BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(3), 1083—1084 (1975)

The Spin-Statistical Contribution in Redox Chemiluminescence Quantum Efficiency

Csaba P. Keszthelyi

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, U.S.A.

(Received June 18, 1974)

Synopsis. The theoretical upper limit of the quantum efficiency of Redox Chemiluminescence is shown to be 1.0 for both energy sufficient and energy deficient systems; whether the oxidant and reductant are generated *in situ* (as in ECL) has no effect on the chemiluminescence efficiency.

Electron transfer or redox chemiluminescence involves the conversion of chemical energy to light. The early experimental inquiries[1)] were augmented by the theoretical considerations put forth by Marcus[2)] and Hoytink.[3)] The most common light producing sequence involves radical ions ($A^{\bar{\cdot}}$ and $D^{\overset{+}{\cdot}}$) undergoing a homogeneous electron transfer reaction in fluid solution:

$$A^{\bar{\cdot}} + D^{\overset{+}{\cdot}} \rightarrow A + D + h\nu. \qquad (1)$$

The nature of the emitted light ($h\nu$) has allowed identification of the luminescors in many systems as $^1A^*$, $^1D^*$, $(AD)^*$ or $(A)_2^*$.[4,5)] It is convenient to classify redox chemiluminescence systems as energy sufficient or energy deficient, depending on whether the enthalpy of Eq. 1 is greater or smaller than the first excited singlet energy (E_s) of the luminescor parent compound. Ways for obtaining singlet emission from an energy deficient system will be discussed further on in this paper.

An important property of all useful redox chemiluminescent systems is the quantum efficiency, Φ_{CL}, defined as the number of photons emitted per radical ion annihilation. It has recently been demonstrated that Φ_F, the fluorescence quantum efficiency determined from optical excitation, does not represent an upper limit for Φ_{CL}, because the chemiluminescence excitation reaction path may be more efficient than the optical excitation route.[6)]

Recent papers dealing with redox chemiluminescors have examined their practical applicability as display devices[7–9)] or a new type of laser.[10,11)] While exploring practical applicability, some of the new papers have introduced a number of contradictory claims which involve erroneous interpretation of the theoretical work of Hoytink and Marcus. For example, the paper by Schwartz, Blakeley, and Robinson[8)] claims that the maximum theoretical efficiency of an energy sufficient ECL system is 0.828, while that of an energy deficient (T-route) system is 0.414. This is contradicted by Pighin[9)] who reported that the maximum theoretical efficiency of an energy deficient system is 6.6% (based on photons/electron). Rather than retracing the lines of thought that lead to the erroneous numbers 0.828 0.414, and 0.066, which are amply documented in the original papers themselves, we should briefly establish the correct conclusions based on the work of Marcus and Hoytink primarily.

The radical ions themselves are doublets, hence the pure spin-statistical prediction for Eq. 1 is

$$A^{\bar{\cdot}} + D^{\overset{+}{\cdot}} \rightarrow \frac{1}{4}S + \frac{3}{4}T, \qquad (2)$$

where S stands for singlet and T stands for triplet. Although it is possible to trace the quantum efficiency from Eq. 2, it would, in effect, be totally unwarranted. In the theory of Marcus the spin-statistical contribution is subject to the rate constant k for the electron transfer

$$k = \mathscr{H}_{\rho} Z \exp\{-\Delta G^{\neq}/k_b T\}, \qquad (3)$$

and the potential energy curves (*G vs.* Reaction Coordinate) incorporate the 'orientation polarization' factor. The activation barrier in the electron transfer step is strongly affected by the 'orientation polarization', which in turn may involve a transition state with a virtual charge distribution corresponding to $(A^{2-}\cdots D^{2+})$ for example.[2)] Not only does Marcus' theory mitigate against blind reliance on the simplicistic spin-statistical approach when dealing with fluid solution media, but it would specifically make quick dissipation of ~3 eV unlikely by non-radiative means - such as required by Eq. 2 in case of an energy deficient system for 25% of the redox events; *i.e.*, producing $^1S_0$ rather than $^1S^*$ in the present notation.

Hoytink expresses the rate constants as

$$K_{\mathrm{singlet}^*} = \frac{1}{4}K_d \exp\{-\Delta H_s^*/kT\} \qquad (3a)$$

and

$$K_{\mathrm{triplet}} = \frac{3}{4}K_d \exp\{-\Delta H_t^*/kT\} \qquad (3b)$$

Hence only for the special case when the exponential terms are equal would Hoytink's work support Eq. 2. Once we emphasize the importance of specific terms that vary from system to system, we can proceed to set maximum quantum efficiency limits.

