

# THEORY OF CHEMIEXCITATION: PHOTONIC vs. CHARGE TRANSFER EXCITATION

By

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The creation of electronically excited moieties in fluid solution in certain redox processes, commonly termed ECL, has been systematically investigated for over a decade. The heterogeneous and the homogeneous charge transfer steps are generally separable; the former can be classically treated according to electrochemistry, and the latter as molecular fluorescence. Attention is focussed presently on a series of ECL quantum efficiency determinations which indicate that the time scale difference between the photon absorption and diffusional homogeneous charge transfer can lead to very large variations in quenching losses stemming from intersystem crossing.

The creation of electronically excited moieties by certain redox processes in fluid solution was reviewed at the Athens International Conference on Chemiluminescence and Bioluminescence by HOJTINK [1] who was generally credited as the first to propose the path



Experimental evidence of characteristic solute fluorescence under conditions of Eq. (1) was presented by HERCULES [2] and a number of other investigators subsequently. A general survey of the principal reactions of electrogenerated chemiluminescence (ECL) is presented in Table I. It should be remarked at the outset that, although the heterogeneous charge transfer steps comprise a relatively small part of Table I, many of the complexities, peculiarities, and outright difficulties of the ECL process are inherently related to the electrochemical reactions. Accordingly, *in situ* generation of the ECL parent ions by cyclic square waves at inert metal electrodes has paralleled advances in non-aqueous solvents and instrumentation [3]. The workable range in any given solvent-supporting electrolyte system, the "electrochemical window" as indicated in Table II, is of fundamental concern, and requires rigorous exclusion of oxygen and moisture.

The diffusion controlled character of the electrogeneration of  $R^-$  and  $R^+$  has been recognized early, and this recognition has led to rigorous mathematical models of the ECL process [4-11]. Apart from minor observations of „pre-annihilation”

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Table I

## Principal Reactions of Electrogenerated Chemiluminescence

Reaction	Comment
$R + e_{(e1)} \rightarrow R^-$	electroreduction at cathode to monoanion
$R + 2e_{(e1)} \rightarrow R^{=}$	electroreduction at cathode to dianion
$R - e_{(e1)} \rightarrow R^+$	electrooxidation at anode to monocation
$R - 2e_{(e1)} \rightarrow R^{++}$	electrooxidation at anode to dication
$R^- - e_{(e1)} \rightarrow R$	electrooxidation of anion to parent at anode
$R^{=} - 2e_{(e1)} \rightarrow R$	electrooxidation of dianion to parent at anode
$R^+ + e_{(e1)} \rightarrow R$	electroreduction of monoanion to parent at cathode
$R^{++} + 2e_{(e1)} \rightarrow R$	electroreduction of dication to parent at cathode
$A + e_{(e1)} \rightarrow A^-$	electroreduction at cathode to monoanion in a MIXED ECL SYSTEM
$D - e_{(e1)} \rightarrow D^+$	electrooxidation at anode to monoanion
$R^- + R^+ \rightarrow 2R + hv$	over-all scheme of ECL light generating step
$A^- + D^+ \rightarrow A + D + hv$	over-all scheme of ECL light generating step in a MIXED ECL SYSTEM
$A^- + D^+ \rightarrow {}^1A^* + D$	formation of excited singlet of $A$ in homogeneous charge transfer step
$A^- + D^+ \rightarrow A + {}^1D^*$	formation of excited singlet of $D$ in homogeneous charge transfer step
$A^- + D^+ \rightarrow A + {}^3D^*$	formation of triplet of $A$ in homogeneous charge transfer step
${}^3A^* + D \rightarrow A + {}^3D^*$	formation of triplet of $D$ via sensitization
$A + {}^3D^* \rightarrow {}^3A^* + D$	formation of triplet of $A$ via sensitization (direction ECL system dependent)
${}^3A^* + {}^3A^* \rightarrow {}^1A^* + A$	triplet-triplet fusion (TTF)
${}^3D^* + {}^3D^* \rightarrow {}^1D^* + D$	TTF
${}^1A^* + A \rightarrow {}^1(A)_2^*$	excimer formation in Singlet-route step
${}^3A^* + {}^3A^* \rightarrow {}^1(A)_2^*$	excimer formation in TTF step
${}^3D^* + {}^3D^* \rightarrow {}^1(D)_2^*$	excimer formation in TTF step
$A^- + D^+ \rightarrow [A^- \dots D^+]$	solvent separated ion pair formation in MIXED ECL SYSTEM
$A^- + D^+ \rightarrow {}^1(AD)^*$	exciplex formation in redox step
${}^1A^* + D \rightarrow {}^1(AD)^*$	exciplex formation from ${}^1A^*$
$A + {}^1D^* \rightarrow {}^1(AD)^*$	exciplex formation from ${}^1D^*$
${}^1A^* + Q \rightarrow A + Q + q$	thermal quenching of ${}^1A^*$
${}^1D^* + Q \rightarrow D + Q + q$	thermal quenching of ${}^1D^*$
${}^3A^* + Q \rightarrow A + Q + q$	thermal quenching of ${}^3A^*$
${}^3D^* + Q \rightarrow D + Q + q$	thermal quenching of ${}^3D^*$
${}^1(AD)^* + Q \rightarrow A + D + Q + q$	thermal quenching of ${}^1(AD)^*$
${}^1(D)_2^* + Q \rightarrow 2D + Q + q$	thermal quenching of ${}^1(D)_2^*$
${}^1(A)_2^* \sim {}^3A^*$	intersystem crossing of ${}^1A^*$
${}^1D^* \sim {}^3D^*$	intersystem crossing of ${}^1D^*$
$R^- + Q \rightarrow X$	decomposition of anion
$R^+ + Q \rightarrow X$	decomposition of cation
$X \xrightarrow{e} X^*$	excitation of decomposition product by ECL intermediers
$R^- + R^+ \rightarrow R + R + q$	general representation of 'dark path' in ECL
${}^1A^* \rightarrow A + hv$	fluorescence of $A$
${}^1D^* \rightarrow D + hv$	fluorescence of $D$
${}^1(AD)^* \rightarrow A + D + hv$	exciplex fluorescence
${}^1(A)_2^* \rightarrow 2A + hv$	excimer fluorescence
${}^1(D)_2^* \rightarrow 2D + hv$	excimer fluorescence
$X^* \rightarrow X + hv$	decomposition product fluorescence
${}^3A^* \rightarrow A + hv$	phosphorescence in ECL (rare)
${}^3D^* \rightarrow D + hv$	phosphorescence in ECL (rare)

