Reversible formation of excited states in intramolecular donor assisted chemiluminescence reactions of dioxetanes†

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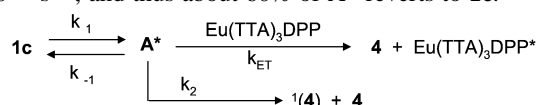
Data are presented requiring that the currently accepted CIEEL mechanism for the chemiluminescence of electron donor substituted dioxetanes be modified to include reversible thermal population of a dioxetane excited charge transfer state that undergoes ring scission with excited product formation which is accelerated by energy acceptors.

Chemiluminescent and bioluminescent reactions frequently proceed by electron donor catalyzed decomposition of dioxetanes. Donors with low oxidation potentials accelerate the decay rates and increase chemiexcited singlet to triplet product ratios. These reactions are regarded as proceeding by electron transfer to an O–O σ* orbital which initiates immediate dissociation of the dioxetane ring.[1–3] However it has been argued that this chemically initiated electron exchange luminescence "CIEEL" mechanism fails to rationalize the effect of structure on rates and multiplicity.[3] For example, electron donor substituents of dioxetanes **1** and **2** produce rate accelerations (Table 1) which correlate poorly with their oxidation potentials.[4–6] The aminophenyl groups in **1b–e** effect over a 200-fold range of decay rates, all of which are much below that produced by the less readily oxidized amine and thioether groups in **2a–c**.
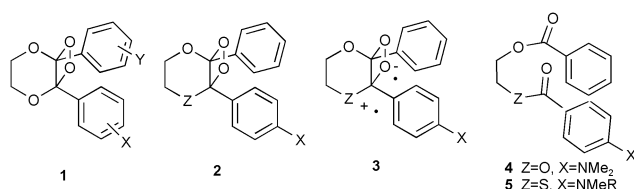
It is reported that **1c** decays quantitatively to diester **4** with a chemiluminescence quantum yield of $\Phi_{CL} = 0.021$ and a chemiexcitation efficiency of $\Phi_{CE} = 0.21$.[5] We now find that the decay rate of **1c** is increased with europium tris(4,4,4-trifluoro-1-thienyl-1,3-butadione)-4,7-diphenyl-1,10-phenanthroline [Eu(TTA)$_3$DPP][7] but approaches a plateau with increasing Eu concentrations. This suggests that Eu(TTA)$_3$DPP catalyzes the decay of an intermediate, A*, that is in thermal equilibrium with **1c**. The kinetics of this process is given by eqn. 1. When k_1 was taken as 4.72×10^{-4} s^{-1} a plot of $1/(k_1 - k_{obs})$ versus [Eu] was linear with a slope to intercept ratio of $k_{ET}/(k_{-1}$

Table 1 Dioxetane decay rates $\times 10^4$ s^{-1} in xylene at 25 °C

	Y	X	k_{obs}		Z	X	k_{obs}
1a	H	H	0.017[a]	**2a**	NPh	H	170[b]
1b	*m*-NMe$_2$	*m*-NMe$_2$	0.090[a]	**2b**	NMe	H	2300[b]
1c	H	*p*-NMe$_2$	3.7[a]	**2c**	S	H	2800[b]
1d	*p*-NMe$_2$	*p*-NMe$_2$	6.2[a]	**2d**:R = Me	S	NMeR	3500[e]
1e	CN	*p*-NMe$_2$	19[a]	**2d**:R = PA[c]	S	NMeR	3900[e]
				2d:R = BP[d]	S	NMeR	3900[e]

[a] Ref. 4. [b] Ref. 5. [c] PA = 9-(phenanthryl)CH$_2$N(C$_8$H$_{17}$)CO(CH$_2$)$_4$–. [d] BP = 2-(9,10-bisphenylethynylanthracyl)-NHCO(CH$_2$)$_4$–. [e] Measured in toluene. Rates were independent of concentration.

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b304245f/

$+ k_2) = 1380$ M^{-1}. In the absence of Eu(TTA)$_3$DPP k_{obs} was 1.9×10^{-4} s^{-1}, and thus about 60% of A* reverts to **1c**.

$$\mathbf{1c} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{A^*} \xrightarrow[k_{ET}]{Eu(TTA)_3DPP} \mathbf{4} + Eu(TTA)_3DPP^*$$
$$\mathbf{A^*} \xrightarrow{k_2} {}^1(\mathbf{4}) + \mathbf{4}$$

