



Organic superbase-induced chemiluminescent decomposition of a hydroxyaryl-substituted dioxetane: Unique effect of a bifunctional guanidine base on the chemiluminescence profile of a bicyclic dioxetane bearing a 4-(benzoxazol-2-yl)-3,5-dihydroxyphenyl moiety

Nobuko Watanabe*, Ayu Wakatsuki, Hisako K. Ijuin, Yoshio Kabe, Masakatsu Matsumoto*

Department of Chemistry, Kanagawa University, Tsuchiya, Hiratsuka, Kanagawa 259-1293, Japan

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ABSTRACT

Organic superbases represented by TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) effectively induced the decomposition of hydroxyaryl-substituted dioxetanes in acetonitrile to give bright light. The color of the chemiluminescence from a dioxetane bearing a 4-(benzoxazol-2-yl)-3,5-dihydroxyphenyl moiety varied depending on the base used. In addition to this change in the color of emission, TBD increased the chemiluminescence efficiency 2- to 5-fold compared to the results with other base systems and accelerated decomposition of the dioxetane. These unique effects of TBD may be due to its “bifunctional” character, which is different from those of other organic superbases. Chemiluminescent decomposition of the dioxetane was effectively induced by superbases even in apolar *p*-xylene.

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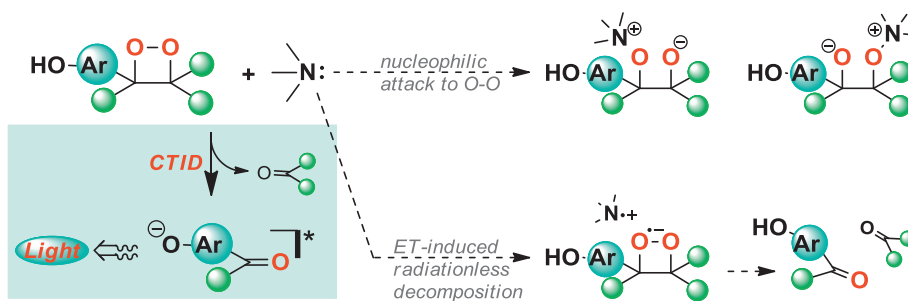
A hydroxyaryl-substituted dioxetane undergoes base-induced decomposition accompanied by the emission of bright light by a CTID (charge-transfer-induced decomposition) mechanism (Scheme 1).^{1–7} This phenomenon has received considerable attention based on interest in the mechanisms of chemiluminescence and bioluminescence as well as regarding potential applications in modern biological and clinical analyses.^{8,9} For base-induced decomposition, inorganic ionic bases, such as OH[−] and F[−], and alkaline metal alkoxides have generally been used. On the other hand, neutral organic bases have been used relatively little, presumably because of their possible nucleophilicity to dioxetane O–O and/or their ability as an electron-donor, which could lead to the radiationless decomposition of dioxetane (Scheme 1).^{10,11} However, neutral organic bases have the advantage of being soluble even in an apolar solvent and are rather easy to handle under water-free conditions. Furthermore, so-called superbases, which are stronger than OH[−] and F[−], have recently been developed and effectively used in various base-catalyzed reactions.^{12–14} This prompted us to investigate whether organic superbases could effectively induce the chemiluminescent decomposition of hydroxyaryl-substituted dioxetanes.

The dioxetanes selected for the present investigation were the parent bicyclic dioxetane, 1-(3-hydroxyphenyl)-4,4-dimethyl-5-*tert*-butyl-2,6,7-trioxabicyclo[3.2.0]heptane **1**,^{4a} and its derivatives in which the phenolic moiety was further modified to a 4-(benzoxazol-2-yl)-3-hydroxyphenyl **2a**, 4-(benzoxazol-2-yl)-3-hydroxy-5-methoxyphenyl **2b**, or 4-(benzoxazol-2-yl)-3,5-dihydroxyphenyl moiety **2c** (Fig. 1). **2a** and **2b** have been preliminarily reported to be two of the most effective CTID-active dioxetanes,¹⁵ while **2c** was designed with the expectation of unprecedented color-tuning in chemiluminescence due to mono-oxido/di-oxidoaryl anion species: **2c** was prepared by single-oxygenation of the corresponding 5-[4-(benzoxazol-2-yl)-3,5-dihydroxyphenyl]dihydrofuran, which was easily synthesized from a precursor dihydrofuran used to prepare **2b** (see SD). Dioxetanes **2a–2c** were sufficiently thermally stable to permit handling at room temperature, quantitatively decomposed to the respective keto esters **3a–3c** in hot *p*-xylene. We selected as a trigger five typical superbases, BTPP [(*tert*-butylimino)tris(pyrrolydino)phosphorene], TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene), MTBD (7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), and TMG (1,1,3,3-tetramethylguanidine), together with TBAF (tetrabutylammonium fluoride) as a reference (Fig. 1).

First, we investigated chemiluminescent decomposition of the parent dioxetane **1** in acetonitrile using the five organic superbases selected. When **1** (3.3×10^{-5} M) in acetonitrile at 25 °C was

* Corresponding authors.

E-mail addresses: nwatanab@kanagawa-u.ac.jp (N. Watanabe), matsumo-chem@kanagawa-u.ac.jp (M. Matsumoto).



Scheme 1. Decomposition of a hydroxyaryl-substituted dioxetane with an amine.

