



Chemiexcitation efficiency for the charge-transfer-induced chemiluminescent decomposition of 3-hydroxyphenyl-substituted dioxetanes in an aqueous system



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ABSTRACT

The decomposition of 3-oxyphenyl-3-methoxy-4-(2'-spiroadamantane)-1,2-dioxetane (**A**) and 5-*tert*-butyl-4,4-dimethyl-1-(3-oxyphenyl)bicyclo[3.2.0]heptane (**B**) in NaOH/H₂O gives light in poor yield, which is several orders of magnitude lower than that in aprotic solvents. To understand the poor chemiluminescence efficiency in NaOH/H₂O, we investigated the behaviors of the authentic emitters, methyl 3-oxidobenzoate (**C**) and 2,2,4,4-tetramethyl-3-oxopentyl 3-oxidobenzoate (**D**). We found that **D** was weakly fluorescent though hydrolyzed in NaOH/H₂O, and estimated that the singlet-chemiexcitation efficiency Φ_S was 6.1×10^{-3} for the decomposition of **B** in NaOH/H₂O. On the other hand, Φ_S for **A** could not be estimated, since **C** was hydrolyzed too rapidly to observe its fluorescence.

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The intramolecular charge-transfer-induced decomposition (CTID) of oxidophenyl-substituted dioxetanes has received considerable attention due to interest in the mechanisms of bioluminescence and chemiluminescence and because of possible applications in modern biological and clinical analyses using chemiluminescence.^{1–4} Typical examples are adamantylidene-substituted dioxetanes **1** and bicyclic dioxetanes **2**, which undergo chemiluminescent CTID through unstable oxidophenyl-substituted dioxetane **3** or **4** produced by deprotonation or deprotection (Scheme 1).^{2,5,6} Although dioxetanes **1** and **2** both effectively emit light in an aprotic polar medium, they give light in quite poor yield in an aqueous medium: the chemiluminescence efficiency Φ^{CL} in H₂O versus CH₃CN was ca. 1/16,000 for **1**, and ca. 1/10,000 for **2**.

This significant defect has been considerably improved through the addition of a fluorescer and/or a surfactant for practical use in an aqueous system.^{7,8} However, it is still unclear whether the markedly low Φ^{CL} is mainly due to poor singlet-chemiexcitation efficiency Φ_S and/or to poor fluorescence efficiency Φ^f of the emitter produced for CTID of **1** or **2** in H₂O. Since Φ^{CL} is given as $\Phi_S \times \Phi^f$ for dioxetane-based chemiluminescence, it is important for the estimation of Φ_S to characterize the emitter and to understand its fluorescence properties. Thus, we can first reliably

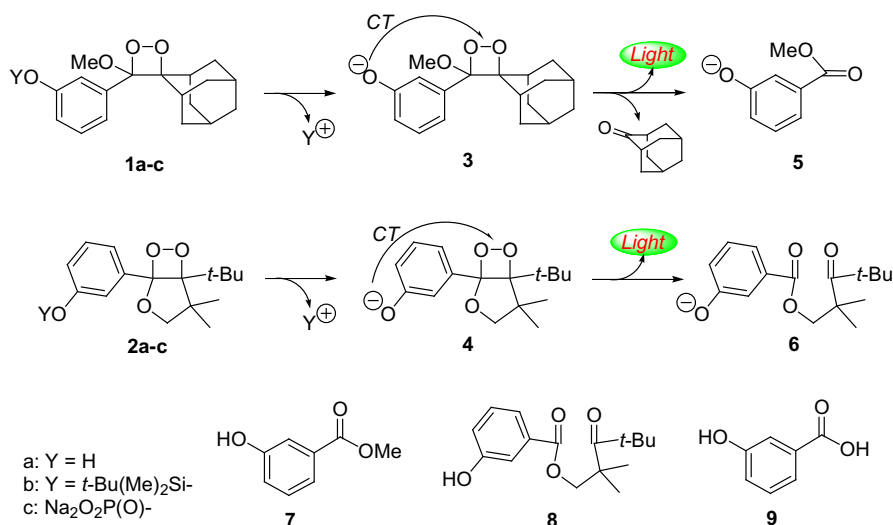
estimate Φ_S as well as Φ^f , when the fluorescence spectrum of the authentic emitter coincides with the chemiluminescence spectrum.

