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Solvent-promoted chemiluminescent decomposition of a bicyclic dioxetane bearing a 4-(benzothiazol-2-yl)-3-hydroxyphenyl moiety

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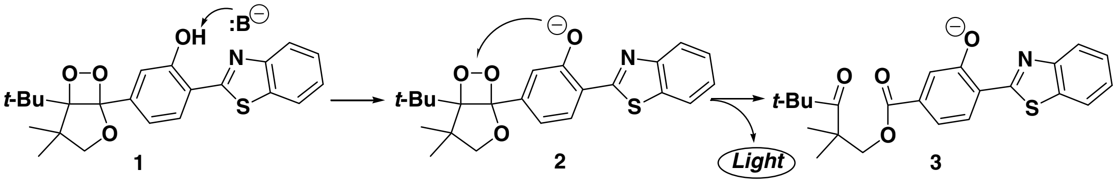
ABSTRACT

An aprotic polar solvent such as *N*-methylpyrrolidone (NMP) promoted the thermal decomposition of bicyclic dioxetane bearing a 4-(benzothiazol-2-yl)-3-hydroxyphenyl moiety **1** without the addition of any base. This solvent-promoted decomposition (SPD) gave light as effectively as the base-induced decomposition (BID) in an aprotic polar solvent. SPD caused intramolecular CT-induced chemiluminescence similar to BID, but, in contrast to BID, SPD proceeded through a pathway with a large negative entropy of activation. Dioxetane **1** was also shown to give light due to excited state intramolecular proton transfer (ESIPT) upon heating in *p*-xylene.

Dioxetanes bearing an electron donor such as oxidophenyl anion undergo intramolecular charge-transfer (CT)-induced decomposition to effectively give a singlet-excited carbonyl fragment that emits light.[1–4] On the other hand, uncatalyzed thermal decomposition (TD) of dioxetanes gives mainly a triplet-excited species, so that bright light emission is hardly expected.[5,6] In addition to these two types of decomposition, we report here the aprotic polar solvent-promoted decomposition (SPD) of dioxetane bearing a 4-(benzothiazol-2-yl)-3-hydroxyphenyl moiety **1** accompanied by the emission of bright light, and that this SPD resembled the base-induced decomposition (BID) of **1**,[7,8] which proceeds through unstable anionic dioxetane **2** to keto ester **3**; however, the entropy of activation for SPD had a large negative value, which was in sharp contrast to BID (Scheme 1). Furthermore, we report that the uncatalyzed TD of **1** gave light due to excited state intramolecular proton transfer (ESIPT) in a nonpolar solvent.[9,10]

In the course of our investigation of high-performance chemiluminescence compounds, we found that dioxetane **1** emitted weak green light when dissolved in DMSO at room temperature. Such chemiluminescence was apparently caused by solvent-promoted decomposition (SPD), although this was hardly observed for a parent dioxetane **4** bearing a simple 3-hydroxyphenyl group. Thus, we investigated the behavior of **1** in hot DMSO. Thermal decomposition of **1** in DMSO at 100 °C exhibited the emission of green light with maximum wavelength $\lambda_{max} = 497$ nm and half-life $t_{1/2} = 320$ s, although the chemiluminescence efficiency, Φ, was only 0.0013. From the mixture that followed the thermal decomposition of **1**, epoxide **5**[11] was isolated in high yield along with a trace amount of keto ester **6** (Scheme 2). The formation of dimethyl sulfone was also observed by ^{1}H NMR analysis of the reaction mixture. These results show that **1** was consumed predominantly by reduction with DMSO but not by SPD to give **6**. Therefore, we next sought to examine the SPD of **1** in an aprotic polar solvent, which is far more resistant to oxidation than DMSO.

The solvent selected was *N*-methylpyrrolidone (NMP), which is used as frequently as DMSO. First, the BID of **1** was examined.



Scheme 1. Base-induced decomposition (BID).

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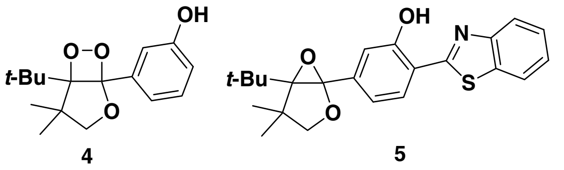


Scheme 2.