Table II

Electrochemical Window of Some of the Solvents Used in ECL Research

Solvent (MP)	Electrolyte <sup>a</sup>	Oxidation-Reduction Limit <sup>b</sup> (V. vs. Ag Reference Electrode)
DMF	TBAP	+1.5/-2.7
ACN	TBAP	+2.2/-2.8
THF	TBAP	+1.5/-3.0
PPO (70-72)	TBAP	+1.5/-2.2
PHEN (100-101)	TBAP	+1.4/-2.2
PPD (140-141)	TBAP	+1.8/-2.0
TH (154-156)	TBAP	+1.2/-2.4
TBAP (217-218)	—	+2.8/-3.0

*Abbreviations:* DMF: N,N-dimethylformamide, ACN: acetonitrile; THF: tetrahydrofuran; PPO: 2,5-diphenyloxazole; PHEN: phenanthrene; PPD: 2,5-diphenyl-1,3,4-oxadiazole; TH: thianthrene; TBAP: tetra-*n*-butylammonium perchlorate.

- a) The supporting electrolyte concentration was 0.10 M in all cases.  
 b) The potential where current due to background decomposition (in the absence of added solute, using a current setting that would have been typical if 3 mM solute were present) was at least 1/10th the  $i_p$  current usually observed in a 3 mM DPA solution at the same 100 mV/sec CV scan rate.

type ECL [12-14], the thermodynamics of the homogeneous charge transfer process Eq. (1) is determined by the heterogeneous charge transfer steps. Quantitatively,

$$-\Delta H_r^0 = E_{R/R^+}^0 - E_{R/R^-}^0 - 0.10 \text{ eV} \quad (2)$$

at room temperature, where the first term is the reaction enthalpy, the second and third terms give the standard redox potentials of the ECL parent (solute), and the last term is the commonly used estimate of entropy losses. When  $|\Delta H_r^0| \cong E_s$ , where  $E_s$  is the first excited singlet energy of the ECL emitter, the system described in Eq. (1) is called "energy sufficient", otherwise as "energy deficient". A novel possibility arises in "mixed" ECL systems, where the cation and anion are derived from different compounds (cf. Table I): now the redox reaction may be energy sufficient with respect to one emitter, yet remain energy deficient with respect to the other [15].