For the CTID of **3** and **4**, the emitters produced are methyl 3-oxidobenzoate **5** and its 2,2,4,4-tetramethyl-3-oxopentyl analog **6**, respectively. However, both the fluorescence spectrum of the authentic emitter **5** and the chemiluminescence spectrum of **3** have been reported to be considerably different from each other in NaOH/H₂O, while they are similar in an aprotic polar solvent such as DMSO or acetonitrile.⁹ A similar discrepancy has also been reported between CTID emission from **4** and fluorescence of **6**.¹⁰ It has very recently been reported that **5** undergoes rapid hydrolysis to give a dianion **15** (vide infra) of 3-hydroxybenzoic acid **9**, which shows a strong fluorescence with $\lambda_{max}^f = 412$ nm in a basic aqueous solution.¹¹ This work prompted us to report our findings that may lead to a better understanding of the markedly low Φ^{CL} for CTID of **3** and **4** in an aqueous system.

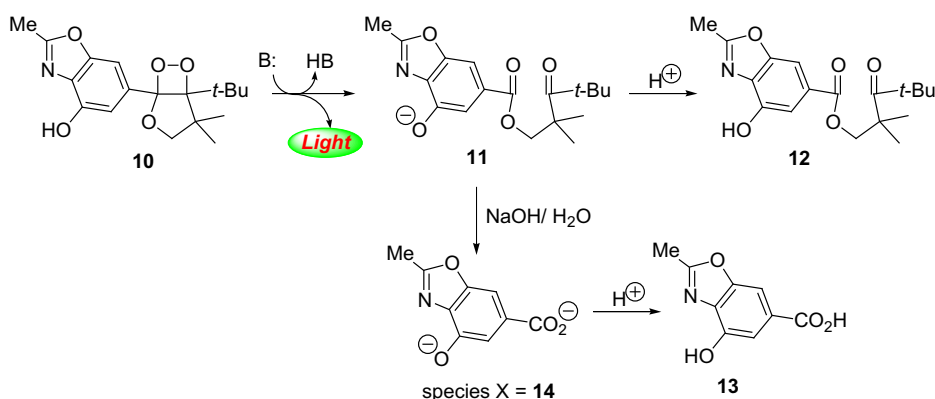
Bicyclic dioxetane **10** bearing a 4-hydroxy-2-methylbenzoxazole-6-yl group has been reported to show Φ^{CL} that is considerably higher than that for **2** in a NaOH/H₂O system.¹² As in the case of **1** and **2**, the fluorescence spectrum of the spent reaction mixture does not coincide with the chemiluminescence spectrum of **10** in NaOH/H₂O (Scheme 2). The authentic emitter **11** prepared by dissolving 2,2,4,4-tetramethyl-3-oxopentyl 4-hydroxy-2-methylbenzoxazole-6-carboxylate (**12**) in NaOH/H₂O showed fluorescence ($\lambda_{max}^f = 413$ nm), the spectrum of which resembled that of the spent

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Scheme 1. Base-induced chemiluminescent decomposition of 3-oxophenyl-substituted 1,2-dioxetanes.



Scheme 2. Base-induced chemiluminescent decomposition of bicyclic dioxetane **10** bearing a 4-hydroxy-2-methylbenzoxazol-6-yl group.

reaction mixture when it was irradiated with light of $\lambda_{\text{ex}} = 313$ nm. Furthermore, fluorescence with $\lambda_{\text{max}}^{\text{fl}} = 413$ nm increased gradually as time passed. On the other hand, when the solution of **11** was irradiated with light of $\lambda_{\text{ex}} = 370$ nm, it showed weak fluorescence with $\lambda_{\text{max}}^{\text{fl}} = 469$ nm, the spectrum of which coincided with that of chemiluminescence from **10** (Fig. 1).

