Electronic Supplementary Information

Chemiluminescence Efficiency of Catalyzed 1,2-Dioxetanone Decomposition Determined by Steric Effects

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Tables Section

Table S1. Initial emission intensity (I_0), observed decay rate constant (k_{obs}), chemiluminescence quantum yield (Φ_{CL}) and singlet excited state formation quantum yield (Φ_S) for the ACT-catalyzed decomposition of *spiro*-cyclopentyl-1.2-dioxetanone (**3**, 3.0 µmol L^{-1}) in toluene at 25.0 °C; mean values ± sd for three replicates.

ACT	ACT (mmol L^{-1})	I_0 (10^{-16} E s^{-1})	k_{obs} (10^{-4} s^{-1})	Φ_{CL} (10^{-4} E mol^{-1})	Φ_S (10^{-4} E mol^{-1})
RUB	0 [a]	0.19 ± 0.02	13 ± 3	0.11 ± 0.03	-
	0.1	3.6 ± 0.2	10 ± 2	1.7 ± 0.3	1.8 ± 0.3
	0.2	6.4 ± 0.3	11.5 ± 0.3	2.3 ± 0.4	2.3 ± 0.4
	0.4	6.8 ± 0.4	10 ± 2	3.3 ± 0.5	3.4 ± 0.5
	0.6	8.0 ± 0.6	10 ± 2	3.9 ± 0.6	4.0 ± 0.6
	0.8	6.2 ± 0.2	8.7 ± 0.4	2.7 ± 0.3	2.8 ± 0.3
PER	0 [a]	0.16 ± 0.03	10 ± 1	0.11 ± 0.04	-
	0.1	0.43 ± 0.06	8.0 ± 2.0	0.36 ± 0.01	0.41 ± 0.01
	0.2	0.81 ± 0.01	9.0 ± 2.0	0.60 ± 0.10	0.70 ± 0.20
	0.4	1.2 ± 0.1	8.0 ± 0.3	0.90 ± 0.10	1.10 ± 0.10
	0.6	1.5 ± 0.3	8.0 ± 1.0	1.15 ± 0.03	1.32 ± 0.04
	0.8	2.0 ± 0.1	7.0 ± 1.0	1.80 ± 0.20	2.10 ± 0.30
	1.0	1.7 ± 0.4	7.4 ± 0.1	1.60 ± 0.30	1.80 ± 0.40
DPA	0 [a]	0.11 ± 0.01	6.1 ± 0.1	0.11 ± 0.01	-
	0.6	0.97 ± 0.04	5.9 ± 0.1	1.01 ± 0.04	1.11 ± 0.04
	1.2	1.55 ± 0.07	5.6 ± 0.1	1.70 ± 0.10	1.90 ± 0.10
	1.8	1.89 ± 0.04	5.5 ± 0.2	2.10 ± 0.10	2.30 ± 0.10
	2.4	2.52 ± 0.02	6.3 ± 0.9	2.50 ± 0.30	2.80 ± 0.30
	3.0	2.70 ± 0.10	6.0 ± 0.4	2.78 ± 0.05	3.05 ± 0.06
ANT	0 [a]	0.05 ± 0.02	9.0 ± 0.2	0.05 ± 0.02	-
	1.0	0.3 ± 0.1	8.0 ± 0.7	0.4 ± 0.2	1.7 ± 0.3
	3.0	0.44 ± 0.04	6.2 ± 0.4	0.7 ± 0.1	2.3 ± 0.4
	5.0	0.61 ± 0.02	5.84 ± 0.04	1.00 ± 0.03	3.3 ± 0.1
DBA	0 [a]	0.07 ± 0.01	8.5 ± 0.9	0.07 ± 0.01	-
	1.0	1.11 ± 0.01	14.8 ± 0.7	0.63 ± 0.05	6.7 ± 0.5
	2.0	2.07 ± 0.08	19.0 ± 0.6	1.0 ± 0.2	10 ± 3
	3.0	2.43 ± 0.02	11.8 ± 0.8	1.8 ± 0.1	19 ± 2
	4.0	2.64 ± 0.09	11.0 ± 2.0	2.2 ± 0.3	23 ± 3

[a]Without ACT, for the thermal unimolecular decomposition.