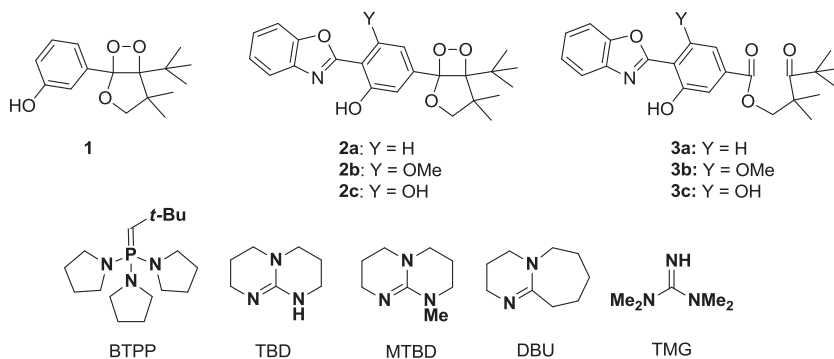


Fig. 1. Bicyclic dioxetanes bearing a 3-hydroxyphenyl or 3,5-dihydroxyphenyl moiety and neutral organic superbases.

treated with a large excess (200 eq.) of BTPP, which is the strongest base ($^{\text{AN}}\text{pK}_a$: pK_a in acetonitrile = 28.4) among the five,¹⁴ **1** decomposed according to pseudo-first order kinetics to give blue light (maximum wavelength: $\lambda_{\text{max}}^{\text{CL}} = 471$ nm, rate constant of CTID: $k^{\text{CTID}} = 5.4 \times 10^{-2} \text{ s}^{-1}$, and half-life of CTID: $t_{1/2} = 13$ s) with chemiluminescence efficiency $\phi^{\text{CL}} = 0.13$.^{16,17} When these results were compared to the chemiluminescence of **1** in a TBAF system,^{4a} ϕ^{CL} was rather higher and $t_{1/2}$ was shorter with BTPP than with TBAF, though the $\lambda_{\text{max}}^{\text{CL}}$ values were the same. Chemiluminescent decomposition of **1** was similarly carried out with the use of TBD, MTBD, DBU or TMG: the respective $^{\text{AN}}\text{pK}_a$ values were 26.0, 25.5, 24.3, and 23.4.¹⁴ These results are summarized in Table 1 and the chemiluminescence spectra are shown in Fig. 2(A). As

shown in Table 1, i) all of the superbases except TMG were more effective as a trigger than TBAF with respect to ϕ^{CL} , ii) from a practical perspective, $\lambda_{\text{max}}^{\text{CL}}$ did not vary with the base used, and, iii) k^{CTID} decreased in the order of the strength of the bases: BTTP > TBD > MTBD > DBU > TMG.

Next, we investigated the chemiluminescent decomposition of dioxetane bearing a benzoxazolylphenol moiety **2a** triggered by organic superbases as in the case of **1**, though the reaction temperature was elevated to 45 °C. As shown in Table 1 and Fig. 2(B), **2a** displayed chemiluminescence with $\lambda_{\text{max}}^{\text{CL}} = 490$ nm and a high ϕ^{CL} (0.26–0.34) regardless of the base used. However, TBD appeared to affect the rate of decomposition differently from the other bases: the order of k^{CTID} for **2a** was BTTP > MTBD > TBD > DBU > TMG,

Table 1
Chemiluminescence properties of the organic superbase-induced decomposition of dioxetanes **1** and **2a–2c** in acetonitrile.^a

	Base	BTTP	TBD	MTBD	DBU	TMG	TBAF
1	$^{\text{AN}}\text{pK}_a^b$	28.4	26.0	25.5	24.3	23.4	–
	$\lambda_{\text{max}}^{\text{CL}}/\text{nm}$	471	471	471	471	471	469
	ϕ^{CL}	0.13	0.14	0.11	0.12	0.086	0.10
	$k^{\text{CTID}}/\text{s}^{-1}$	5.4×10^{-2}	2.5×10^{-2}	6.9×10^{-3}	1.3×10^{-3}	8.5×10^{-4}	3.6×10^{-2}
	$t_{1/2}/\text{s}$	13	28	100	530	820	19
2a (45 °C)	$\lambda_{\text{max}}^{\text{CL}}/\text{nm}$	490	490	490	490	490	490
	ϕ^{CL}	0.32	0.34	0.30	0.33	0.26	0.33
	$k^{\text{CTID}}/\text{s}^{-1}$	1.5×10^{-3}	7.0×10^{-4}	7.8×10^{-4}	5.9×10^{-4}	2.8×10^{-4}	1.5×10^{-3}
	$t_{1/2}/\text{s}$	470	990	890	1200	2500	470
	2b (45 °C)	$\lambda_{\text{max}}^{\text{CL}}/\text{nm}$	487	487	487	487	487
ϕ^{CL}		0.25	0.25	0.23	0.23	0.18	0.24
$k^{\text{CTID}}/\text{s}^{-1}$		1.8×10^{-3}	8.2×10^{-4}	1.0×10^{-3}	9.3×10^{-4}	6.3×10^{-4}	1.7×10^{-3}
$t_{1/2}/\text{s}$		380	840	690	750	1100	410
2c		$\lambda_{\text{max}}^{\text{CL}}/\text{nm}$	560	535	535	498	495
	ϕ^{CL}	0.0091	0.031	0.015	0.0077	0.0057	0.012
	$k^{\text{CTID}}/\text{s}^{-1}$	4.8×10^{-2}	9.7×10^{-2}	2.2×10^{-3}	8.8×10^{-4}	8.1×10^{-4}	6.0×10^{-1}
	$t_{1/2}/\text{s}$	14	7.1	320	790	850	1.2

^a A solution of a dioxetane in acetonitrile (1.0×10^{-4} M, 1 mL) was added to a solution of a base in acetonitrile (1.0×10^{-2} M, 2 mL) at 25 °C.

^b Ref. 14.

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