Thus, we first attempted to carefully investigate the time-course of absorption and the fluorescence spectra for freshly prepared **11** in NaOH/H₂O at 25 °C.¹³ Figure 2 shows that the absorption at $\lambda^{\text{abs}} = 337$ nm decreased while the absorption at $\lambda^{\text{abs}} = 320$ nm increased over time. On the other hand, Figure 3 shows fluorescence spectra ($\lambda_{\text{ex}} = 370$ nm) in which a peak at $\lambda_{\text{max}}^{\text{fl}} = 469$ nm decreased while a peak at $\lambda_{\text{max}}^{\text{fl}} = 413$ nm increased over time. Irradiation of the same sample with light of $\lambda_{\text{ex}} = 313$ nm gave only fluorescence with $\lambda_{\text{max}}^{\text{fl}}$ at 413 nm that increased over time, as shown in Figure 4.

These results strongly suggested that **11** with an absorption maximum $\lambda_{\text{max}}^{\text{abs}}$ at 337 nm and a fluorescence maximum $\lambda_{\text{max}}^{\text{fl}}$ at 469 nm changed gradually into a species X with $\lambda_{\text{max}}^{\text{abs}}$ at 320 nm and $\lambda_{\text{max}}^{\text{fl}}$ at 413 nm in NaOH/H₂O: species X was presumed to be a dianion **14** of 4-hydroxy-2-methylbenzoxazole-6-carboxylic acid **13** based on the findings in a previous report (Scheme 2).¹¹ Thus, we subjected keto ester **12** to hydrolysis with NaOH in aqueous EtOH to effectively give authentic **13**: for the hydrolysis of **12** in NaOH/H₂O as a control experiment, the isolation of pure **12** was quite hazardous. As expected, the authentic **13** showed strong fluorescence with $\lambda_{\text{max}}^{\text{fl}}$ at 413 nm when it was dissolved in NaOH/H₂O.

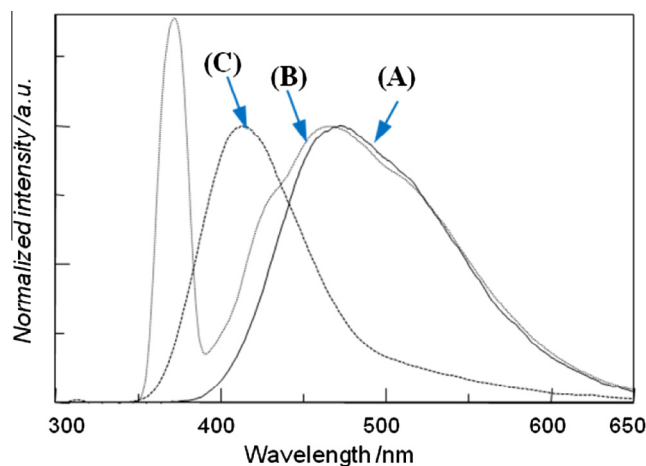


Figure 1. (A) Chemiluminescence spectrum of **10**, (B) fluorescence spectrum of authentic keto ester **11** ($\lambda_{\text{ex}} = 370$ nm), and (C) fluorescence spectrum of **11** ($\lambda_{\text{ex}} = 313$ nm) in NaOH/H₂O.

The above results prompted us to reinvestigate the absorption and fluorescence spectra of **6**, as the authentic emitter for CTID of **2**, prepared from ester **8** in NaOH/H₂O. When a freshly prepared solution of **6** was irradiated with light of $\lambda_{\text{ex}} = 370$ nm, it showed

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