JOC Article
pubs.acs.org/joc

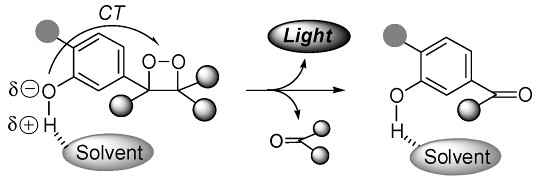
Intramolecular Charge-Transfer-Induced Decomposition Promoted by an Aprotic Polar Solvent for Bicyclic Dioxetanes Bearing a 4-(Benzothiazol-2-yl)-3-hydroxyphenyl Moiety

Masatoshi Tanimura, Nobuko Watanabe, Hisako K. Ijuin, and Masakatsu Matsumoto*

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

matsumo-chem@kanagawa-u.ac.jp

Received November 3, 2010



Bicyclic dioxetanes **3a**−**d** bearing a 4-(benzothiazol-2-yl)-3-hydroxyphenyl group decomposed to give the corresponding keto esters **4a**−**d** accompanied by the emission of bright light when simply dissolved in an aprotic polar solvent such as *N*-methylpyrrolidone (NMP) or DMF at 50−100 °C. This solvent-promoted decomposition (SPD) was effectively a chemiluminescence process caused by the hydrogen bonding of a phenolic OH with a solvent molecule(s). The characteristics of the chemiluminescence in SPD resembled those in base-induced decomposition (BID), which occurs through an oxidoaryl-substituted dioxetane **5** by an intramolecular charge-transfer-induced decomposition (CTID) mechanism. Both free energies of activation, $\Delta G^{\ddagger}_{\mathrm{SPD}}$ and $\Delta G^{\ddagger}_{\mathrm{BID}}$, increased in the order **3a** < **3b** < **3c** < **3d**, and were linearly correlated with each other. However, SPD showed features different from those of BID in terms of enthalpy of activation and entropy of activation. SPD had large negative values for $\Delta S^{\ddagger}$ (ca. −71 J mol^{-1} K^{-1}) regardless of the substituent R at the 5-position for **3a**−**d**, while the $\Delta S^{\ddagger}$ values for BID changed from 0.5 to −22 J mol^{-1} K^{-1} as R became smaller. The enthalpy of activation $\Delta H^{\ddagger}$ for SPD was 14−21 kJ mol^{-1} smaller than that for BID.

Introduction

The high-energy molecule 1,2-dioxetane typically undergoes two types of decomposition leading to chemiexcitation. The first is uncatalyzed thermal decomposition (TD), which mainly gives a triplet-excited carbonyl fragment, and the emission of bright light is hardly expected.[1,2] The other is the intramolecular charge-transfer-induced decomposition (CTID) of a dioxetane bearing an aromatic electron donor, which effectively gives a singlet-excited species.[1,3−7] For example, the deprotonation of hydroxyaryl-substituted dioxetane **1** with a base produces unstable dioxetane **2** bearing an oxidoaryl anion as an excellent electron donor that undergoes CTID accompanied by the emission of bright light (Scheme 1).[3,8] In addition to such base-induced CTID (BID), we have identified a new type of CTID, which we call solvent-promoted decomposition (SPD). For SPD, dioxetane **1**