The energy doubling process leading to fluorescence in the energy deficient case is termed "triplet-triplet annihilation", or, preferably, "triplet-triplet fusion" [16] to emphasize the energy building aspect of



The intermediacy of triplets has been also proposed for those puzzling ECL systems which work under a step function excitation, *i.e.* only a DC reduction potential needs to be applied [17-19]. Luminescence properties of several ambient and elevated temperature ECL systems are presented in Tables III and IV, respectively. Such results are typical for general investigation of new ECL systems. One of the recognized aims of preliminary investigations is to find efficient ECL systems, *i.e.* where excited state production according to Eq. (1) is a significant reaction channel in comparison

*Table III*  
*Luminescence Properties of Several ECL Systems at Room Temperature*

ECL System <sup>#</sup>	Emitters <sup>c</sup>	Relative* Intensity	Comments <sup>&amp;</sup>
PPD/TH	$1_{A^+}, 1_{D^+}, (AD)^*$	1.00	2-electrode, 3-electrode mode of electrogeneration
PPO/TH	$1_{A^+}, 1_{D^+}, 1(A)_{\frac{1}{2}}^*$ (?)	0.1	2-el, 3-el, unstable $A^+$ ; in all these mixed systems the 4300 Å emission, attributed to ${}^1TH^*$ , was the most intense emission peak
PPO	$1_{A^+}, 1(A)_{\frac{1}{2}}^*$ (?)	0.01	2-el, 3-el; $A^+$ is unstable; filming upon oxidation
PPO	$1_{A^+}, 1(A)_{\frac{1}{2}}^*$ (?)	0.005	DMF solvent, 2-el, 3-el; very unstable $A^+$ ; spectral shifts, complications
PPO/WB	$1_{A^+}, 1(A)_{\frac{1}{2}}^*$ (?), $X^*$ (?), $D^*$ (?), $(AD)^*$ (?)	0.05	2-el, 3-el; broad emission structureless; stable ions
PPO/WB	$1_{A^+}, 1(A)_{\frac{1}{2}}^*$ (?), $(AD)^*$ , ${}^1D^*$ (?)	0.05	DMF solvent, 2-el, 3-el, stable ions
$\alpha$ -NPO	$1_{A^+}, X^*$ (?)	0.1	stable $A^+$ , filming upon generating $A^+$ ; light intensity drops quickly
POPOP	$1_{A^+}, X^*$ (?)	0.01	stable $A^+$ , filming upon generating $A^+$ ; ECL intensity falls rapidly
POPOP	$1_{A^+}$ (?), $X^*$	0.01	DMF solvent; stable $A^+$
BBOT	$1_{A^+}, X^*$ (?)	0.05	solubility problem; $A^+$ film very strongly
BBOT/TH	$1_{A^+}, 1_{D^+}, X^*$ (?)	0.1	2-el, 3-el; BBOT interferes with $D^+$
BBOT/WB	$1_{A^+}, X^*$ (?)	0.1	2-el, 3-el; there is significant broadening of the spectrum, exact cause cannot be specified from data
PTP	$1_{A^+}, X^*$ (?)	0.005	the cathodic limit of ACN is insufficient for reducing this compound, the emission is under undesirable electro-chemical conditions

Table III—CONT.

ECL System <sup>#</sup>	Emitters <sup>c</sup>	Relative* Intensity	Comments <sup>&amp;</sup>
FTD	$1A^*, X^* (?)$	0.01	2-el, 3-el; anodic reaction leads to filming
FTD	$1A^*, X^* (?)$	0.005	DMF solvent; anodic range available in DMF is too short, the process is in the 'background'
ATD	$1A^*, X^* (?)$	0.01	2-el, 3-el; $A^+$ highly unstable
APD	$1A^*, X^* (?)$	0.05	2-el, 3-el; $A^+$ is relatively stable (compared to PPD)
BTD	$1A^*, X^* (?)$	0.005	2-el, 3-el; severe filming of the electrode, the ECL intensity is falling
FTD/TH	$1A^*, 1D^*, (AD)^* (?), X^* (?)$	0.5	2-el, 3-el; stable emission
ATD/TH	$1A^*, 1D^*, X^* (?)$	0.5	2-el, 3-el; $1A^*$ emission is very small
APD/TH	$1A^*, 1D^*, X^* (?)$	1.1	2-el, 3-el; very stable ECL emission
BTD/TH	$1A^*, 1D^*, X^* (?)$	1.0	2-el, 3-el; very stable ECL emission
APD/WB	$1A^*, X^*$	0.01	2-el, 3-el; as in most similar systems, the ECL ascribable to $1A^*$ is of a very low intensity by comparison to the rest of the structureless band

<sup>#</sup> The concentration of *A* and *D* was 1 mM unless solubility problems existed; the supporting electrolyte was 0.1 M TBAP or TBABF<sub>4</sub>. The frequency of electrogeneration was always swept between 1 Hz and 1 kHz, the maximum ECL emission usually occurring between 50 and 200 Hz. Unless specified as 2-electrode ("2-el"), 3-electrode ("3-el"), only the controlled potential mode of electrogeneration was used.

