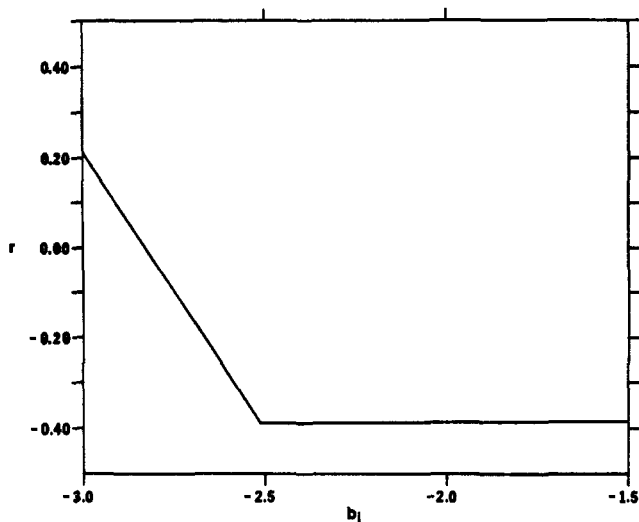


Figure 1. Working curve relating r to b_i for T-route systems.

It is very important to recognize here a difference in definition between this work and Feldberg's with regard to β . Feldberg defined β as a parameter relating t_f , k_a , τ , and C , but he chose to consider f and ϕ_f separately. However, f , ϕ_f , and the equivalent factor to Feldberg's β (as well as $\phi_{tr}/(1-g)^2$) are not independently determinable from luminescence decay curves, so we have chosen to combine them all into a single newly defined β , which continues to reflect the competitiveness of triplet quenching with respect to annihilation.

Comparison of eq 2 and 8 shows that while the direct production of luminescent molecules in S-route ecl implies that the accompanying luminescence can be described by the single parameter ϕ_{ecl} , the intermediate steps in the T route necessitate the use of two composite parameters α and β in the description of emission. Of course, N is directly calculable from the simulation (without the need to consider any processes other than diffusion and charge transfer); hence it is possible to obtain expected luminescence decay curves for various values of α and β . Such a procedure produces curves for $(\alpha/\beta) > 0.1$ that can be linearized in the usual logarithmic form

$$\log \omega_i = a_i + b_i(t_r/t_f)^{1/2} \quad (9)$$

One can therefore obtain working curves depicting the variations of α and β with a_i and b_i , and by the procedure outlined below one can utilize this information to provide α and β from experimental Feldberg parameters.

So that the working curves would be as accurate as possible, a_n and b_n of eq 1 were recalculated in a 1000 iteration/step simulation, which was written in Fortran IVD for an IBM 360/65 computer. The program was basically similar to the one presented by Cruser^{19,20} and operated on the assumptions that the diffusion coefficients of all species were equal and that within the volume element containing the electrode, the homogeneous charge transfer preceded the heterogeneous process. The latter innovation was the major

(19) S. A. Cruser, Ph.D. Thesis, The University of Texas at Austin, 1968.

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

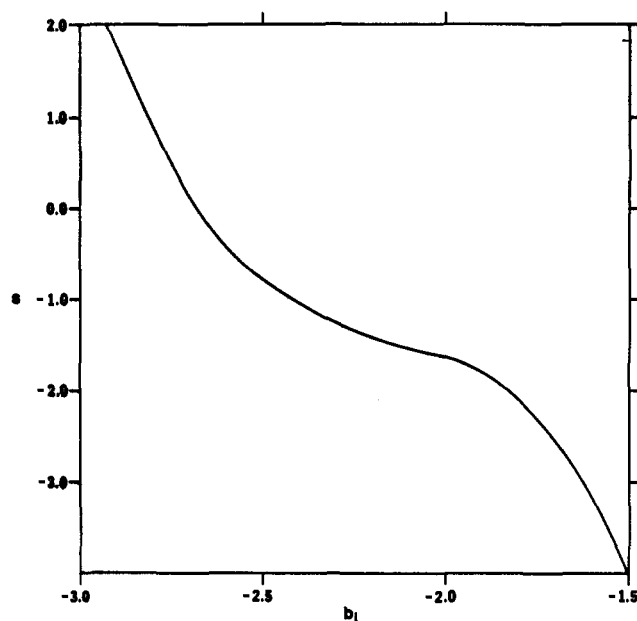


Figure 2. Working curve relating s to b_i for T-route systems.

difference between the programs used in this work and that given by Cruser. Somewhat more satisfactory from a kinetic viewpoint, it was also found to decrease markedly the computation time required to obtain results of a specified precision. The final 800 data points of the second simulated step, *i.e.*, $0.20 < (t_r/t_f) < 1.0$, were fitted to a straight line by a least-squares procedure; the results, $a_n = 0.724$ and $b_n = -1.483$, were used to prepare the working curves.