---

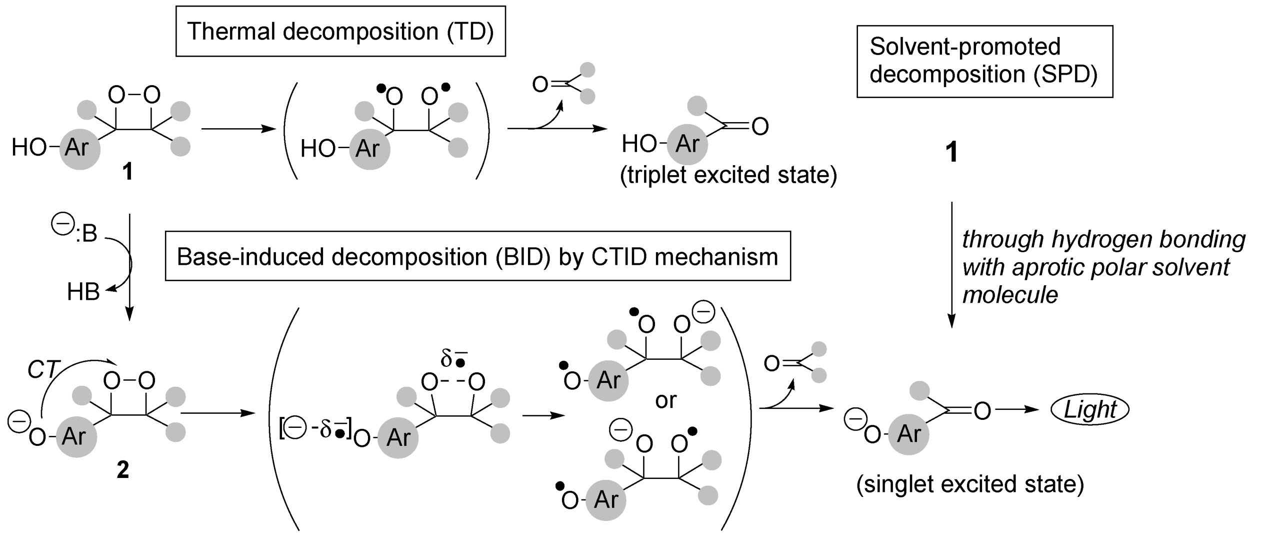
[1] (a) Bartlett, P. D.; Landis, M. E. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; pp 243−286. (b) Adam, W. In *The Chemistry of Peroxide*; Patai, S., Ed.; Wiley: New York, 1983; pp 829−920. (c) Adam, W. In *Small Ring Heterocycles*; Hassner, A., Ed.; Wiley: New York, 1986; pp 351−429. (d) Adam, W.; Heil, M.; Mosandl, T.; Saha-Möller, C. R. In *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1992; pp 221−254. (e) Saha-Möller, C. R.; Adam, W. In *Comprehensive Heterocyclic Chemistry II. A Review of the Literature 1982−1995*; Padwa, A., Ed.; Pergamon: New York, 1996; pp 1041−1082. (f) Adam, W.; Trofimov, A. V. In *The Chemistry of Peroxides*; Rappoport, Z., Ed.; Wiley: New York, 2006; Vol. 2, pp 1171−1209. (g) Baader, W. J.; Stevani, C. V.; Bastos, E. L. In *The Chemistry of Peroxides*; Rappoport, Z., Ed.; Wiley: New York, 2006; Vol. 2, pp 1211−1278.

[2] (a) Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1974**, *96*, 7578–7589. (b) Turro, N. J.; Lechtken, P.; Shore, N. E.; Schuster, G.; Steinmetzer, H.-C.; Yekta, A. *Acc. Chem. Res.* **1974**, *7*, 105–106. (c) Adam, W.; Baader, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 410–416. (d) Reguero, M.; Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M. *J. Am. Chem. Soc.* **1991**, *113*, 1566–1572. (e) Wilson, T.; Halpern, A. M. *J. Phys. Org. Chem.* **1995**, *8*, 359–363. (f) Vasil'ev, R. F. *J. Biolumin. Chemilumin.* **1998**, *13*, 69–74. (g) Tanaka, C.; Tanaka, J. *J. Phys. Chem. A* **2000**, *104*, 2078–2090.

[3] (a) Beck, S.; Köster, H. *Anal. Chem.* **1990**, *62*, 2258–2270. (b) Adam, W.; Reihardt, D.; Saha-Möller, C. R. *Analyst* **1996**, *121*, 1527–1531. (c) Matsumoto, M. *J. Photochem. Photobiol., C* **2004**, *5*, 27–53. (d) Matsumoto, M.; Watanabe, N. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1899–1920. (e) Adam, W.; Trofimov, A. V. In *The Chemistry of Peroxides*; Rappoport, Z., Ed.; Wiley: New York, 2006; Vol. 2, pp 1171−1209.

DOI: 10.1021/jo1021822

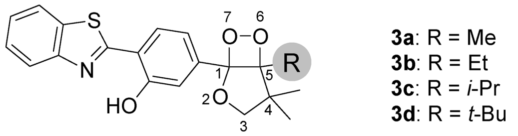
SCHEME 1. **Thermal Decomposition, Base-Induced Decomposition, and Solvent-Promoted Decomposition by a CTID Mechanism for a Hydroxyaryl-Substituted Dioxetane**



decomposed to give bright light without the aid of a strong base in an aprotic polar solvent.[9,10] We report here the detailed features of SPD and the differences in its thermodynamic aspects compared to those of BID.