When **1** was treated with tetrabutylammonium fluoride (TBAF) in NMP at 45 °C, chemiluminescence occurred effectively with $\lambda_{max}^{BID} = 498$ nm, $\Phi^{BID} = 0.29$, and rate constant $k^{BID} = \ln 2/t_{1/2}^{BID} = 2.5 \times 10^{-4}\ s^{-1}$ (vide infra). The BID of **1** also proceeded to give bright light in acetonitrile,[8] DMF, and DMSO. These results are summarized in Table 1, and the chemiluminescence spectra of **1** are illustrated in Figure 1.

Next, SPD was investigated in NMP. When **1** was heated without any strong base in NMP at 100 °C, **1** decomposed to exclusively give **6** accompanied by the emission of green light with $\lambda_{max}^{SPD} = 498$ nm, $\Phi^{SPD} = 0.25$, and $k^{SPD} = 8.0 \times 10^{-3}$ s. Thus, the chemiluminescence spectrum coincided with that for the BID of **1**, as illustrated in Figure 2, and Φ^{SPD} was comparable to that for BID as shown in Table 1. These results suggested that the SPD of **1** in NMP should proceed through dioxetane bearing an oxidophenyl anion **2** to give anionic keto ester **3** in the excited state or a closely related species such as a solvated anion by a mechanism similar to the case of BID. This effective SPD chemiluminescence of **1** was also observed in aprotic polar solvents, such as DMF, *N,N′*-dimethylpropyleneurea (DMPU), and propylene carbonate (PPC) at 100 °C. The results are summarized in Table 1, and the chemiluminescence spectra are illustrated in Figure 2.

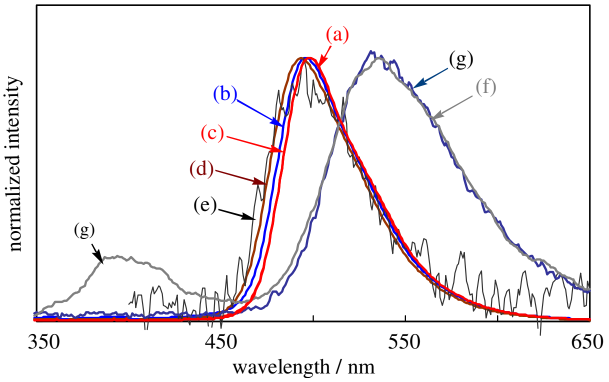


Figure 2. Chemiluminescence spectra for the SPD of **1** in (a) NMP, (b) DMF, (c) DMPU, (d) PPC, and (e) acetonitrile, and for the TD in (f) *p*-xylene and (g) DGM.

Table 1
Base-induced decomposition (BID) and solvent-promoted decomposition (SPD) of dioxetane **1**

Mode	Solvent[a]	Temp (°C)	λ_{max}^{CL} (nm)	Φ^{CL}[b]	$t_{1/2}$ (s)	k (s^{-1})
BID	NMP	45	498	0.29	2800	2.5×10^{-4}
BID	CH_3CN	45	492	0.28	1600	4.2×10^{-4}
BID	DMF	45	496	0.29	2200	3.1×10^{-4}
BID	DMSO	45	495	0.35	1600	4.3×10^{-4}
SPD	NMP	100	498	0.25	87	8.0×10^{-3}
SPD	DMF	100	496	0.23	57	1.2×10^{-2}
SPD	DMPU	100	498	0.25	270	2.6×10^{-3}
SPD	PPC	100	493	0.24	290	2.4×10^{-3}
SPD	CH_3CN	60	494	–[c]	–[c]	–[c]
TD	*p*-XL	100	536	0.0008	60000	1.2×10^{-5}
TD	DGM	100	403,535	–[c]	–[c]	–[c]

[a] NMP: *N*-methylpyrrolidone, DMPU: *N,N′*-dimethylaminopropyleneurea, PPC: propylene carbonate, *p*-XL: *p*-xylene, DGM: diethylene glycol dimethyl ether.