It is convenient that the numerical description of ω_i with α and β can be fitted to two families of straight lines, all of which have a unit slope

$$\log \alpha = r + a_i \quad (10)$$

$$\log \beta = s + a_i \quad (11)$$

The intercepts of these lines depend strongly upon b_i , a fact which is shown graphically in Figures 1 and 2. It is plain that one can straightforwardly calculate α and β from the experimental a_i value for a real system once the proper r and s values have been chosen from the measured value of b_i .

Of these two composite quantities, α is undoubtedly the one of greater interest because it is proportional to ϕ_t , which is the single most fundamental description of the redox process. Certainly it would be most informative if one could extract the triplet yield from α , but doing so requires knowledge of the product $\phi_t\phi_{tr}/(1-g)$. Although very precise estimates of this factor's value cannot be made with present data, enough information is available to permit a useful indication of its size for many cases of interest. First, Parker and his coworkers have, in effect, measured k_s for a variety of triplet-triplet annihilation reactions.²¹ They have chosen to present their data in terms of a quantity p_c , which is defined as the ratio of k_s to the pertinent Smoluchowski-Debye diffusion-controlled rate constant.^{17,22} These ratios are usually on the order of

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

(22) M. V. Smoluchowski, *Z. Phys. Chem.*, **92**, 129 (1917).

0.04 for aromatic hydrocarbons and related compounds. In complement, the flash experiments of Porter and Wright have indicated that k_a is ordinarily very close to the Smoluchowski-Debye constant,^{23,24} a conclusion which has been recently corroborated by Avakian, *et al.*²⁵ If triplet-triplet annihilation is indeed diffusion controlled, then Parker's p_c data are essentially ϕ_{tt} values. Unfortunately, experimental studies bearing on $(1 - g)$ are far less abundant. Groff, Merrifield, and Avakian have suggested that in the absence of activation effects,²⁶ the statistical factors accompanying the angular momentum selection rules will lead to $(k_g + k_s)/k_a = 0.25$. Moreover, their magnetic field studies of anthracene triplet exciton fusion have indicated that $(k_g + k_s)/k_a$ is 0.22 ± 0.01 . Thus k_t/k_a seems likely to lie in the range 0.6-0.8, and $(1 - g)$ is probably 0.6-0.7. In the absence of more extensive data, the statistical value of 0.63 appears an appropriate choice. Obviously the uncertainties in ϕ_{tt} and $(1 - g)$ render the choice of ϕ_t rather uncritical. Unless there is some special reason to choose another value, one can quite reasonably use the efficiency measured by the usual optical means. Even though these considerations can be employed to estimate only the magnitude of ϕ_t , it is important to recognize that α itself can generally be evaluated quite precisely. Thus meaningful and discriminating studies of the variations in ϕ_t with system parameters can ordinarily be carried out as long as all the observations pertain to a single triplet-triplet annihilation process.

Although this method of data analysis allows one to evaluate the quenching parameter β , its usefulness for obtaining estimates of τ is obscured by the parameter's explicit dependence on ϕ_t , ϕ_{tt} , $(1 - g)$, and $f(t)$. The considerations discussed above are helpful with regard to the first three of these quantities, but there really is no satisfactory way to evaluate $f(t)$. Even so, one can estimate its magnitude from the expected diffusional range of the triplet intermediates, which is controlled by their average lifetime. Diffusion theory shows that this range is on the order of $(D\tau)^{1/2}$ (if τ can be taken as the actual triplet lifetime), hence $f(t) \sim 2(\tau/t_t)^{1/2}$. Much experimental evidence suggests that τ will not greatly exceed 1 msec in fluid solutions at room temperature,²¹ so 10^{-1} is probably a reasonable upper limit for $f(t)$. One might ordinarily expect $f(t)$ to be somewhat smaller for several reasons. First, the radical ions are generally effective triplet quenchers,²⁷ and their presence on either side of the reaction zone tends to "wall in" the triplets. Moreover, triplet-triplet annihilation may play a large role in governing the triplet lifetime, and, of course τ may actually be much less than 1 msec. Having recorded these reservations, we consider it satisfying that the use of $f(t) = 0.1$ with β values derived from our work with rubrene systems has produced estimates of τ between 10^{-4} and 10^{-3} sec.²⁸ Feldberg has suggested that $f =$

0.525 and that it is constant with time.¹⁵ However, we feel that radical ion quenching alone renders this an unreasonably large estimate, and we believe it unlikely that a single figure could apply to all systems at all times.