<sup>c</sup> Assignments of longer wavelength emitters are tentative, some of the emitters labeled  $X^* (?)$  may well be dimeric in nature such as  $(A...D)^*$  for example.

\* These are based on 1 mM PPD/1 mM TH in ACN-TBAP as standard; the values reported correspond to the maximum obtainable intensity in a given system by varying *f* or *E<sub>p</sub>* (or  $\Delta E$  in "two-electrode" mode of electrogeneration) in a routine manner.

<sup>&</sup> For structures of additional scintillator materials cf. I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, N. Y., 1965.

*Table IV*  
*Luminescence Properties of Several ECL Systems at Elevated Temperatures*

No.	Solvent <sup>a</sup>	Electrolyte	Solute(s)	Temperature <sup>b</sup> T °C	Exp. Conditions	Results and Remarks
1	TBAP	—	—	220	CV; potential steps; voltage pulses	no luminescence detected
2	TBAP	—	RUB	220	CV; potential steps; voltage pulses	no luminescence; unstable RUB cation and anion
3	TBAP	—	DPA	220	CV; potential steps; voltage pulses	no luminescence; unstable DPA cation and anion
4	TBACl	—	DPA	80	CV; potential steps	no luminescence; stable DPA <sup>-</sup> , TBACl unsuitable for DPA <sup>+</sup>
5	PPO	TBAP	—	80	potential steps; voltage pulses	no luminescence
6	PPO	TBAP	RUB	80	CV	stable R <sup>+</sup> and R <sup>-</sup> ;
7	PPO	TBAP	RUB	80	potential steps	RUB ECL detected
8	PPO	TBAP	RUB	80	voltage pulses	RUB ECL, brighter than above
9	PPO	TBAP	RUB	80	voltage pulses sine wave at 60 cps	RUB ECL for 30 days continuous, intensity fell
10	PPO	TBAPF	RUB	80	voltage pulses	RUB ECL
11	PPO	TMABF	RUB	80	voltage pulses	RUB ECL
12	PPO	TEAP	RUB	80	voltage pulses	RUB ECL
13	PPO	TMAP	RUB	80	voltage pulses	RUB ECL
14	PPC	TBAP	TH and PPD	80	potential steps	no luminescence
15	PPO	TBAP	DPA	80	CV; potential steps, voltage pulses	stable R <sup>+</sup> and R <sup>-</sup> ; DPA ECL
16	PPO/PPD	TBAP	RUB	115	voltage pulses	RUB ECL
17	PPO/PTP	TBAP	RUB	95	voltage pulses	RUB ECL
18	TH	TBAP	—	150	CV; potential steps	no luminescence
19	TH	TBAP	PPD	150	potential steps	no luminescence
20	PHEN	TBAP	RUB	100	voltage pulses	RUB ECL

21	PPD	TBAP	RUB	140	voltage pulses	RUB ECL
22	PTP	TBAP	RUB	220	voltage pulses	RUB ECL
23	PPO/1-methyl-naphthalene	TBAP	RUB	80	potential steps; voltage pulses	RUB ECL; brighter than using PPO alone
24	PPO/2-methyl-naphthalene	TBAP	RUB	80	potential steps; voltage pulses	RUB ECL; brighter than using PPO alone
25	N,N-diphenyl-formamide	TBAP	RUB	80	voltage pulses	no luminescence
26	PPO	TBAP	TPP	80	CV; potential steps; voltage pulses	TTP ECL of very low intensity

*Abbreviations:* RUB: rubrene; TBABF<sub>4</sub>: tetra-*n*-butylammonium tetrafluoroborate; TBACl: tetra-*n*-butylammonium chloride; TEAP: tetra-*n*-ethylammonium perchlorate; PTP: *p*-terphenyl;

- a) The typical ratio of solvent to electrolyte to solute was 100:10:1, resulting in solutions approximately 5 mM in solute. When a mixed solvent was used, the component added to PPO was approximately 25% by wt.
- b) Estimated sample temperatures in the vicinity of the electrode. The bath temperature was considerably higher than these values, *e.g.*, in the case of molten TBAP the bath had to be higher than 235 °C to prevent solidification of the sample in the vicinity of the electrode. Since the electrodes are good heat conductors, the temperature in the vicinity of the electrode is lower than that of the rest of the ECL solution.

to "dark reactions" (cf. Table I). The various types of ECL efficiency that have been used in the scientific literature are summarized in Table V.