In this work, we investigated SPD and BID for a series of bicyclic dioxetanes possessing an alkyl group on the same skeleton to understand their characteristics from the perspective of a substituent effect. The bicyclic dioxetanes selected for the present investigation were 1-[4-(benzothiazol-2-yl)-3-hydroxyphenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptanes **3a−d** with an alkyl group R at the 5-position: **3a**, R = methyl; **3b**, R = ethyl; **3c**, R = isopropyl; and **3d**, R = *tert*-butyl, as illustrated in Chart 1. For dioxetanes **3a−d**, the thermodynamic aspects of BID in acetonitrile and TD in *p*-xylene have very recently been disclosed.[11] Therefore, we thought that these dioxetanes would be suitable for easily understanding the characteristic features of SPD.

CHART 1. **Bicyclic Dioxetanes 3a−d Bearing a 4-(Benzothiazol-2-yl)-3-hydroxyphenyl Group**



Results and Discussion

1. Solvent-Promoted Decomposition and Base-Induced Decomposition for Bicyclic Dioxetanes Bearing a 4-(Benzothiazol-2-yl)-3-hydroxyphenyl Group. Dioxetanes **3a−d** were thermally stable and essentially did not decompose in a nonpolar solvent such as *p*-xylene at room temperature: their half-lives have been estimated to be 1−43 y at 25 °C in *p*-xylene.[11] However, **3a−d** decomposed to emit weak green light even at room temperature, when they were simply dissolved in NMP (*N*-methylpyrrolidone). Thus, we investigated the properties of the chemiluminescence for this solvent-promoted decomposition (SPD). On heating at 60 °C in NMP, **3a** underwent SPD according to first-order kinetics to give bright light with a maximum wavelength of $\lambda_{max}{}^{SPD}$ = 499 nm, rate of SPD, $k^{SPD} = 1.6 \times 10^{-2}\ s^{-1}$, and chemiluminescence efficiency, $\Phi^{SPD} = 0.25$.[12,13] Dioxetanes **3b−d** similarly decomposed at 60 °C in NMP to give bright light. Their

---

(4) The chemiluminescent (CL) decomposition of dioxetanes bearing an aromatic electron donor has been proposed to proceed via the intramolecular CIEEL (chemically initiated electron exchange luminescence) mechanism,[1,3,5] where an initially formed radical ion pair is annihilated by back electron transfer (BET) to give an excited aromatic carbonyl compound. However, the question of whether such a CL reaction includes BET as a fundamental process is still being argued and remains unclear.[6,7] Therefore, we have recently been using the term CTID, which includes CIEEL and other CT-induced mechanisms.

(5) (a) Koo, J.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1977**, *99*, 6107–6109. (b) Koo, J.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 4496–4503. (c) Zaklika, K. A.; Kissel, T.; Thayer, A. L.; Burns, P. A.; Schaap, A. P. *Photochem. Photobiol.* **1979**, *30*, 35–44. (d) Catalani, L. H.; Wilson, T. *J. Am. Chem. Soc.* **1989**, *111*, 2633–2639. (e) McCapra, F. J. *Photochem. Photobiol., A* **1990**, *51*, 21–28. (f) McCapra, F. In *Chemiluminescence and Bioluminescence*; Hastings, J. W., Kricka, L. J., Stanley, P. E., Eds.; Wiley: New York, 1996; pp 7−15. (g) Adam, W.; Bronstein, I.; Trofimov, T.; Vasil'ev, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 958–961. (h) Adam, W.; Matsumoto, M.; Trofimov, T. *J. Am. Chem. Soc.* **2000**, *122*, 8631–8634. (i) Nery, A. L. P.; Weiss, D.; Catalani, L. H.; Baader, W. J. *Tetrahedron* **2000**, *56*, 5317–5327.

(6) (a) Catalani, L. H.; Wilson, T. *J. Am. Chem. Soc.* **1989**, *111*, 2633–2639. (b) McCapra, F. J. *Photochem. Photobiol., A* **1990**, *51*, 21–28. (c) Wilson, T. *Photochem. Photobiol.* **1995**, *62*, 601–606.