$$1/(k_1 - k_{obs}) = (k_{-1} + k_2 + k_{ET}[Eu])/k_1 k_{-1} \qquad (1)$$

Decomposition of **1c** is accompanied by singlet diester $^1(\mathbf{4})$ emission at 352 and 395 nm. Eu(TTA)$_3$DPP quenches this emission with the appearance of Eu emission at 613 nm and an increase in the chemiexcitation efficiency, $\Phi_{CE\infty} = 0.57$.[8] Sensitization of Eu during catalyzed decay of A* suggests that A* is acting as a triplet energy donor.[9,10] The donor cannot be the product triplet $^3(\mathbf{4})$ because the kinetics show that the donor reconverts to ground state **1c**. Plots of the reciprocal emission intensities at 352 and 613 nm versus 1/[Eu(TTA)$_3$DPP] and [Eu(TTA)$_3$DPP], respectively, were linear with the same slope to intercept ratio, $k_{ET}/(k_{-1} + k_2) = 1300 \pm 100$ M^{-1}, as obtained from the kinetic data. Since energy transfer is limited by the rate of diffusion ($k_{ET} \leq 1 \times 10^{10}$ s^{-1}), the A*/A equilibrium constant, k_1/k_{-1}, is $\geq 1.0 \times 10^{-10}$. An upper limit for k_1/k_{-1} of ≤ 0.05 is estimated from the absence of a detectable light flash on adding Eu(TTA)$_3$DPP to **1c**. Thus k_{-1} is $\leq 4.6 \times 10^6$ and ≥ 0.09 s^{-1} and k_2 is $\leq 3.1 \times 10^6$ and ≥ 0.06 s^{-1}.

Oxathiin **2d**:R = Me decayed much more rapidly to give the diester, **5**:R = Me (Table 1). Although the chemical yield was nearly quantitative, the emission at 367 nm from $^1(\mathbf{5}$:R = Me) was very inefficient, $\Phi_{CL} = 7.7 \times 10^{-6}$ ($\Phi_{CE} = 3.1 \times 10^{-4}$).[11] In contrast to **1c**, decay of **2d**:R = Me was not accelerated by Eu(TTA)$_3$DPP although Eu emission was still efficiently sensitized ($\Phi_{CE\infty} = 0.40$ and $k_{ET}\tau = 550$ M^{-1} where τ is the lifetime of the donor). In the presence of a tracer concentration of Eu(TTA)$_3$DPP (0.15 mM), triplet acceptors having triplet energies of ET = 59–66.6 Kcal mol^{-1} (9-Br-phenanthrene, naphthalene, phenanthrene, and triphenylene)[12] enhanced the Eu emission, while acceptors with ET ≥ 67 Kcal mol^{-1} were without effect. The increase in Eu emission with increasing acceptor concentration was similar to that obtained by increasing the Eu(TTA)$_3$DPP concentration alone, $k_{ET}\tau$ (av) = 430 $\pm$ 100 M^{-1}. None of these compounds affected the chemiluminescence of **2d**:R = Me in the absence of Eu(TTA)$_3$DPP nor did they produce a change in its decay rate.

The triplet energy profile of acceptors that mediate sensitized excitation of Eu emission suggests that **2d**:R = Me decays by way of a triplet intermediate with ET ~ 67 Kcal mol^{-1}. Energy transfer from the ground state is ruled out because it would result in a rate increase. The data do not distinguish between the possible triplet intermediates, $^3(\mathbf{5}$:R = Me) and ^{3}A(**2d**:R = Me). By analogy with **1c** the donor may be ^{3}A(**2d**:R = Me), but the known triplet energy of ~ 67 Kcal mol^{-1} for aminobenzoic esters[12] is consistent with $^3(\mathbf{5}$:R = Me).

In an attempt to maximize energy transfer, acceptors were covalently attached to the dioxetane (**2d**:R = PA or R = BP, Table 1). Unexpectedly each of these derivatives decayed about 11% faster than **2d**:R = Me. The efficiency of energy transfer from **2d**:R = PA to Eu(TTA)$_3$DPP increased ($k_{ET}\tau = 1600$

M^{-1}) but the quantum yield of Eu chemiexcitation was lower, $\Phi_{CE\infty}$ = 0.33 (Table 2). The increased $k_{ET}\tau$ is consistent with energy transfer from a relatively long lived phenanthrene triplet of the product, **5**(R = ^{3}PA). The reduced Eu chemiexcitation and the faster decay with covalently bound phenanthrene suggest that the phenanthrene accelerates non-radiative decay of a very short lived intermediate, ^{1}A(**2d**:R = PA), that is in equilibrium with **2d**:R = PA (Fig. 1).

Decay of **2d**:R = BP resulted in strong BP emission from **5**:R = ^{1}BP (Φ_{CE} = 0.24, Table 2) in contrast to very weak BP emission when free BP was added to **2d**:R = Me. This again suggests an intermediate, ^{1}A(**2d**:R = BP), that is too short lived for interception except by a covalently bound acceptor. Decay of ^{1}A with excitation of BP but not PA can be attributed to the energetic inaccessibility of singlet phenanthrene, 83 Kcal mol^{-1}, *versus* 58 Kcal mol^{-1} for BP. The accelerated decay of **2d**:R = BP again suggests that ^{1}A(**2d**:R = BP) is formed reversibly.