The multi-step ECL process is prone to lose efficiency in a number of ways including the spin-statistical contribution [20], solvent and supporting electrolyte effects [21—22], ion-annihilation at the electrode [23], and intersystem crossing [24]. A large Stokes (0, 0) loss, characteristic of many ECL parent dyes, can also be a source of non-radiative loss of electronic excitation energy [25—26]. Counteracting such losses, endothermic steps are thermodynamically permitted in both the heterogeneous and homogeneous electron transfer reactions; yet on the other hand these were shown [27] to fall in the *ignis fatuus* category for energetically significant utilization with available ECL reactions.

Rigorous determination of the quantum efficiency of an ECL system is an exacting task that makes clear the intersectional nature of this research area: it involves, on the one hand, the standard repertoire of electrochemical techniques [28—31], and, on the other hand, spectroscopic methods and considerations [20], [32—35]. A survey of representative  $\Phi_{ecl}$  values is given in Table VI. By the commonly accepted definition [36—40] the ECL quantum efficiency is

$$\Phi_{ecl} = \frac{\text{number of photons emitted}}{\text{number of } e^- \text{ transferred in the homogeneous (redox) step}} \quad (4)$$

Emphatically,  $\Phi_{ecl}$  is *not* simply based on the number of heterogeneous electron transfer events, but on the number of redox events occurring between electrogenerated cations and anions; hence the occasional notion in the research literature that (photons emitted/electrons input) would be a measure of  $\Phi_{ecl}$  is a mistaken one, and any semblance to the classical definition of fluorescence quantum efficiency

$$\Phi_f = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} \quad (5)$$

is superficial and misleading. How profoundly the electrochemical steps affect the entire ECL process is demonstrated by the variation of  $\Phi_{ecl}$  values as a function of experimental conditions (Table VII); the results plainly indicate that uniformity of results depends on rigorous methodology of the researcher, well beyond the mere selection of suitable fluorscours.

Table V  
Various Types of ECL efficiency

Type & Symbol	<i>I</i> (light intensity)	<i>i</i> (current)	Footnote
Power	$I_t @ eV$	$i_t @ V$	
Practical $\Phi_{prac}$	$I_t$	$i_t$	a)
Electrical $\Phi_{elec}$	$I_c$	$i_t$	b)
Coulombic $\Phi_{coul}$	$I_c$	$i_f$	c)
ECL $\Phi_{ecl}$	$I_c$	$N$	d)

a) Total emitted light/total current.

b)  $I_t$  is corrected for solution losses, reflectivity...

c) The current *i* is corrected for charging and background processes.

d) Correction for number of electrogenerated species which are lost.



Table VI  
A Survey of Representative  $\Phi_{\text{ect}}$  Values

Compound (concentration)	Solvent <sup>a</sup>	Method	Efficiency <sup>b</sup>	Ref.
MADI (1 mM)	DMF	2-elec. 60 Hz sp. wave IS—PM (s. s.)	$\Phi_{\text{prac}} = 0.1-0.2$	d
Rubrene	$\emptyset$ CN	pulsed	$\Phi_{\text{coul}} (?) = 1.5; 0.87^{\circ}$	e
DPA (2 mM)	DMF	RRDE-Direct PM	$\Phi_{\text{ect}} = 0.08$	f
DPA—TMPD (1 mM—1 mM)	DMF	RRDE-Direct PM	$\Phi_{\text{ect}} = 0.006$	f
Rubrene (1 mM)	DMF	RRDE-Direct PM	$\Phi_{\text{ect}} = 0.007$	f
PYRENE—TMPD (3.5 mM—2 mM)	DMF	RRDE-Direct PM	$\Phi_{\text{ect}} = 0.007$	f
DPA (0.27 mM—2.7 mM)	DMF	3-elec. (1 sec. pulses) (2nd pulse used for IS—PM; F-plot)	$\Phi_{\text{ect}} = 0.05-0.15$	g
Rubrene (0.4—1 mM)	DMF	3-elec. (1 sec. pulses) (2nd pulse used for IS—PM; F-plot)	$\Phi_{\text{ect}} = 0.05$	g
Rubrene (0.6—1.2 mM)	$\emptyset$ CN	3-elec. (1 sec. pulses) (2nd pulse used for IS—PM; F-plot)	$\Phi_{\text{ect}} = 0.1$	g
FA-10 MP (0.2—1.5 mM)	DMF	3-elec. (1 sec. pulses) (2nd pulse used for IS—PM; F-plot)	$\Phi_{\text{ect}} = 0.006-0.01$	g