(7) (a) Takano, Y.; Tsunesada, T.; Isobe, H.; Yoshioka, Y.; Yamaguchi, K.; Saito, I. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 213–225. (b) Tanaka, J.; Tanaka, C.; Matsumoto, M. In *Bioluminescence and Chemiluminescence*; Tsuji, A., Matsumoto, M., Maeda, M., Kricka, L. J., Stanley, P. E., Eds.; World Scientific: Singapore, 2004; pp 205−208. (c) Tanaka, C.; Tanaka, J.; Matsumoto, M. In *Bioluminescence and Chemiluminescence*; Tsuji, A., Matsumoto, M., Maeda, M., Kricka, L. J., Stanley, P. E., Eds.; World Scientific: Singapore, 2004; pp 209−212. (d) Isobe, H.; Takano, Y.; Okumura, M.; Kuramitsu, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2005**, *127*, 8667–8679.

(8) (a) Schaap, A. P.; Gagnon, S. D. *J. Am. Chem. Soc.* **1982**, *104*, 3504–3506. (b) Schaap, A. P.; Handley, R. S.; Giri, B. P. *Tetrahedron Lett.* **1987**, *28*, 935–938. (c) Schaap, A. P.; Chen, T. S; Handley, R. S.; DeSilva, R.; Giri, B. P. *Tetrahedron Lett.* **1987**, *28*, 1155–1158.

(9) Part of this work has been reported as a preliminary communication.[10]

(10) Matsumoto, M.; Tanimura, M.; Akimoto, T.; Watanabe, N.; Ijuin, H. K. *Tetrahedron Lett.* **2008**, *49*, 4170–4173.

(11) Tanimura, M.; Watanabe, N.; Ijuin, H. K.; Matsumoto, M. *J. Org. Chem.* **2010**, *75*, 3678–3684.

(12) Φ^{CL} was estimated based on the value 0.29 for the chemiluminescent decomposition of 3-adamantylidene-4-(3-*tert*-butyldimethylsiloxyphenyl)-4-methoxy-1,2-dioxetane in a TBAF/DMSO system.[13]

(13) Trofimov, A. V.; Mielke, K.; Vasil'ev, R. F.; Adam, W. *Photochem. Photobiol.* **1996**, *63*, 463–467.

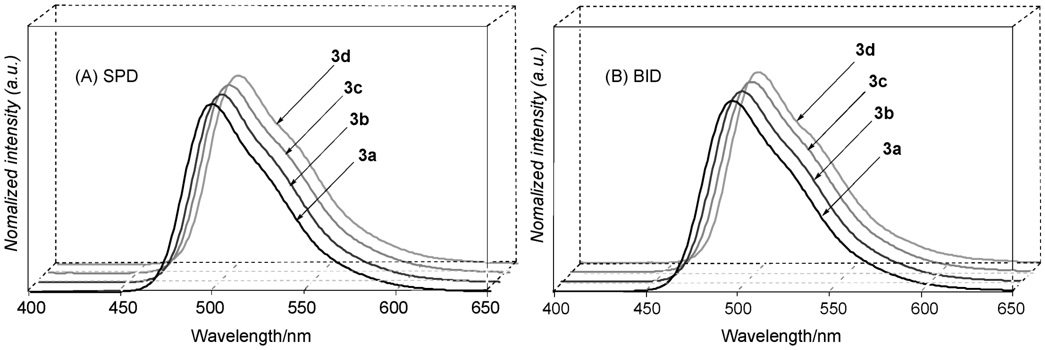


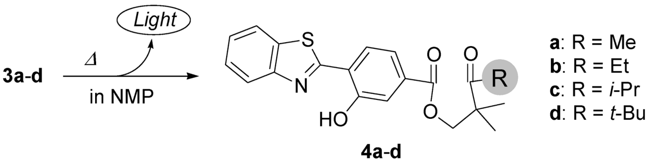
FIGURE 1. Chemiluminescence spectra of dioxetanes **3a**–**d** for SPD in NMP and BID in a TBAF/NMP system.

