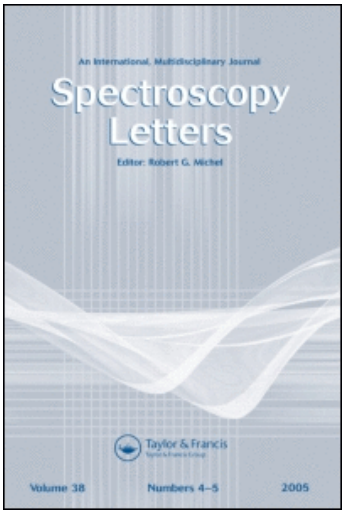

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Chemistry in Lasers. VI. Dimeric Luminophors in Electrogenerated Chemilumines cence

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CHEMISTRY IN LASERS. VI. DIMERIC LUMINOPHORS IN ELECTROGENERATED CHEMILUMINESCENCE

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(ABSTRACT)

Electrogenerated chemiluminescence (ECL) provides an unusually attractive method for producing dimeric luminophors, by comparison to optical pumping of a dye laser, both in terms of dimer/monomer ratio and variety of accessible states. Several dimeric luminophors arising from the homogeneous charge transfer step are discussed, and the customary assignment of full singlet or triplet character to some of the excited moieties is shown to be unwarranted. An error in the literature concerning the kinetics of ECL-dimer formation is pointed out.

The recent paper by Measures[1] on the prospects of developing a laser based on electrochemiluminescence (ECL)[2] calls to attention some advantages of this particular technique for achieving laser action in dye solutions. It was suggested that 9,10-diphenylanthracene (DPA) should be a promising candidate to achieve population inversion in the singlets, whereas 9,10-dimethylanthracene (DMA) and 9,10-dibromoanthracene were judged suitable for a laser based on excimers. The particular advantage

of ECL to produce excimers is inherent to the method: whereas in optical pumping the formation of excimers involves creation of excited monomers followed by diffusion to an interaction sphere, i.e.

$$DMA + h\nu \rightarrow {}^1DMA^* \quad (1)$$

$${}^1DMA^* + DMA \rightarrow {}^1(DMA)_2^* \quad (2),$$

in electrogenerated chemiluminescence the order of the steps is effectively reversed, i.e. diffusion to an interaction sphere precedes creation of the excited state:

$$DMA^{+\cdot} + DMA^{-\cdot} \rightarrow [DMA^{+\cdot}...DMA^{-\cdot}] \rightarrow [DMA...DMA]^* \quad (3)$$

It is readily apparent from Eqs. 1, 2, and 3 that in case of optical excitation the concentration dependence of the {dimer emission intensity/monomer emission intensity} ratio[3] is a well defined function of [DMA], and in ECL the same ratio is seen to be concentration independent as a first approximation. In the following we would like to examine in some detail the formation of dimeric luminophors in ECL, and some related quenching problems. These results complement, rather than contradict in any way, the work of Measures.[1]

Electrogenerated chemiluminescence involves the conversion of electrical energy to chemical energy, for example at a platinum wire or PPDE (planar platinum disk electrode):

$$R + e^-_{electrode} \rightarrow R^{-\cdot} \quad (4)$$

and

$$R \rightarrow e^-_{electrode} + R^{+\cdot} \quad (5)$$

followed by conversion of the chemical energy to light:

$$R^{+\cdot} + R^{-\cdot} \rightarrow 2R + h\nu \quad (6).$$

The chemical energy available from Eq. 6 can be calculated as

$$\Delta H^\circ = \Delta G^\circ - T\Delta S^\circ \quad (7)$$

where ΔG^{O} is the difference between the standard oxidation and reduction potentials of R, and the present literature value of $T\Delta S^{O}$ is 0.10 eV at room temperature.[4] By comparing ΔH^{O} with the first excited singlet energy (E_s) of R, the system in Eq. 6 can be classified as either energy sufficient ($E_s \leq |\Delta H^{O}|$) or energy deficient ($E_s > |\Delta H^{O}|$). In an energy sufficient system Eq. 6 becomes

$$R^{+\cdot} + R^{-\cdot} \rightarrow {}^1R_0 + {}^1R_1 \qquad (8a)$$

followed by fluorescence of $^1R_1$

$$^1R_1 \rightarrow {}^1R_0 + h\nu \qquad (8b).$$

Generally, energy sufficient systems give more intense luminescence than energy deficient ones, as was shown in the first experimental inquiries.[5-7]