Abbreviations: MADI, N-methyl-1,3-p-anisyl-4,7-isoindole; FA, fluoranthene; PM, photomultiplier; F-plot, Feldberg-plot; s. s., steady state; 3-elec., potentiostated electrogeneration; IS, integrating sphere; Direct PM, the ECL intensity was insufficient for direct actinometric calibration, but it was referred back to an actinometric calibration using an artificial light source.

- a) The solvent contained 0.1 M TBAP as supporting electrolyte in all cases.  
 b) The efficiency is given in %, 100% being the possible maximum.  
 c) The efficiency varies with stepping positive or negative.  
 d) A. Zweig: *Advances in Photochemistry*, 6, 425 (1968).  
 e) D. M. Hercules: *Accounts Chem., Res.* 2, 301 (1969); "Physical Methods in Organic Chemistry", 4th ed., Part II, A. Weissberger and B. Rossiter; Eds., Academic Press, New York, N. Y., 1971.  
 f) J. T. Maloy: Ph. D. thesis, The University of Texas at Austin, 1970; J. T. Maloy and A. J. Bard: *J. Amer. Chem. Soc.*, 93, 5968 (1971).  
 g) R. Bezman and L. R. Faulkner: *J. Amer. Chem. Soc.*, 94, 6317, 6324, 6331 (1972).

*Table VII*  
*A Survey of  $\Phi_{ecl}$  Values Obtained*  
*Under Various Experimental Conditions*

ECL System <sup>#</sup> Concentrations (mM)	Method*	$\Phi_{ecl}$ (%)	Comments
DPA/TH (7.77)/(11.11)	Pulsed	18.1	maximum $\Phi_{ecl}$ value, using the same solution that gave 4.9% under steady state (ss) condition ( <i>cf.</i> below in Table)
DPA/TH (7.77)/(11.11)	Pulsed Actinometry Actinometry	4.3 (~10)	75 minute exposure time continuous peak value, estimated from photodiode monitoring
DPA/TH (7.77)/(11.11)	Pulsed ss	3.5	16 hrs continuous
DPA/TH (7.77)/(11.11)	Pulsed ss	2.6	2 hrs at 300 Hz; same solution as in 16 hr experiment
DPA/TH (7.77)/(11.11)	Pulsed ss	4.9	solution in which 18.1% was obtained; the 4.9% refers to a 14 hr experiment, applying optimal potentials
DPA/TH (7.77)/(11.11)	RRDE Actinometry	6.4	975 seconds duration with several 30 second stops (not counted in the 975 seconds) for recovery of ECL intensity
DPA/TH (7.77)/(11.11)	RRDE Actinometry	(~13)	peak value, estimated from photodiode monitoring during actinometry
DPA (7.77) (2.20) (~0)	RRDE RRDE RRDE	5.4 11.3 (~13)	averaged extrapolated maximum in THF, extrapolated;
DMA/TPTA (0.100 mM each) rubrene (2.00)	RRDE Pulsed	(7) 1.3	in benzonitrile solvent

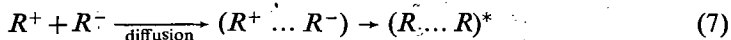
*Abbreviations:* ss: steady state; RRDE: rotating ring-disk electrode; TPTA: tri-*p*-tolylamine.  
<sup>#</sup> Pulsed method implies 60 Hz as the frequency of electrogeneration unless specified otherwise under 'comments'.

\* The solvent — supporting electrolyte system was (50% ACN: 33%  $\text{O}^-\text{H}$ : 17%  $\text{O}^-\text{CH}_3$ ) — 0.1 M TBAP unless specified otherwise under 'comments'.

A fine point with major consequences which needs to be taken into consideration in adoptin fluorescence principles in ECL research stems from a great difference in bimolecular excited state formation; in case of photon absorption, diffusion of the excited molecule ( $R^*$ ) to within the interaction sphere of a suitable moiety ( $R$ ) follows creation of  $R^*$ :



whereas in ECL the order is reversed:



similar considerations obviously extend to mixed ECL systems and creation of  $(A \dots D)^*$ , indicating that the redox path is preferential, in a sense even ideal, for production of excimers and exciplexes. The prominence of dimeric emission has been reported indeed in a number of ECL systems [15], [41—42], well in accord with observations in chemiluminescence [43—45].

