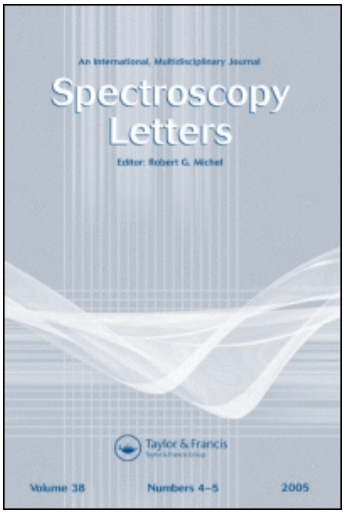

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On the Applicability of the Relative Excimer Yield Equation to Electrogenerated Chemiluminescence

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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, Keszthelyi[1] claims that our application[2] of the well-known equation used to describe the relative yield of excimer and monomer emission in spectroscopic studies[3,4]

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

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

$$\lim_{\alpha \to 0} \frac{\Phi_D}{\Phi_M} = \frac{k'_f \tau'_D k_a}{k_f} [A] = m_1[A] \qquad (2)$$

Simple rearrangement of Equation 1 yields

$$\frac{\Phi_D}{\Phi_M} = \frac{k'_f}{k_f} \frac{\tau'_D}{\alpha^{-1} + \tau'_D k_d} \left(\frac{1}{\tau'_M} + (\alpha^{-1} + 1) k_a [A] \right) \qquad (3)$$

so that

$$\lim_{\alpha \to \infty} \frac{\Phi_D}{\Phi_M} = \frac{k'_f}{k_f k_d} \left(\frac{1}{\tau'_M} + k_a [A] \right) \qquad (4)$$

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

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

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

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

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.

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