Table S2. Fluorescence quantum yields (Φ_{FL}) and voltammetric half-peak oxidation potentials ($E^{ox}_{1/2}$) for the activators, k_{CAT}/k_D ratio obtained from the double-reciprocal plots with Φ_S and [ACT] (Figures S1 and S2) and thermal unimolecular decomposition rate constant (k_D) for 1,2-dioxetanones **2** and **3**.

ACT	Φ_{FL} [a]	$E^{ox}_{1/2}$ [b] (V *vs.* SCE)	**2**		**3**	
			k_{CAT}/k_D [c] (10^2 L^{-1} mol)	k_D [c,d] (10^{-3} s^{-1})	k_{CAT}/k_D [e] (10^2 L^{-1} mol)	k_D [d,e] (10^{-4} s^{-1})
RUB	0.98	0.61	1.78 ± 0.57	8.83 ± 0.19	78 ± 10	9.0 ± 1.0
PER	0.87	0.88	3.20 ± 0.16	5.64 ± 0.09	16.0 ± 0.7	8.0 ± 0.6
DPA	0.91	1.06	1.27 ± 0.40	6.38 ± 0.06	4.48 ± 0.05	5.9 ± 0.4
ANT	0.30	1.18	1.23 ± 0.33	6.47 ± 0.07	12 ± 3	7.0 ± 1.0
DBA	0.094	1.42	-	-	1.8 ± 0.3	13 ± 4
PPO	0.70	1.46	0.89 ± 0.18	5.99 ± 0.07	-	-

[a]Values taken from S. L. Murov, I. Carmichael, G. L. Hug, in *Handbook of Photochemistry*, 2nd ed., Marcel Decker Inc., New York, 1993.
[b]In acetonitrile, SCE: saturated calomel electrodes; values taken from C. Stevani, S. M. Silva and W. J. Baader, *Eur. J. Org. Chem.*, 2000, 4037 and L. F. M. L. Ciscato, F. H. Bartoloni, E. L. Bastos and W. J. Baader, *J. Org. Chem.*, 2009, **74**, 8974.
[c]Determined in toluene at 50 °C.
[d]It was assumed that $k_D \approx k_{obs}$ for the catalysed decomposition assays, once that $k_D >> k_{CAT}$[ACT].
[e]Determined in toluene at 25 °C.

Table S3. Singlet excited state energy (E_S) of the ACTs and free energy balance of the electron back-transfer step between the ketone radical anion and the activator radical cation, on the ACT-catalyzed chemiluminescent decomposition of peroxides **2** and **3**.

ACT	E_S [a] (kJ mol^{-1})	**2**		**3**	
		ΔG_{EBT} [b] (kJ mol^{-1})	ΔG^*_{EBT} [c] (kJ mol^{-1})	ΔG_{EBT} [b] (kJ mol^{-1})	ΔG^*_{EBT} [c] (kJ mol^{-1})
RUB	221	–343	–122	–331	–110
PER	273	–369	–96	–357	–84
DBA	295	-	-	–409	–114
DPA	305	–386	–81	–374	–69
ANT	319	–398	–79	–386	–67
PPO	356	–425	–69	-	-

[a]Values taken from S. L. Murov, I. Carmichael, G. L. Hug, in *Handbook of Photochemistry*, 2nd ed., Marcel Decker Inc., New York, 1993.
[b]$\Delta G_{EBT} = -F[E^{ox}_{1/2}(ACT) - E^{red}_{1/2}(ketone)]$; $E^{red}_{1/2}$(adamantanone) = –3.18 and (cyclopentanone) = –3.06 V *vs.* SHE, values taken from J.-E. Dubois, P. Bader and S. Briand, *Tetrahedron Lett.*, 1988, **29**, 3935 and *CRC Handbook of Chemistry and Physics*, 95th ed., 2015, respectively; $E^{ox}_{1/2}$(ACT) from Table S2 vs. SHE (standard hydrogen electrode, SCE vs. SHE = –0.24 V).
[c]$\Delta G^*_{EBT} = \Delta G_{EBT} + E_S$.