Purposeful variations, and enhancement of  $\Phi_{\text{ect}}$  is an important topic on both theoretical and practical grounds. The systematic increase of  $\Phi_{\text{ect}}$  in case of the 9,10-dimethylantracene/tri-*p*-tolylamine/tetra-*n*-butylammonium perchlorate/tetrahydrofuran system (Table VIII) suggests that the supporting electrolyte concentration has an unusually significant role in this system. An explanation of the empirical observation stems from increase of the reaction enthalpy,  $\Delta H_r^0$ , with decreasing concentration of the tetra-*n*-butylammonium perchlorate supporting electrolyte (Table IX), whereby the formerly triplet-route ECL system becomes energy sufficient with respect to the 9,10-dimethylantracene first excited single state ( $E_s = 3.06$  eV). The by-passing of quenching problems associated with the triplet state are, in turn, demonstrated by these selfsame results. It would be unlikely to encounter a similar quantum yield increase in photonic excitation, where the  $A^-$  and  $D^+$  energetics do not enter via Eq. (2).

A further distinction between photonic and redox excitation concerns the time-evolution of the energetic molecules [46—47]. The homogeneous electron transfer in fluid solution occurs several orders of magnitude slower than the photon absorption, shown by the potential energy curves ( $G$  vs. Reaction Coordinate) in the cohesive theoretical formulations of MARCUS [48—50]. Yet in attempting to approach the ECL problem from the fluorescence side, we find that the quantum yield of fluorescent solutions as given by Stepanov's formula [51—52], or its corrected version [53]

$$f(\nu) = C n_q(\nu) k(\nu) \nu^3 e^{-h\nu/kT} \quad (8)$$

where  $f(\nu)$  is the normalized fluorescence energy spectrum,  $C$  a constant,  $k(\nu)$  the

Table VIII

Increase of  $\Phi_{\text{ect}}$  as Function of Supporting Electrolyte Concentration in the 9,10-dimethylantracene/tri-*p*-tolylamine/tetra-*n*-butylammonium perchlorate/tetrahydrofuran System

DMA <sup>a</sup>	TPTA <sup>a</sup>	TBAP <sup>a</sup>	$\Phi_{\text{ect}}$ <sup>b</sup>
0.100	0.100	200	0.6
0.100	0.100	120	2.5
0.100	0.100	60.0	4
0.100	0.100	5.00	6

a) All concentrations are in mM.

b) Measured at  $f = 0.5$  Hz,  $\lambda = 4300$  Å

Table IX

Increase of ECL Reaction Enthalpy as a Function of Supporting Electrolyte Concentration in the 9,10-dimethylantracene/tri-*p*-tolylamine/tetra-*n*-butylammonium perchlorate/tetrahydrofuran System

TBAP (mM)	DMA (mM)	TPTA (mM)	mV/sec	$-E_{P_c}$ (mV)	$E_{P_a}$	$\Delta E_{P_c}$ (mV)	$\Delta E_{P_a}$	$\Delta H_r^0$ (eV)
200	1.00	1.00	100	2.165	—	70	—	
100	1.00	1.00	200	—	0.856	—	70	2.86
10	1.00	1.00	200	2.675	—	843	—	
200	0.100	0.100	200	2.160	—	68	—	
200	0.100	0.100	200	—	0.940	—	80	2.94
200	0.100	0.100	100	2.116	—	78	—	
200	0.100	0.100	100	—	0.921	—	75	2.88
120	0.100	0.100	50	2.155	—	70	—	
120	0.100	0.100	50	—	0.883	—	67	2.88
100	0.100	0.100	100	2.106	—	57	—	
100	0.100	0.100	100	—	0.893	—	73	2.84
60.0	0.100	0.100	100	1.269	—	67	—	
60.0	0.100	0.100	100	—	0.860	—	83	2.97
10.0	0.100	0.100	100	2.294	—	169	—	
10.0	0.100	0.100	100	—	1.004	—	116	3.05
10.0	0.100	0.100	200	2.228	—	166	—	
10.0	0.100	0.100	200	—	1.019	—	134	3.09
1.0	0.100	0.100	200	2.357	—	522	—	