TABLE 1. Solvent-Promoted Decomposition (SPD) of Dioxetanes 3a–d

dioxetane	solvent[a]	temp/°C	λ_{max}^{SPD}/nm	Φ^{SPD} [b]	k^{SPD}/s^{-1}
3a	NMP	60	499	0.25	1.6×10^{-2}
3b	NMP	60	499	0.25	1.1×10^{-2}
3c	NMP	60	498	0.25	2.8×10^{-3}
3d	NMP	60	498	0.23	6.3×10^{-4}
3c	NMP	100	498	0.23	3.0×10^{-2}
3d	NMP	100	498	0.23[c]	1.5×10^{-2} [c]
3d	DMSO	100	497	1.3×10^{-3}	–[d]
3c	DMF	100	496	0.22	3.6×10^{-2}
3d	DMF	100	496	0.23	1.2×10^{-2}
3c	DMPU	100	498	0.25	1.0×10^{-2}
3d	DMPU	100	498	0.25	2.6×10^{-3}
3c	PPC	100	493	0.25	8.2×10^{-3}
3d	PPC	100	493	0.24	2.4×10^{-3}
3d	EGM	100	498	7.3×10^{-5}	8.0×10^{-4}

[a] NMP: *N*-methylpyrrolidone. DMPU: *N*,*N*′-dimethylpropyleneurea. PPC: propylene carbonate. EGM: ethylene glycol monomethyl 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.[12,13] [c] Values reported in ref 10 are revised. [d] Not estimated.

SCHEME 2. Solvent-Promoted Chemiluminescent Decomposition of Bicyclic Dioxetanes 3a–d in NMP



chemiluminescence spectra and properties are summarized together with those for **3a** in Figure 1A and Table 1, respectively. Table 1 shows that SPD was an effective chemiluminescence process for **3a**–**d**. Note that the reaction mixture of **3a**–**d** after SPD exclusively gave the corresponding keto esters **4a**–**d** (Scheme 2).

One of our initial interests was to determine what kind of solvent promoted the chemiluminescent decomposition of dioxetanes **3**. Thus, SPD was examined with **3d** as a representative compound at 100 °C in various solvents. As shown in Figure 2 and Table 1, aprotic polar solvents such as DMF, DMPU (*N*,*N*′-dimethylpropyleneurea), and PPC (propylene carbonate) were as equally effective as NMP for SPD of **3d**. DMSO was not suitable for SPD, since **3d** was effectively reduced to an epoxide (Supporting Information): Φ^{SPD} was only 1/180 of that in NMP. When the reaction mixture was heated in ethylene glycol monomethyl ether (EGM) as a representative protic solvent with a high boiling point, the decomposition of **3d** occurred, although Φ^{SPD} was quite low, as shown in Table 1. Dioxetane **3c** as another representative also effectively underwent CTID in DMF, DMPU, or PPC as shown in Table 1.

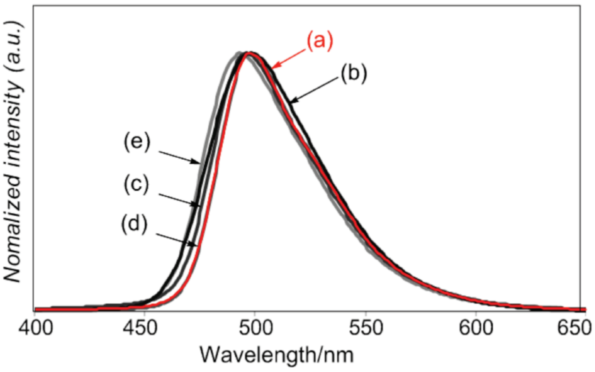


FIGURE 2. Chemiluminescence spectra for the SPD of dioxetane **3d** in (a) NMP, (b) DMSO, (c) DMF, (d) DMPU, and (e) PPC.

TABLE 2. Base-Induced Decomposition (BID) of Dioxetanes 3a–d in a TBAF/NMP System[a]

dioxetane	λ_{max}^{BID}/nm	Φ^{BID} [b]	k^{BID}/s^{-1}	$t_{1/2}^{BID}$/s[c]
3a	498	0.25	5.3×10^{-3}	130
3b	498	0.24	3.9×10^{-3}	180
3c	498	0.24	8.0×10^{-4}	870
3d	497	0.24	1.5×10^{-4}	4500

[a] BID was carried out at 40 °C. [b] Based on a value reported for the BID of 3-adamantylidene-4-(3-*tert*-butyldimethylsiloxyphenyl)-4-methoxy-1,2-dioxetane in TBAF/DMSO.[12,13] [c] Half-life = ln 2/k^{BID}.