[b] Based on a value reported for the BID of 3-adamantylidene-4-(3-*tert*-butyldimethylsiloxyphenyl)-4-methoxy-1,2-dioxetane in TBAF/DMSO.[12]

[c] Not estimated.

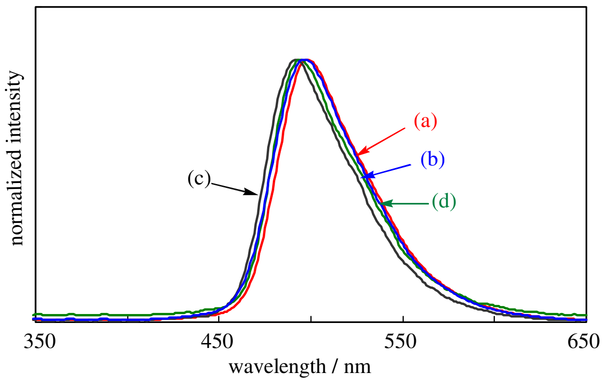
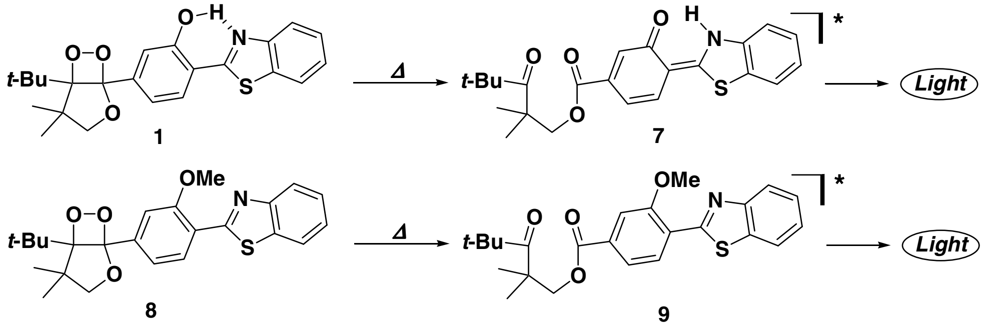


Figure 1. Chemiluminescence spectra for the BID of **1** in (a) NMP, (b) DMF, (c) acetonitrile, and (d) DMSO.

p-Xylene is a typical nonpolar solvent that is used often to examine the uncatalyzed thermal decomposition of dioxetanes.[13] Thus, we carried out the thermal decomposition (TD) of **1** in *p*-xylene to compare the behavior with that in an aprotic polar solvent. In *p*-xylene at 100 °C, dioxetane **1** decomposed to afford **6** with the emission of yellow light ($\lambda_{max}^{TD} = 536$ nm), though the efficiency, Φ^{TD}, was only 8×10^{-4} and the rate was very slow (rate constant $k^{TD} = 1.2 \times 10^{-5}\ s^{-1}$) (Table 1, Fig. 2). The small value for k^{TD} indicates that **1** underwent typical uncatalyzed TD in *p*-xylene, as reported for various analogs of dioxetane **1**,[14] in contrast to SPD. However, the chemiluminescence for the TD of **1** was observed at a longer wavelength than those for BID and SPD. This result was rather unexpected, since the chemiluminescence of TD due to a neutral hydroxybenzoate emitter generally shows a λ_{max}^{TD} shorter than that for the corresponding BID. In fact, the chemiluminescence spectrum for the TD of **4** appeared at a wavelength shorter than that for the BID: $\lambda_{max}^{TD} = 410$ nm, while $\lambda_{max}^{BID} = 466$–$470$ nm for **4**.[8] Based on reports that 2-(benzothiazol-2-yl)phenols display fluorescence due to ESIPT,[9,10] the emission of yellow light for the TD of **1** in *p*-xylene is presumably attributed to excited quinone methide **7** (Scheme 3). This idea was supported by the fact that methoxyphenyl-analog **8** of **1** underwent TD in *p*-xylene at 100 °C to give weak violet light with $\lambda_{max}^{TD} = 390$ nm, $\Phi^{TD} = 9.2 \times 10^{-4}$, and $k^{TD} = 4.3 \times 10^{-4}\ s^{-1}$ (Scheme 3). This result suggested that the TD of **1** would show chemiluminescence with λ_{max}^{TD} near 390 nm, if ESIPT did not occur. This expectation was realized when the TD of **1** was carried out in diethylene glycol dimethyl ether (diglyme) at 100 °C. As illustrated in Figure 2, the chemiluminescence spectrum showed a peak at 403 nm in addition to a peak at 535 nm due to ESIPT.