absorption coefficient, does not carry a temporal factor. Irrelevant as it may be for the photon-in/photon-out reaction channel, which for a given species, solvent conditions and temperature, is uniquely defined, the ECL process in general is not well approximated without the time scale. The reason is that molecular geometry changes and solvent cage shifts occur *after* creation of  $R^*$  in the case of photonic excitation, but may be significantly complete *before* creation of  $R^*$  in ECL. Due to this timescale inhomogeneity of the two reaction channels, it has been reported that the ECL quantum efficiency cannot be expressed properly as a product of an efficiency quotient leading to  $R^*$  production and  $\Phi_f$ , the ordinary fluorescence quantum yield of the ECL emitter [54]; hence the interaction between electrochemistry and spectroscopy in ECL is a higher order one, and, mathematically speaking, the variables are not separable. Paraphrased, the set of relevant quantum states that describe the time-evolution of  $R^*$  depends on the reaction channel. Such a set of quantum states has been formally treated as a *Markov chain* [25], or the problem can be approached by adopting the multicomponent luminescent solution treatment of KETSSEMÉTY [55]. It should be noted that, unlike in ordinary multi-component luminescent systems, in the ECL reaction some transient components contribute according to their lifetime, *i.e.*, appear in the summation with an extra Gaussian or pre-exponential factor.

How significant are the issues raised here can best be gauged from direct experiments, where the time-scale inhomogeneity between the photonic and redox reaction channel leads to conspicuous changes. A promising system to demonstrate the difference would (1) have a large change in solute geometry between the ground ( $R$ ) and excited ( $R^*$ ) state, (2) the time-evolution of  $R^*$  should bypass in an unequivocal manner (at least some) of the quantum states that cause the loss in efficiency. This opens the exciting possibility that  $\Phi_{ecl} > \Phi_f$  may be observed, although the losses commonly encountered in charge transfer excitation mitigate against this very strongly.

Mixed ECL systems based on the solute thianthrene (TH) meet the rather specific requirements set forth: (1) TH has a large change in geometry in going from  $R$  to  $R^*$  [56], (2) the geometry change upon photon absorption leads to very dominant inter system crossing (Bonnier and Jardon report 96% triplet yield and only 3.6% singlet yield), (3) the redox excitation path avoids the large geometry change and concomitant

Table X

*Increase of  $\Phi_{ecl}$  as a Function of Reaction Enthalpy in Mixed ECL Systems Based on the Thianthrene Cation and Different Anions*

Anion <sup>a</sup>	$E_{1/2}$ (V vs. SCE)	$-\Delta H_r^0$ (eV)	$\Phi_{ecl}$
DPA	-1.85	2.97	1
PPD	-2.14	3.26	0.1
PPO	-2.25	3.37	0.01
PHEN	-2.41	3.53	0.005
TH	-2.54	3.66	0.0005

<sup>a</sup> All solute concentrations were 7 mM in dry, de-aerated ACN—0.1 M TBAP, except [DPA] was 0.75 mM due to low solubility.

intersystem crossing that follows photonic excitation, because the order of planarity is  $TH^+ > TH^* > TH$  [15]. An extensive study [24] summarizes the results of a series of ECL efficiency determinations; it seems conspicuously evident that as the chemical excitation energy ( $\Delta H_r^0$ ) is lowered towards 2,86 eV (the first excited singlet energy of thianthrene as determined from fluorescence emission), the photon yield increases (Table X.). The experimental observations demonstrate that the excitation process in electrochemiluminescence can differ profoundly from photon absorption, the effective fluorescence quantum yield of a solute may vary significantly pending both mode of excitation and chemical energy input, and that the relatively slow time scale of charge transfer excitation can play an important role. In closing it is comfortable to note that the diametrically opposite relationship between  $\Delta H_r^0$  and  $\Phi_{ecl}$ , as seen from Tables VIII—IX vs. X, is not outside the realm of scientific explanation; indeed they provide valuable insight into the multifarious ECL process.

\* \* \*

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## ТЕОРИЯ ХИМИЧЕСКОГО ВОЗБУЖДЕНИЯ: СРАВНЕНИЕ ФОТОННОГО И ЭЛЕКТРОННОГО ВОЗБУЖДЕНИЙ

Ч. П. Кестхели

Больше десятилетия изучают уже регулярно в жидких растворах возникновение электронно-возбужденного состояния в некоторых окислительно-восстановительных процессах (ЕСЛ). Гетерогенную и гомогенную передачу заряда обычно удается разделить, первую можно рассмотреть с позиций классической теории электрохимических явлений, вторую как молекулярную флюоресценцию. Результаты полученные по изучению квантового выхода показывают, что смешение времени между адсорбцией фотонов и гомогенной диффузионной передачей заряда может привести к значительно отличающимся потерям гашения, происхождения межсистемных переходов.