When the system described by Eq. 6 is energy deficient, the homogeneous electron transfer step yields triplets (T):

$$R^{+\cdot} + R^{-\cdot} \rightarrow {}^1R_0 + {}^3R_1 \qquad (9).$$

As most ECL experiments are carried out at room temperature, direct phosphorescence is unlikely in most systems, and the luminescence requires an additional step. Endothermic intersystem crossing to the excited singlet

$$T \rightarrow S^{*} \qquad (10)$$

is unlikely to occur in these systems due to the short triplet lifetime in the presence of formidable concentrations of radical ion quenchers, hence the commonly postulated "energy doubling" mechanism is triplet-triplet annihilation (TTA)

$$T + T \rightarrow S + S^{*} \qquad (11).$$

Analogous considerations apply to the chemiluminescence studies of Weller,[8] who prepare the ions as sodium and perchlorate salts for example, and observe luminescence upon mixing.

Although some of the early inquiries assumed[9] that every redox event in solution leads to an electronically excited state, this view is

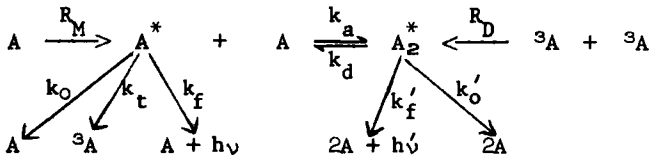
clearly untenable in case of many very weakly luminescing systems, where much faster than diffusion controlled quenching would be required to account for the low ECL efficiency. On the other hand, formation of a bimolecular "encounter complex" in Eq. 6 can explain such low efficiencies via Eq. 3:

$$\begin{array}{ccccccc} [R^{+}...R^{-}] & \rightleftharpoons & [R...R]^{*} & \rightleftharpoons & R + R^{*} \\ & & \downarrow\uparrow & & \downarrow Q \\ & & [R...R]^{\dagger} & \rightarrow & R + R \end{array} \qquad (12)$$

It should be pointed out that although Marcus' theory[10] would not favor quick dissipation of all the excitation energy of $[R...R]^{*}$ to the solvent cage, these considerations do not apply if loss of librational quanta leads to a high vibrational state of the ground state dimer $[R...R]^{\dagger}$. The encounter complex $[R...R]^{*}$ may be thought of as a short lived precursor of the excimer $(R)_2^{*}$, and its contribution to the total luminescence intensity should be small, if any. Hence in the simplest ECL system, one in which direct production of excited singlets occurs (S-route) as in Eq. 8, only $^1R_1$ and $^1(R)_2^{*}$ fluorescence is expected. A mixed ECL system is one in which the cation and anion (ct. Eq. 4 and 5) are derived from different parent compounds. In a mixed S-route system, involving R_1^{+} and R_2^{-}, both excimer and exciplex emission can contribute. A mixed S,T-route system has also been reported in the literature, in which case $E_{s(R_1)} > |\Delta H^{o}| > E_{s(R_2)}$,[11] and the ECL emission consisted of three distinct peaks ($^1R_1^{*}$, $^1R_2^{*}$, and $(R_2)_2^{*}$ or $(R_1R_2)^{*}$).

Before proceeding to examine the various dimeric luminophors in T-route ECL systems, we should make mention of the kinetic treatment of T-route ECL systems as it appears in the literature.[12] This appears to be especially desirable in view of the fact that the literature treatment contains a serious error, as will be shown in the following. Parker[13] and Birks[14] considered the kinetic aspects of delayed fluorescence arising

from triplet-triplet annihilation, using the scheme



(13)

where k_o and k_o' are the respective rate constants for radiationless conversion, k_t is the rate constant for triplet formation, and k_f and k_f' are the rate constants for the radiative transitions of the monomer and the excimer. The steady-state distribution between the excited species is determined by $k_a[A]$ and k_d, while the rate of formation of A^* and A_2^* are given by R_M and R_D. In the steady-state treatment τ_M and τ_D, the lifetimes of the monomer and excimer respectively, are related to the rate constants as

$$1/\tau_M = k_f + k_o + k_t \tag{14}$$

and

$$1/\tau_D = k_f' + k_o' + k_D \tag{15}$$

Consequently, the steady-state equation for the general mechanism involving monomers becomes:

$$R_M + k_d[A_2^*] = ([1/\tau_M] + k_a[A])[A^*] \tag{16}$$

and for dimers:

$$R_D + k_a[A][A^*] = [A_2^*]/\tau_D \tag{17}$$

By defining the special symbol $\alpha \equiv R_D/R_M$ we may express ϕ_D/ϕ_M, the excimer/monomer emission ratio, as

$$\frac{\phi_D}{\phi_M} \equiv \frac{k_f'[A_2^*]}{k_f[A^*]} = \frac{k_f'}{k_f}\frac{\tau_D}{1 + \alpha\tau_D k_D}\left(\frac{\alpha}{\tau_M} + (1 + \alpha)\, k_a[A]\right) \tag{18}$$

It can be readily seen that for prompt fluorescence the relative excimer emission is directly proportional to the bulk concentration of the hydrocarbon, i.e. Eq. 18 reduces to

$$\frac{\phi_D}{\phi_M} = m_1[A] \qquad (19)$$

a straight line of slope m_1 passing thru the origin. When $R_D \neq 0$, the line will have an intercept $(k_f'/k_f)(\tau_D/\tau_M)[\alpha/(1 + \alpha\tau_D k_d)]$, whereas the slope m_1' will be $[(1 + \alpha)/(1 + \alpha\tau_D k_d)](k_f'/k_f)\tau_D k_a$. By incorporating the quenching reactions

$$A^* + Q \xrightarrow{k_1} A + Q \qquad (20)$$

$$A_2^* + Q \xrightarrow{k_2} 2A + Q \qquad (21)$$

the T-route ECL treatment[12] made a specific allowance for a quencher Q, and incorporated it in the excited state lifetimes as

$$1/\tau_M' = k_f + k_o + k_t + k_1[Q] \qquad (22)$$

and

$$1/\tau_D' = k_f' + k_o' + k_d + k_2[Q] \qquad (23)$$

In terms of Eq. 18 the relative excimer emission became[12]

$$\frac{\phi_D}{\phi_M} = \frac{k_f'}{k_f}\frac{\tau_D'}{1 + \alpha\tau_D' k_d}\left(\frac{\alpha}{\tau_M'} + (1 + \alpha)k_a[A]\right) \qquad (24)$$

Regrettably in a T-route ECL system $R_M = 0$, hence $\alpha \equiv \frac{R_D}{R_M}$ is undefined (or "∞"), and Eq. 24 given by Maloy[12] is mathematically invalid. We must emphasize that the treatment given by Parker[13] and Birks[14] is correct, except that it can not be carried over to T-route ECL. Due to the absence of R_M the entire treatment is actually simplified, starting with Eq. 16 which should be $k_d[A_2^*] = ([1/\tau_M] + k_a[A])[A^*]$.

In proceeding to delineating the various dimeric luminophors in T-route ECL systems, we should recall that an ECL encounter complex, being a precursor to the excimer, was regarded to make a small contribution at best to the total luminescence intensity. Similarly, a TTA encounter complex should be regarded as a precursor to the excimer, though by extending the treatment of Goldschmidt and co-workers,[15] the two

types of encounter complex for the same parent compound (ECL vs. TTA) need not coincide in general. Consequently, in the following a distinction is made between the ECL-type $[R\cdots R]^*$ and TTA-type $(R\cdots R)^*$.

The T-route system described by Figure 1 is a simple one component system. The use of symbols is both conventional and self-explanatory, for example, Φ_δ refers to dimer emission efficiency, whereas Φ_F is the fluorescence efficiency. Besides monomer fluorescence arising from TTA, the expected spectrum contains three peaks of dimeric origin, $h\nu_{R_2}^*$ being dominant.

A rather complex emission pattern holds for a mixed ECL system that is energy deficient with respect to both luminescor parent compounds (R_1 and R_2); this is indicated in Figure 2. In addition to the two excited singlet bands due to R_1^* and R_2^*, we have included possible bands corresponding to monomer phosphorescence, although in this case only a few compounds could be in the category. On the other hand, the ECL encounter complex $[R_1\cdots R_2]^*$, the TTA types $(^3R_1\cdots{}^3R_1)^*$, $(^3R_2\cdots{}^3R_2)^*$, and $(^3R_1\ldots{}^3R_2)^*$, and the triplet excimers or exciplex $^3(R_1)_2^*$, $^3(R_2)_2^*$, and $^3(R_1R_2)$, can be expected to emit photons due to their probable mixed singlet-triplet character. Such mixed singlet-triplet character has been discussed by Matsen[16] for example, who demonstrated that in a higher than zero-order treatment, the symmetry state designations, Γ_A and Γ_B, pertaining to isolated noninteracting molecules, are only approximately valid, and local-point group symmetry allows mixed singlet and triplet character for chemical species such as $[R\ldots R]^*$.