The effects of solvent on the thermal chemiluminescent decomposition of **1** described above are summarized as follows. First, SPD proceeded in an aprotic polar solvent to afford bright light with



Scheme 3. Thermal decomposition (TD) of **1** emitting light due to ESIPT and TD of **8**.

$\lambda_{max}^{SPD} = 492–498$ nm similar to BID by a CT-induced decomposition mechanism. Second, **1** underwent uncatalyzed TD to give excited **7** which emitted yellow light with $\lambda_{max}^{TD} = 536$ nm due to ESIPT in nonpolar *p*-xylene. In addition to the chemiluminescence due to ESIPT, light emission from neutral phenol **6** in the excited state was observed at $\lambda_{max}^{TD} = 403$ nm in diglyme.

It was important to elucidate whether SPD is mechanistically different from BID. Thus, the kinetics of the SPD of **1** was investigated in NMP as a representative solvent. SPD should be a consecutive reaction, which consists of the reversible formation of dioxetane bearing an oxidophenyl anion **2** or its solvated species that undergo CT-induced decomposition to give light. However, the reaction proceeded following practically first-order kinetics at 60–100 °C, as shown in Figure 3. On the other hand, both λ_{max}^{SPD} and Φ^{SPD} changed scarcely with the SPD reaction temperature. These results suggested that the thermodynamic profile of the reaction could be simply but meaningfully analyzed in terms of pseudo-first order kinetics. Based on the thus-measured rate constants, k^{SPD}s, at 60–100 °C, the thermodynamic parameters for the SPD of **1** in NMP were estimated from the Arrhenius plots to be free energy of activation $\Delta G^{\ddagger} = 99.3$ kJ mol^{-1}, enthalpy of activation $\Delta H^{\ddagger} = 82.4$ kJ mol^{-1}, and entropy of activation $\Delta S^{\ddagger} = -56.8$ J K^{-1} mol^{-1}.

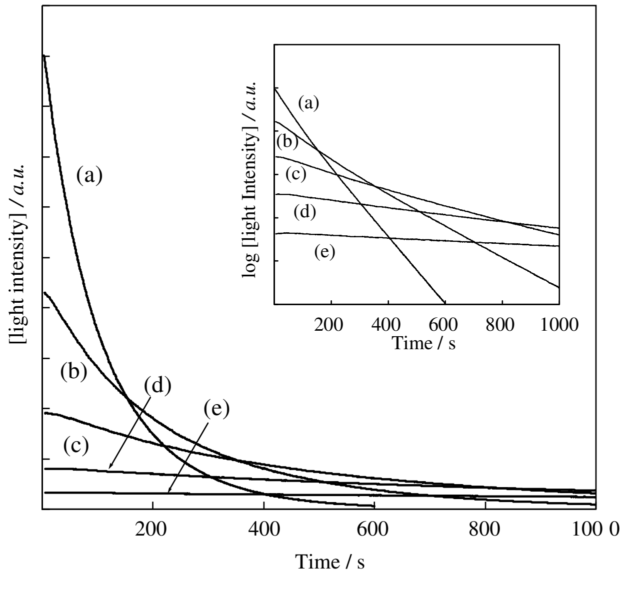
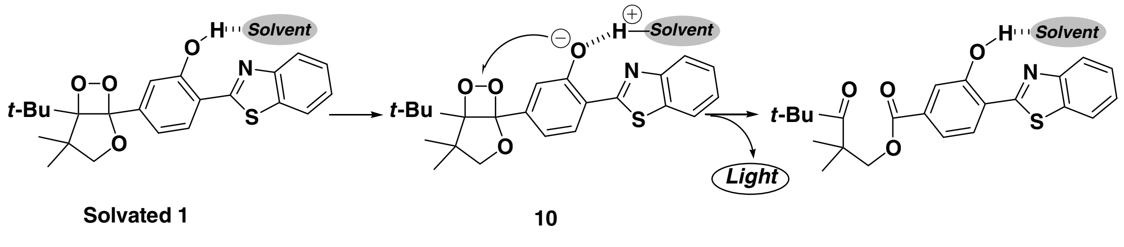