Notably, acetonitrile hardly functioned as a solvent for SPD of **3a**–**d**, although it is a typical aprotic polar solvent with a dielectric constant that is as large as that of NMP.[14] This finding and the results summarized in Table 1 show that chemiluminescent SPD appeared to effectively take place only in an aprotic polar solvent that was a strong proton acceptor and a weak proton donor.[15–17] Thus, SPD should proceed under the strong participation of hydrogen bonding between a phenolic hydroxyl group of **3** and solvent molecule(s).

---

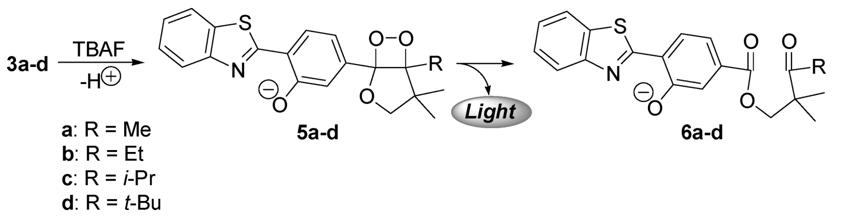
(14) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; Wiley-VCH: Weinheim, Germany, 2003.

(15) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interaction*; Plenum Press: New York, 1978.

(16) Chastrette, M. *Tetrahedron* **1979**, *35*, 1441–1448.

(17) Maria, P.-C.; Gal, J.-F.; de Franceschi, J.; Fargin, E. *J. Am. Chem. Soc.* **1987**, *109*, 483–492.

SCHEME 3. TBAF-Induced Decomposition of Dioxetanes 3a−d



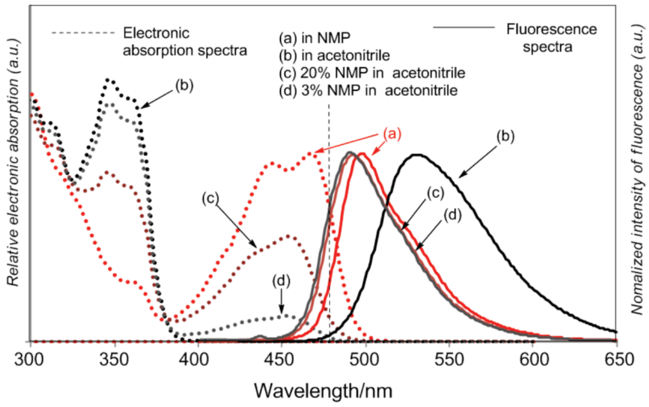


FIGURE 3. Electronic absorption spectra and fluorescence spectra of **4c** in (a) NMP, (b) acetonitrle, and (c, d) NMP/acetonitrile mixed solvent.

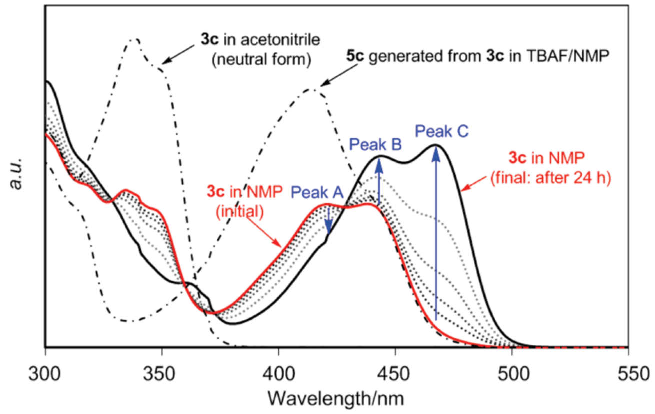


FIGURE 4. Time course for SPD of dioxetane **3c** monitored by electronic absorption spectrum in NMP.