By comparison to S-route systems, T-route ECL systems, where formation of dimeric luminophors is heavily favored, present many complexities for kinetic analysis. Due to the different reaction path involved, the logically pleasing recourse to comparison with spectra obtained from optical excitation may not always be justified. Yet, as recent results indi-

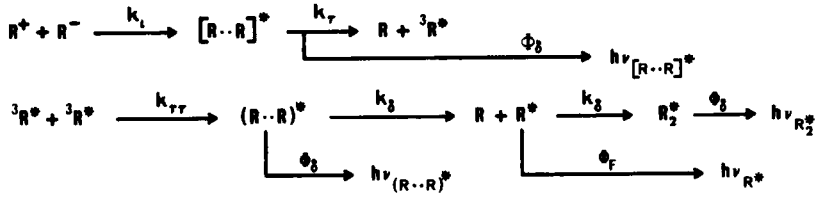


Fig. 1. A simple energy deficient (T-route) ECL system. Initial cation-anion (R^+/R^-) annihilation produces the ECL encounter complex $[R\cdot\cdot R]^*$ which may emit a photon with efficiency Φ_δ or dissociate to give the triplet $^3R^*$; cf. Text for triplet-triplet annihilation (TTA) and related emission (quenching steps and singlet superscripts are not shown in Figures).

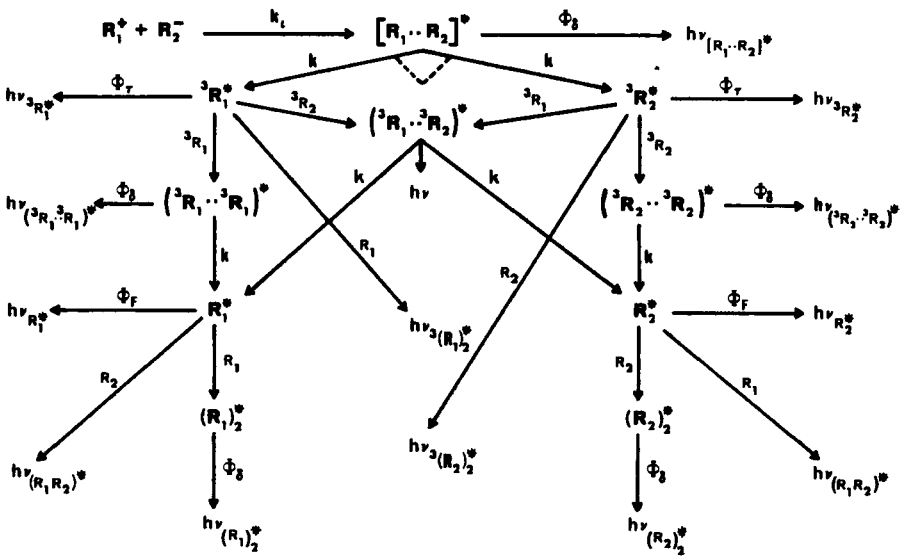


Fig. 2. A mixed energy deficient (T-route) ECL system where the initial cation-anion annihilation results in the encounter complex $[R_1\cdot\cdot R_2]^*$ capable of dissociating to give either $^3R_1^*$ or $^3R_2^*$; cf. Text and Figure 1 also.

cating the hyper-polarizability of dye molecules in lasers[17] suggest, chemistry in lasers also involves molecular states that can differ significantly from the ordinary fluorescence situation. Consequently, the states arising from ECL have unusual significance in considering dye lasers. On the one hand, some of these dimeric luminophors may be suitable to support laser action; on the other hand, their presence must be taken into account in estimating cavity losses, and what has usually been blamed on "triplet build-up" often could have had a more complex molecular history, as Figure 2 suggests. In addition to the time-evolution problem discussed earlier in this series,[18] dimeric luminophors are also potential contributors to the apparent anti-Stokes drop in the quantum yield of luminescence of dyes,[19] found to adversely affect their laser efficiency.

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