Figure 3. Time-course for SPD of **1** in NMP at (a) 100, (b) 90, (c) 80, (d) 70, and (e) 60 °C.

BID using TBAF in an aprotic polar solvent has been known to proceed following pseudo-first order kinetics independent of the concentration of TBAF when a large excess of TBAF is used. Thus, rate constants k^{BID} for **1** were measured using a large excess of TBAF in NMP at five points from 35 to 55 °C. The Arrhenius plots revealed that the activation parameters for BID were $\Delta G^{\ddagger} = 97.3$ kJ mol^{-1}, $\Delta H^{\ddagger} = 99.8$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 8.2$ J K^{-1} mol^{-1}. If we compare these activation parameters with those for SPD, we see that the entropy term of SPD has a large negative value in contrast to that of the BID. These results reveal that SPD proceeded through a transition state with considerably less disorder than that for BID. This is presumably attributed to the participation of hydrogen-bonding (HB) between NMP molecule(s) and a phenolic OH of **1**. Thus, an intermediary anionic dioxetane **10** was produced through HB as an ion pair with protonated NMP molecule(s) to cause SPD. A model scheme is illustrated in Scheme 4. On the other hand, the intermediary anion **2** should be slightly solvated or naked as an extreme for BID in an aprotic polar solvent such as NMP and DMSO especially with the use of TBAF.

According to the above suggestion, SPD is presumed to proceed effectively only in aprotic solvent with high ability of electron-pair donor (EPD) (proton acceptor) and low ability of electron-pair acceptor (EPA) (proton donor). This idea was consistent with the SPD in acetonitrile, as described below. Although acetonitrile (bp 81.6 °C) is an aprotic polar solvent that is suited for BID as shown in Table 1, it possesses lower ability of EPD and higher ability of EPA than NMP.[15–18] Upon heating in acetonitrile at 60 °C, the SPD of **1** also took place though very slowly and emission of light with λ_{max}^{SPD} at 494 nm was so weak that the Φ^{SPD} could not be estimated.



Scheme 4. Solvent-promoted decomposition (SPD).

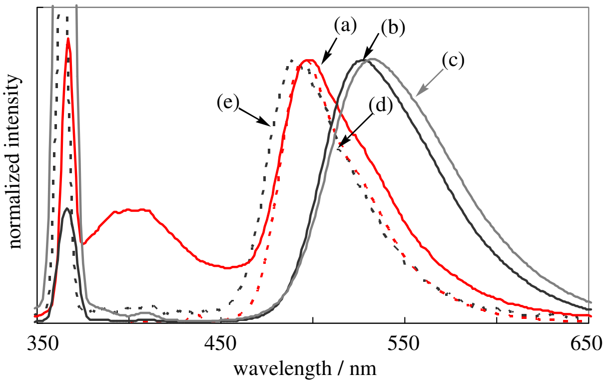


Figure 4. Fluorescence spectra of authentic **6** in (a) NMP, (b) acetonitrile, (c) *p*-xylene, and **3** generated from **6** in situ in (d) NMP and (e) acetonitrile.