We next investigated the base-induced decomposition (BID) of **3a−d** in NMP to understand how it compared to the less-common SPD. Upon treatment with a large excess of tetrabutylammonium fluoride (TBAF) in NMP at 40 °C, **3a−d** decomposed according to pseudo-first-order kinetics to effectively give light, the spectrum of which is shown in Figure 1B.[11,18] As summarized in Table 2, the results show that both the efficiency and maximum wavelength of chemiluminescence for BID in NMP coincided with those for SPD (Table 1). The spent reaction mixtures of **3a−d** gave the corresponding keto esters **4a−d** in high yields after careful neutralization. When authentic keto esters **4a−d** were dissolved in a TBAF/NMP solution, they showed fluorescence, the spectra of which coincided with the chemiluminescence spectra for BID of **3a−d** in NMP. These results strongly suggest that BID of **3a−d** produced an oxido anion of keto esters **6a−d** in an excited state through dioxetanes **5a−d** bearing an oxidophenyl anion (Scheme 3).

Thus, the electronic absorption and fluorescence spectra of keto ester **4** were investigated to clarify the situation of **4** dissolved without any base in NMP (SPD conditions). When **4c** as a representative was simply dissolved in NMP at 25 °C, an electronic absorption spectrum was observed at $\lambda_{max}{}^{ab}$ = 444 and 467 nm and a fluorescence spectrum was observed at $\lambda_{max}{}^{fl}$ = 498 nm (Figure 3). Both spectra coincided with those for **6c** generated from **4c** in a TBAF/NMP system. These results strongly suggested that **4c** existed as anion **6c** or its closely related species even when dissolved simply in NMP. On the other hand, when dissolved in acetonitrile, **4c** showed an absorption spectrum at $\lambda_{max}{}^{ab}$ = 347 and 360 nm, which was considerably different than that in NMP, and a fluorescence spectrum at $\lambda_{max}{}^{fl}$ = 530 nm, rather than at $\lambda_{max}{}^{fl}$ = 498 nm, due to ESIPT (excited state intramolecular proton transfer).[19] Figure 3 shows these differences in the electronic spectra of **4c** between NMP and acetonitrile. Figure 3 shows also that the electronic absorption and fluorescence spectra of **4c** changed depending on the concentration of NMP in acetonitrile, and only 3 w/w % NMP was needed to generate **6c** or its closely related species to some extent.

We next attempted to understand the features of dioxetane **3c** dissolved in NMP. We expected that **3c** would exist in a concentration that was sufficient to show characteristic electronic absorption spectrum,[20] since **3c** was estimated to have a moderate lifetime at 25 °C ($t_{1/2} \approx 2$ h, vide infra) in NMP, though a solution of **3c** in NMP always included decomposition product **4c**. A freshly prepared solution of **3c** in NMP showed an absorption spectrum with peak **A** at $\lambda_{max}{}^{ab}$ = 420 nm and peak **B** at $\lambda_{max}{}^{ab}$ = 438 nm. The time-course of the electronic absorption spectrum monitored for SPD of **3c** in NMP showed that peak **A** gradually decreased and finally disappeared, while peak **B** increased with accompanying slight red-shift, and a new peak **C** due to **6c** appeared and increased (Figure 4).

As a reference, we measured an electronic absorption spectrum of anionic dioxetane **5c**, which was generated from **3c** by using a large excess of TBAF in NMP: **5c** was

---

[18] BID of **3a−d** has been reported to show $\lambda_{max}{}^{CL}$ = 492 nm and Φ^{CL} = 0.27−0.28 in a TBAF/acetonitrile system.[11]

[19] (a) Ikegami, M.; Arai, T. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1296–1301. (b) Rodembusch, F. S.; Campo, L. F.; Stefani, V.; Rigacci, A. *J. Mater. Chem.* **2005**, *15*, 1537–1541. See also references cited therein.

[20] The fluorescence spectrum due to **3c** itself dissolved in NMP could not be observed: even an NMP solution with freshly dissolved **3c** showed a fluorescence and/or chemiluminesnce spectrum with $\lambda_{max}{}^{CL}$ = 498 nm due to **6c** and/or SPD of **3c**.

[21] When **3** is treated with a large excess of TBAF in acetonitrile or NMP, **5** would be exclusively produced.

