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On the Applicability of the Relative Excimer Yield Equation to Electrogenerated Chemiluminescence

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ON THE APPLICABILITY OF THE RELATIVE EXCIMER YIELD
EQUATION TO ELECTROGENERATED CHEMILUMINESCENCE

Key words: Luminescence, Fluorescence, Singlet, Triplet, Algebra

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In a recent communication, Keszthelyi¹ claims that our application² of the well-known equation used to describe the relative yield of excimer and monomer emission in spectroscopic studies^{3,4}

$$\frac{\phi_D}{\phi_M} = \frac{k'_f}{k_f} \frac{\tau'_D}{1 + \alpha \tau'_D k_d} \left(\frac{\alpha}{\tau'_M} + (1 + \alpha) k_a [A] \right) \quad (1)$$

to electrogenerated chemiluminescence (ECL) studies in the presence of a quenching agent (Q) is "mathematically invalid" because the treatment does not apply when $\alpha = R_D/R_M$ (where R_D is the rate of excimer formation and R_M is the rate of formation of the excited singlet state monomer) approaches infinity. As we have pointed out,² however, this treatment is perfectly general for all steady state luminescent processes, independent of the mode of excitation, and holds for any value of α . Direct substitution in Equation 1 reveals that

$$\lim_{\alpha \rightarrow 0} \frac{\phi_D}{\phi_M} = \frac{k'_f \tau' D k_a}{k_f} [A] = m_1 [A] \quad (2)$$

Simple rearrangement of Equation 1 yields

$$\frac{\phi_D}{\phi_M} = \frac{k'_f}{k_f} \frac{\tau' D}{\frac{1}{\alpha^{-1} + \tau' D k_d} \left(\frac{1}{\tau' M} + (a^{-1} + 1) k_a [A] \right)} \quad (3)$$

so that

$$\lim_{\alpha \rightarrow \infty} \frac{\phi_D}{\phi_M} = \frac{k'_f}{k_f k_d} \left(\frac{1}{\tau' M} + k_a [A] \right) \quad (4)$$

Thus, for the case of "pure" T-route ECL, a plot of ϕ_D/ϕ_M vs. $[A]$ has a slope of $k'_f k_a / k_f k_d$ (which is independent of $[Q]$) and an intercept of $k'_f / k_f k_d \tau' M$ (which may have a minimum value of $k'_f / k_f k_d \tau' M$ when $[Q]$ is zero). The slope may also be written as

$$\frac{k'_f k_a}{k_f k_d} = \frac{m_1}{k_d \tau_D} \quad (5)$$

where m_1 is the slope obtained in the prompt fluorescence experiment ($\alpha \rightarrow 0$).

Since

$$k_d \tau' D = \frac{k_d}{k'_f + k'_o + k_d + k_2 [Q]} \quad (7)$$

it is obvious that the slope of the ϕ_D/ϕ_M vs. $[A]$ plot in "pure" T-route ECL may never be less than that obtained in prompt fluorescence studies.

We have no comments on the remainder of the communication at issue; most of these concepts have been discussed previously elsewhere (see reference 1, and references contained therein). We maintain, however, that our treatment of excimer emission in the presence of a quenching agent in the ECL experiment is valid.

RELATIVE EXCIMER YIELD EQUATION

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