A critical difference was seen in the fluorescence of authentic emitter keto ester **6** when dissolved in NMP, acetonitrile, and *p*-xylene. The fluorescence spectra of oxido anion **3** prepared from **6** in situ coincided with the corresponding chemiluminescence spectra for the BID of **1** in both NMP and acetonitrile (Fig. 4). On the other hand, the fluorescence of **6** showed a peak at $\lambda_{max} = 497$ nm together with a peak at $\lambda_{max} = 403$ nm due to neutral **6** in NMP without any additive base, while the fluorescence of **6** in acetonitrile ($\lambda_{max} = 527$ nm) resembled that in *p*-xylene ($\lambda_{max} = 530$ nm) rather than that in NMP (Fig. 4). These results show that considerable amount of oxido anion **3** existed together with neutral **6** in hot NMP, though little **3** exists in acetonitrile. These and the SPD results suggest that acetonitrile molecule(s) was capable of abstracting a phenolic proton of **1** to cause SPD, but the resulting excited species was quenched or the chemiexcitation process did not function effectively by backward protonation from acetonitrile molecule(s) or its protonated species. Anyway, SPD apparently related closely to characteristics as electron-pair donor (EPD)/electron-pair acceptor (EPA) and/or hydrogen-bond donor (HBD)/hydrogen-bond acceptor (HBA) for aprotic polar solvents, as illustrated typically by Gutmann's DN (donor number) and AN (acceptor number).[15–18] However, simple correlation between these parameters and chemiluminescence properties especially k^{SPD} could not be observed at present.

In conclusion, a variety of aprotic polar solvents were shown to promote the decomposition (SPD) of bicyclic dioxetane bearing a 4-(benzothiazol-2-yl)-3-hydroxyphenyl moiety **1** to emit light as effectively as the BID of **1** in an aprotic polar solvent. SPD caused intramolecular CT-induced chemiluminescence, similar to BID, though the SPD reaction proceeded through a pathway with a large negative entropy of activation in contrast to BID. Furthermore, uncatalyzed decomposition of dioxetane **1** was found to occur to give light due to ESIPT in *p*-xylene.

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References and notes

1. Beck, S.; Köster, H. *Anal. Chem.* **1990**, *62*, 2258–2270.
2. Adam, W.; Reihardt, D.; Saha-Möller, C. R. *Analyst* **1996**, *121*, 1527–1531.
3. Matsumoto, M. *J. Photochem. Photobiol. C: Photochem. Rev.* **2004**, *5*, 27–53.
4. Matsumoto, M.; Watanabe, N. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1899–1920.
5. Adam, W. In *The Chemistry of Peroxide*; Patai, S., Ed.; Wiley: New York, 1983; p 829.
6. Adam, W. In *Small Ring Heterocycles*; Hassner, A., Ed.; Wiley: New York, 1986; p 351.
7. The BID of **1** has been reported to show chemiluminescence effectively in acetonitrile and even in water.[8]
8. Matsumoto, M.; Akimoto, T.; Matsumoto, Y.; Watanabe, N. *Tetrahedron Lett.* **2005**, *46*, 6075–6078.
9. Ikegami, M.; Arai, T. *J. Chem. Soc., Perkin Trans.* **2002**, *2*, 1296–1301. See also references cited therein.
10. Rodembusch, F. S.; Campo, L. F.; Stefani, V.; Rigacci, A. *J. Mater. Chem.* **2005**, *15*, 1537–1541. See also references cited therein.
11. Authentic epoxide **5** was exclusively produced by reduction of **1** with triphenyl phosphine.
12. Trofimov, A. V.; Mielke, K.; Vasil'ev, R. F.; Adam, W. *Photochem. Photobiol.* **1996**, *63*, 463–467.
13. Baumstark, A. L. In *The 1,2-Dioxetane Ring System: Preparation, Thermolysis, and Insertion Reactions in Singlet O2*; Frimer, A. A., Ed.; CRC: Florida, 1985; Vol. II, pp 1–35.
14. Matsumoto, M.; Murakami, H.; Watanabe, N. *Chem. Commun.* **1998**, 2319–2320.
15. Gutmann, V. *The Donor–Acceptor Approach to Molecular Interaction*; Plenum Press: New York, 1978.
16. Reichardt, C. *Solvent Effects in Organic Chemistry*; Chemie: Weinheim, 1987.
17. Chastrette, M. *Tetrahedron* **1979**, *35*, 1441–1448.
18. Maria, P.-C.; Gal, J.-F.; de Franceschi, J.; Fargin, E. *J. Am. Chem. Soc.* **1987**, *109*, 483–492.