As we have already noted, there is no *a priori* reason to suggest that $f(t)$ is constant; hence one must face a possible time dependence in β . This question is magnified by the possibility that varying triplet quencher concentrations (such as those of the radical ions) may produce a time-dependent τ . It is possible to show from the data in Figures 1 and 2 and from eq 10 and 11 that β is the key factor determining the Feldberg slope b_1 . If β does not remain fairly constant during the course of the luminescence decay, one must therefore observe a nonlinear Feldberg plot. Because it has been our experience and that of others to observe linear plots for T-route systems,^{8,28} we conclude that β is not grossly time dependent in the region of the decay curve ordinarily considered ($t_r/t_t > 0.1$). Thus $f(t)$ and τ may actually be relatively constant, or, alternately, the quotient $f(t)/\tau^2$ may compensate for individual changes in $f(t)$ and τ . Indeed the declining radical ion and triplet concentrations with time could produce a simultaneous, progressive enlargement of both quantities.

From this analysis, it is clear that if a system can be shown to proceed by the T route, one can readily measure a pair of parameters, α and β , which completely describe the quantitative relationships between the homogeneous electron transfer and the resulting luminescence. Even though α is probably the more generally useful of the measurable quantities, the sensitivity of β to a variety of effects, chiefly quenching processes, means that its variation with experimental variables can be helpful for elucidating certain aspects of mechanism. It is interesting to note that typical experimental conditions seem to lead to $10^{-4} < \beta < 10^{-2}$;²⁸ hence the observation of b_1 in the range from -1.9 to -2.5 seems an excellent first indication that a system proceeds by the T route. However, it is important to recognize that a Feldberg slope in this range can also be produced by homogeneous reactant decomposition, an effect discussed below.

Analysis of Total Quantum Output. A consideration of the total luminescence generated in a triple-step experiment as compared to the total number of reactant ions generated is a valuable complement to the analysis of decay curves because it indicates the overall efficiency of the ecl process. The most convenient way to express the results of a total output measurement is as a coulombic efficiency, ϕ_{eoul} , which is defined here as the ratio of total quantum output to the number of reactant ions produced in the system in the forward step. But inspection of boundary conditions for the triple-step experiment shows that ϕ_{eoul} is not a true measure of the efficiency of ecl, because some of the reactant produced in the forward step is consumed electrolytically in the second. For this reason, the allied quantity, ϕ_{ecl} , which expresses the photon emission probability per homogeneous charge-transfer event, is more useful. Accounting for the difference between these two efficiencies was accomplished with a simulation program in which θ , the ratio of the number of charges transferred during the first step to the total number of homogeneous re-

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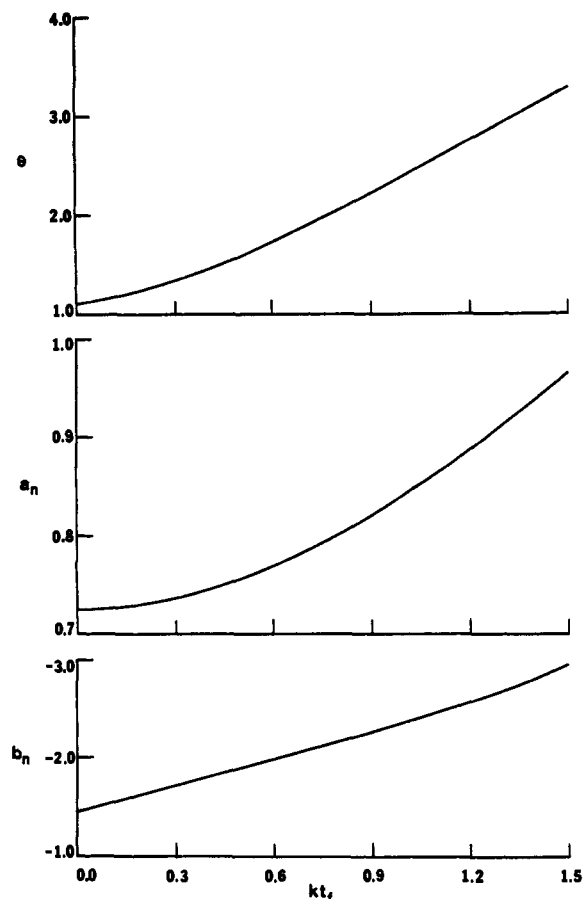


Figure 3. Working curves depicting the effects of an unstable reactant generated in the forward step on θ and on a_n and b_n .

action events, was computed. For the triple-step mode of ecl generation, θ was found to be 1.078, and since it is essentially $\phi_{\text{ecl}}/\phi_{\text{cou1}}$, the calculation of ϕ_{ecl} from experimental data is quite simple.