Addition of Eu(TTA)$_3$DPP to **2d**:R = BP produced Eu emission, $\Phi_{CE\infty}$ = 0.12, without affecting the BP emission. Since BP does not photosensitize Eu(TTA)$_3$DPP fluorescence, the energy donor is ^{3}A(**2d**:R = BP) or ^{3}(**5**:R = BP). The reduced excitation of Eu (Table 2) suggests that interception of ^{1}A(**2d**:R = BP) by BP competes with formation of the donor. The donor does not revert back to ^{1}A(**2d**:R = BP) since Eu(TTA)$_3$DPP did not affect the BP emission (Fig. 1).

A troublesome feature of these observations is the nearly identical $k_{ET}\tau$ values for the excitation of Eu by **2d**:R = Me and **2d**:R = BP. This requires that BP does not affect the triplet intermediate lifetime despite intramolecular energy transfer being exothermic by ~ 25 Kcal mol^{-1} (BP triplet energy ~ 42 Kcal mol^{-1}).[12] Moreover, unlike the other triplet acceptors that shuttle triplet energy to Eu, thioxanthone (ET = 65.5 Kcal mol^{-1})[12] and biphenyl (ET = 65 Kcal mol^{-1})[13] did not affect the excitation of Eu(TTA)$_3$DPP during decay of **2d**:R = Me. A possible source of these inefficiencies is the combination of a large reorganizational energy associated with simultaneous decay of a twisted excited state of ^{3}**5**:R = BP [or dioxetane ring scission in ^{3}A(**2d**:R = BP)] and energy transfer to acceptors having low energy[14] or non-planar ground states.[15]

Table 2 Chemiexcitation efficiencies of oxathiin dioxetanes in toluene (25 °C) with and without added Eu(TTA)$_3$DPP

	λ_{CL}/nm	Φ_{CE} (−Eu)	$\Phi_{CE\infty}$ (+Eu)	$k_{ET}/(k_{-1} + k_2)$/M^{-1}
2d, R = Me	367	0.00031	0.41	540
2d, R = PA	370	0.00008	0.33	1600
2d, R = BP	490, 525	0.24^a	0.12	650

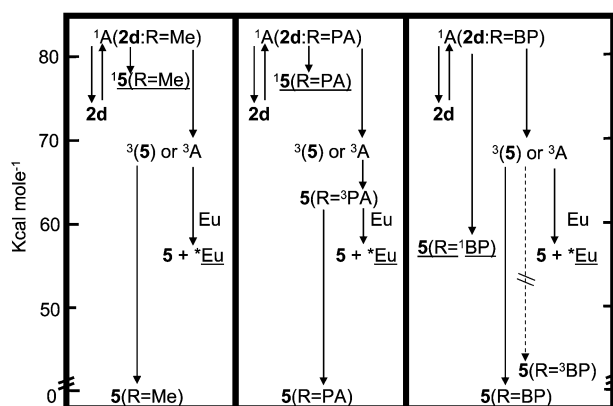^{a} 490 and 525 nm emission unaffected by Eu(TTA)$_3$DPP.

Fig. 1 Intermediates in chemiluminescent decay of oxathiins **2d**. Energies are based on fluorescence wavelength, acceptor triplet energies, and the required energy for triplet sensitized excitation of Eu fluorescence.[9] Energies for **2d** and ^{1}A(**2d**) are not established. Emission observed from underlined species.

The oxathiin dioxetane, **2d**, transitions are summarized in Fig. 1. Decay of dioxane dioxetane, **1c**, appears to be similar except that A* may be degenerate singlet and triplet states. Possible structures for A include a 1,4-diradical produced by O–O or C–C bond cleavage or the internal charge transfer excited state, **3**. The much higher rates of decay of **2a–d** relative to **1b–e** are not easily rationalized if A* is the diradical formed from unassisted O–O cleavage. Initial C–C cleavage might explain the substituent effects but is energetically unlikely since equally strained aminophenyl oxiranes and aziranes are stable.[16] On the other hand faster conversion of **2a–d** to intermediate **3** is consistent with smaller charge separation upon internal electron transfer from a ring N or S. Reversible formation of **3** requires a modification of the usual CIEEL hypothesis in which O–O bond scission is assumed to be concurrent with electron transfer.

Although O–O radical ions have not previously been observed, *ab initio* calculations predict energy minima for the H$_2$O$_2$ radical anion at elongated O–O bond lengths ranging from ~ 2.15 Å to 2.29 Å.[17] Additionally RS–SR radical anions have relatively high energy S–S bonds and cleave reversibly.[18]

An excited dioxetane charge transfer state that reverts to ground state in competition with intersystem crossing and ring cleavage provides a basis for understanding the effect of structure on the rates, multiplicity and quantum yield of dioxetane chemiluminescence products. An important example is the puzzling preponderance of singlet products from dioxetanes with strong electron donors. This behavior would be unexceptional if a metastable singlet charge transfer state is formed that undergoes accelerated substituent-assisted ring scission in competition with intersystem crossing. The possibility that the triplet intermediate observed here is ^{3}A(**2d**) should therefore not be discounted.

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