Considering Eq. 1 in some detail, we find that the over-all light production scheme involves competing reaction paths:

$$\left.\begin{aligned} A^{\bar{\cdot}} + D^{\overset{+}{\cdot}} &\xrightarrow{k_S} {}^1S^* + {}^1S_0 \\ &\xrightarrow{k_t} {}^3T^* + {}^1S_0 \\ &\xrightarrow{k_Q} {}^1S_0 + {}^1S_0 \end{aligned}\right\} \qquad (4)$$

For an energy sufficient system utilizing an efficient fluorescor parent compound, the upper limit of Φ_{CL} or Φ_{ECL} is 1.0 when $k_s \gg k_t + k_Q$. For an energy deficient system when $k_t \gg k_s + k_Q$, the number of redox events also represents the upper limit of triplets produced. In this case, corresponding to E-Type delayed fluorescence,[12)] thermal activation of $^3T^*$ gives

$$^3T^* \xrightarrow[\text{activation}]{\text{thermal}} {}^1S^* \tag{5}$$

Consequently the maximum quantum efficiency of an energy deficient system is also 1.0.

We must emphasize the tenacious nature of Eq. 5 at this point; the type of thermal activation occurring in the case of eosin is not characteristic of many other systems. Also, and this is perhaps even more important, the presence of ionic species in the chemiluminescence solution (and the additional presence of a large excess of supporting electrolyte ions in an ECL system) can be expected to quench some of the triplets, hence cut the efficiency of possible thermal activation. Therefore, we should consider an alternative 'energy-doubling' process, triplet-triple annihilation or TTA:12)

$$^3T^* + {}^3T^* \rightarrow {}^1S^* + {}^1S_0. \tag{6}$$

This would lead to the production of one excited singlet per two redox events, giving Φ_{CL} or $\Phi_{ECL}=0.5$ as the maximum value. Reliance on spin-statistics only (ignoring quintets) gives $1/4\ {}^1S^*+3/4\ {}^3T^*$ per TTA, a prediction which is once again unwarranted.

In closing, we should re-emphasize that various types of losses do occur in actual chemiluminescence and ECL systems. One loss that does not occur at practical concentrations of luminescor parents is electrochemical destruction of cations at the anion-generating pulse and *vice-versa* (except at the very first instant when the pulse is switched). The losses in the 'triple step' experiments of Faulkner13) do not carry over to the typical double potential step mode of electrogeneration.

Combining the recent calculations of Measures11) with the 20% efficient ECL system available,10,14) one finds that laser action is not improbable in these systems; further investigations and improvements should be conducted, nevertheless, by observing the proper relationship between spin-statistics and chemiluminescence quantum efficiency.

Support of this work by the Louisiana State University Council on Research is gratefully acknowledged.

References

1) (a) D. M. Hercules, *Science*, **145**, 808 (1964); (b) R.E. Visco and E. A. Chandross, *J. Amer. Chem. Soc.*, **86**, 5350 (1964); (c) K. S. V. Santhanam and A. J. Bard, *ibid.*, **87**, 139 (1965). (d) A. Weller and K. Zachariasse, *J. Chem. Phys.*, **46**, 4984 (1967).

2) R. A. Marcus, (a) *Ann. Rev. Phys. Chem.*, **15**, 155 (1964); (b) *J. Chem. Phys.*, **43**, 679, 2654 (1965).

3) G. J. Hoytink, *Discus. Faraday Soc.*, **45**, 14 (1968).

4) (a) T. Matsumoto, M. Sato, S. Hirayama, and S. Uemura, This Bulletin, **44**, 1450 (1971); (b) T. Matsumoto, M. Sato, and S. Hirayama, *ibid.*, **46**, 369 (1973).

5) C. P. Keszthelyi, H. Tachikawa, and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 1522 (1972); C. P. Keszthelyi and A. J. Bard, *Chem. Phys. Lett.*, **24**, 300 (1974); *J. Org. Chem.*, **39**, 2936 (1974).

6) C. P. Keszthelyi, *J. Amer. Chem. Soc.*, **96**, 1243 (1974).

7) C. P. Keszthelyi and A. J. Bard, *Extended Abstracts*, **72—1**, p. 275; *J. Electrochem. Soc.*, **120**, 241 (1973).

8) P. M. Schwartz, R. A. Blakeley, and B. B. Robinson, *J. Phys. Chem.*, **76**, 1868 (1972).

9) A. Pighin, *Can. J. Chem.*, **51**, 3467 (1973).

10) (a) C. P. Keszthelyi, *J. Electrochem. Soc.*, **120**, 39C (1973); (b) *Appl. Optics*, **14** (1975—in press).

11) R. M. Measures, *Appl. Optics*, **13**, 1121 (1974).

12) C. A. Parker, "Photoluminescence of Solutions," Elsevier Publ. Co., (1968), Chapter 2.

13) R. Bezman and L. R. Faulkner, *J. Amer. Chem. Soc.*, **94**, 3699, 6317, 7324, 7331 (1972).

14) C. P. Keszthelyi, N. E. Tokel, and A. J. Bard, *Anal. Chem.*, **47**, 249 (1975).