Effect of Reactant Decay. All of the methods given above for analyzing ecl data have carried the implicit assumption that the reacting ions are completely stable on the time scale of the experimental measurements. Since this premise is often invalid, we have also investigated the effect of reactant instability on the slopes and intercepts of plots of $\log \omega_n$ vs. $(t_r/t_f)^{1/2}$ and on θ . Figures 3 and 4 display the results of the simulations for various values of kt_f , where k is the pseudo-first-order rate constant for decay of the unstable reactant to inactive products. Obviously the instability profoundly alters ecl behavior, and, as expected, the alterations are much more severe when the unstable ion is produced in the forward step.

If ion decomposition is known to occur in a particular system, eq 1 is best considered as

$$\log \omega_n = a_n(kt_f) + b_n(kt_f) \times (t_r/t_f)^{1/2} \quad (12)$$

Applying the results of Figures 3 and 4 to T-route intensity-time data is quite tedious, because one must first measure kt_f , then evaluate $a_n(kt_f)$ and $b_n(kt_f)$, and finally construct new working curves analogous to Figures 1 and 2. With S-route systems, the procedure is quite simple. One can determine kt_f either by electrochemical means or from the experimental b_i value via the curves of Figures 3 and 4; hence one can obtain

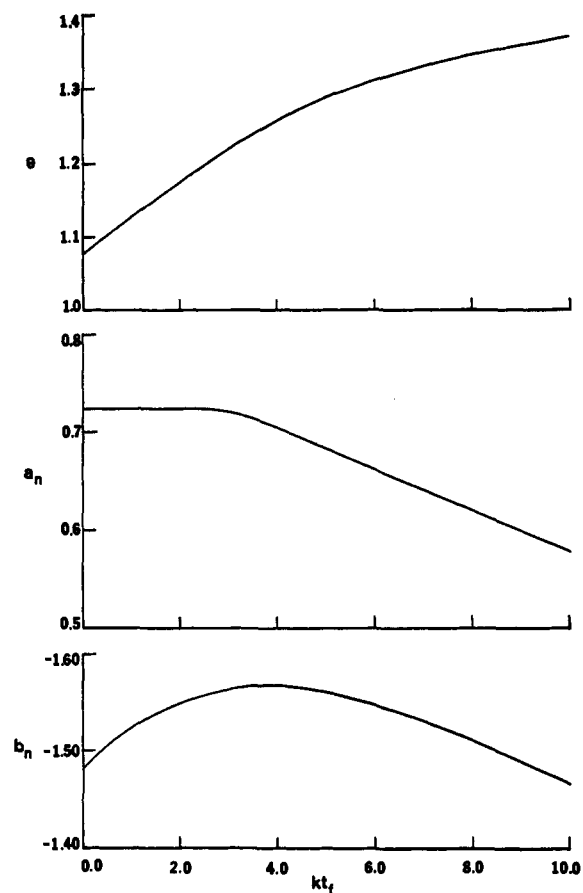


Figure 4. Working curves depicting the effects of an unstable reactant generated in the reversal step on θ and on a_n and b_n .

$a_n(kt_f)$ and

$$\log \phi_{\text{ecl}} = a_i - a_n(kt_f) \quad (13)$$

For either kind of system, one can extract ϕ_{ecl} from total quantum output data by the relation

$$\phi_{\text{ecl}} = \theta(kt_f) \times \phi_{\text{cou1}} \quad (14)$$

Of course one must first know kt_f so that $\theta(kt_f)$ can be obtained from the working curves. For S-route systems involving an unstable reactant, as for those featuring only stable reactants, two measures of ϕ_{ecl} are therefore available. However, the fact that kt_f will often be obtained from $b_i(kt_f)$ means that estimates of ϕ_{ecl} derived from intensity-time and total quantum output data are not strictly independent.

It is important to note from these results that if $|b_i| > 1.5$, it is difficult to decide without a fair amount of additional data whether the large negative slope results from the participation of a triplet pathway to luminescence or from slight ion instability. Mechanistic hypotheses derived from intensity-time curves must therefore always be carefully formulated on the basis of a variety of experiments featuring a range of step times and alternation of the ion generation sequence.

Practical Aspects of Data Extraction. The procedures for analyzing data from ecl experiments have been shown ultimately to depend upon the computation of two types of parameter, $\omega_i = I(t)t_f^{1/2}/AD^{1/2}C$ and $\phi_{\text{cou1}} = (F/Q_i) \int_{t_f}^{\infty} I(t) dt$. While the photometric component of each of these can be measured directly with an ap-

appropriate instrument, the acquisition of reliable values of $AD^{1/2}$ and Q_f is more difficult. A method for greatly simplifying the former problem was suggested by Feldberg,¹⁴ who recognized that because the Cottrell equation describes the faradaic current in the forward step, one can write $\omega_i = I(t)F/\pi^{1/2}i_t$, where i_t is the faradaic current at $t = t_f$. Thus the computation of both ω_i and ϕ_{ecl} depends only on an accurate quantitative description of the electrolysis that occurs during the first step of each experiment.

Anson has investigated chronocoulometric behavior for potential-step electrolyses at microelectrodes²⁹ and has demonstrated that for a constant step time and a constant difference between the initial and step potentials one can express the total charge as follows.

$$\begin{aligned} Q_{\text{total}} &= Q_r + Q_{\text{Cottrell}} \\ &= Q_r + 2nFAD^{1/2}Ct_f^{1/2}/\pi^{1/2} \\ &= Q_r + KC \end{aligned} \quad (15)$$

In this relation, Q_r is a constant residual charge resulting from processes other than generation of the first reactant (mostly double-layer charging), and K is a constant of proportionality. A plot of Q_{total} vs. C is linear, and from the experimental slope, K , one can evaluate Q_f and i_t conveniently and precisely from $Q_f = KC$ and $i_t = KC/2t_f$.

Conclusion

The foregoing discussion has yielded a number of important conclusions concerning the experimental measurement of ecl process efficiencies, although the most significant are perhaps the following. (1) One can readily obtain much information about an ecl system from data acquired by the relatively simple alternating potential step technique. (2) A concise set of parameters for communicating information about the quantitative nature of an ecl process has been defined. For both S- and T-route systems, the excited-state formation efficiency supplies fundamental information about the homogeneous charge-transfer reaction. Though these quantities cannot be measured directly, they can often be extracted from the measurable composite efficiency parameters ϕ_{ecl} and α . For T-route systems alone, a second parameter, β , has also been defined to quantify the degree to which the triplet intermediates are quenched prior to engaging in the energy-transfer process that leads to luminescence. (3) A unified group of data acquisition and analysis procedures has been detailed, from which one can determine the applicable parameters among ϕ_{ecl} , α , and β . (4) By employing appropriate working curves, one can quantitatively account for the effects of reactant decomposition on intensity-time curves and on θ .

The principal limitation of the analysis procedure is that it requires the system of interest to produce luminescence by either the S or the T route, and further, that the investigator know which applies. However, it seems reasonable to assume, with the knowledge of recent evidence,^{1,10-13} that if the luminescence from an energy-deficient system is identical with the fluorescence of the parent compound, luminescence arises by the T route. Unfortunately, energy-sufficient systems are more complex, and in such cases mechanistic

confirmation requires information from other sources, such as observations of the effect of magnetic fields^{10,11} and the effect of triplet quenchers on luminescence decay curves.

Specific examples of the use of the techniques outlined in this work have been avoided so that important principles would not be obscured by interesting results. However, the methods have been successfully applied to a number of prominent ecl systems, and considerable useful and intriguing information has been obtained. The actual results and the conclusions based upon them will be presented shortly.

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Appendix

For convenient reference, the important special parameters used for the data analysis are collected here with their definitions.

Symbol	Definition	Dimensions
\bar{N}	Overall rate of homogeneous electron-transfer events	mol/sec
L	Overall rate of excited-state formation	mol/sec
I	Overall rate of light emission	einsteins/sec
ϕ_s, ϕ_t	Probabilities of singlet and triplet formation, respectively, per electron-transfer event	none
ϕ_f	Fluorescence efficiency	none
ϕ_{tt}	Probability of excited singlet formation in triplet-triplet annihilation	none
ϕ_{ecl}	Probability of emission per electron-transfer event	none
V_r	Volume of the ecl reaction zone	cm ³
T	Triplet concentration	mol/cm ³
τ	Triplet lifetime in the absence of triplet-triplet annihilation	sec
$f(t)$	Average width of the reaction zone	none
k_s, k_g, k_t	Rate constants for excited singlet, ground state, and triplet channels in triplet-triplet annihilation	cm ³ /(mol sec)
k_a	Overall rate constant for triplet-triplet annihilation, $k_s + k_g + k_t$	cm ³ /(mol sec)
g	$k_t/2k_a$	none
k	Pseudo-first-order rate constant for unstable reactant decay	sec ⁻¹
θ	Ratio of total charge-transfer reactions in a potential step experiment to the number of reactant particles produced in the forward step	none

(29) F. C. Anson, *Anal. Chem.*, **38**, 54 (1966).

t_f	Duration of the forward generation step	sec	Coulombic efficiency
t_r	Elapsed time into the second generation step, measured from its beginning	sec	$\phi_{\text{coul}} = (F/Q_f) \int_{t_f}^{\infty} Idt$
A	Working electrode area	cm^2	Intensity parameter (accessible experimentally)
D	Diffusion coefficient of the reaction participants	cm^2/sec	$\omega_i = It_f^{1/2}/AD^{1/2}C$
C	Concentration of the parent substance	mol/cm^3	Redox reaction rate parameter (accessible theoretically)
F	Faraday	coul/equiv	$\omega_n = NIt_f^{1/2}/AD^{1/2}C$
Q_f	Total charge given to reactant ion production in the forward step	coul	T-route efficiency parameter
i_f	Faradaic current attributable to reactant generation at $t = t_f$	amp	$\alpha = \phi_i \phi_{\text{t}} \phi_f / (1 - g)$
r	Intercept of the working curve relating α to a_i	none	T-route quenching parameter
s	Intercept of the working curve relating β and a_i	none	$\beta = f(t) t_f \phi_{\text{t}} \phi_f / 8k_a \tau^2 C (1 - g)^2$

The important dimensionless aggregate parameters have been defined as follows.

Data are plotted according to $\log \omega_y = a_y + b_y(t_r/t_f)^{1/2}$. When $y = i$, a and b refer to values obtained from experimental intensity-time data, and when $y = n$, the plots refer to simulated reaction rate data.

Photochemistry of Phenylcyclopropanes

Kingsley Salisbury

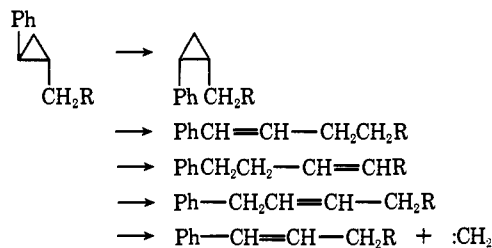
Contribution from the University of Texas at Austin, Austin, Texas 78712.

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Abstract: The gas-phase fluorescence yields of two phenylcyclopropanes show a dramatic increase as compared to monoalkylbenzenes. This increase has been explained by a decrease in the intersystem crossing rate constants. The gas-phase photolysis of *trans*-methylphenylcyclopropane gives the *cis* isomer as the major product and, by a different route, *trans*-1-phenylbut-1-ene and 1-phenyl-2-methylprop-2-ene in much lower quantum yields. The same products, in the same ratio, are obtained on benzene photosensitization. Evidence for and against triplet and singlet mechanisms in the direct photolysis is presented.

There have been several reports of the liquid-phase photolysis of phenylcyclopropanes¹⁻⁷ and in general there seem to be five major reaction paths (Scheme I).

Scheme I



(1) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Amer. Chem. Soc.*, **86**, 2532 (1964).

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On the other hand, sensitization in solution results in clean geometric isomerization with little contribution from any of the other processes.^{1,7} The gas-phase photochemistry of phenylcyclopropanes has received very limited attention. The available data indicate rather similar behavior to the solution photochemistry, but with olefin formation becoming much more important.^{8a} Since almost all the available data on the photochemistry of these molecules are rather qualitative, and the nature of the excited states, from which reactions occur on direct excitation, in many cases remains in doubt, it was decided to make a quantitative study of the gas-phase photochemistry of *trans*-1-phenyl-2-methylcyclopropane (I). This molecule represents the simplest phenylcyclopropane structurally capable of undergoing all the known photochemical reactions of this class. Furthermore, it was felt that a knowledge of the fluorescence of phenylcyclopropanes was necessary to obtain a better understanding of these molecules.

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