TABLE 3. Activation Parameters of SPD, BID, and TD for Dioxetanes 3a−d

	activation parameter	3a	3b	3c	3d[e]
SPD[a]	$\Delta H^{\ddagger}_{SPD}$/kJ mol^{-1}	69.4 ± 0.5	69.8 ± 0.5	74.7 ± 0.3	79.4 ± 0.5
	$\Delta S^{\ddagger}_{SPD}$/J mol^{-1}K^{-1}	−71.8 ± 0.8	−73.6 ± 0.8	−70.7 ± 0.5	−69.1 ± 0.7
	$\Delta G^{\ddagger}_{SPD}$/kJ mol^{-1}	90.8 ± 0.6	91.8 ± 0.6	95.8 ± 0.4	100 ± 0.6
BID[b]	$\Delta H^{\ddagger}_{BID}$/kJ mol^{-1}	83.5 ± 0.5	86.5 ± 0.4	93.2 ± 0.2	99.9 ± 0.3
	$\Delta S^{\ddagger}_{BID}$/J mol^{-1}K^{-1}	−22.0 ± 0.2	−15.2 ± 0.1	−6.9 ± 0.0	0.5 ± 0.0
	$\Delta G^{\ddagger}_{BID}$/kJ mol^{-1}	90.0 ± 0.6	91.0 ± 0.4	95.3 ± 0.2	99.7 ± 0.3
TD[c]	$\Delta H^{\ddagger}_{TD}$/kJ mol^{-1}	115 ± 0	114 ± 1	115 ± 1	124 ± 1
	$\Delta S^{\ddagger}_{TD}$/J mol^{-1}K^{-1}	−6.0 ± 0.0	−10.8 ± 0.1	−21.3 ± 0.3	−8.4 ± 0.1
	$\Delta G^{\ddagger}_{TD}$/kJ mol^{-1}	117.0 ± 0.1	117.4 ± 0.8	121 ± 1	126 ± 1
$-\sigma^{*}$[d]		0	0.10	0.19	0.30
$-E_s$[d]		0	0.08	0.48	1.43

[a] At 50−100 °C in NMP. [b] At 35−60 °C in TBAF/NMP. [c] At 80−120 °C in *p*-xylene.[11] [d] Taft's steric parameters for R. $-\sigma^{*}$: polar substituent constants. $-E_s$: steric substituent constant.[22] R is Me for **3a**, Et for **3b**, *i*-Pr for **3c**, and *t*-Bu for **3d**. [e] Values for SPD and TD of **3d** reported in ref 10 are revised.

estimated to have a half-life of ca. 1.5 h at 25 °C (vide infra). The thus-measured absorption spectrum of **5c** showed $\lambda_{max}{}^{ab}$ at 415 nm (Figure 4). On the other hand, when dissolved in acetonitrile, **3c** showed an absorption spectrum with peaks at $\lambda_{max}{}^{ab}$ = 291 and 338 nm, which was most likely due to neutral dioxetane **3c** itself (Figure 4). These results suggested that the features of **3c** dissolved in NMP were significantly different from those of both anion **5c** and neutral **3c**.

2. Thermodynamic Aspects of Solvent-Promoted Decomposition and Base-Induced Decomposition of Bicyclic Dioxetanes Bearing a 4-(Benzothiazol-2-yl)-3-hydroxyphenyl Group in NMP. We previously stated that SPD resembled BID in terms of its chemiluminescence spectra and efficiencies and that SPD, like BID, proceeded according to (pseudo-)first-order kinetics. On the other hand, experiments of electronic absorption spectra suggested that dioxetane **3c** dissolved in NMP was apparently different from oxido-anion **5c** generated from **3c** in TBAF/NMP or from neutral **3c** in acetonitrile. Thus, we attempted to elucidate how SPD was mechanistically similar to or different from BID.

We investigated the thermodynamic aspects of SPD as well as BID in NMP with regard to the substituent effect for **3a−d**. The time-course of decomposition was monitored at 35−60 °C for BID and at 50−100 °C for SPD. Notably, the reaction temperature did not affect the maximum wavelength or the efficiency of chemiluminescence for either SPD or BID of any of the dioxetanes **3a−d**. By using the measured rate constants, we estimated activation parameters from Eyring plots, i.e., enthalpy of activation $\Delta H^{\ddagger}$, entropy of activation $\Delta S^{\ddagger}$, and free energy of activation $\Delta G^{\ddagger}$. The results are summarized in Table 3, which also shows activation parameters for TD of **3a−d** in *p*-xylene.[11]

Table 3 shows that all of the free energies of activation, i.e., $\Delta G^{\ddagger}_{SPD}$, $\Delta G^{\ddagger}_{BID}$, and $\Delta G^{\ddagger}_{TD}$, increased in the order **3a** < **3b** < **3c** < **3d**. Thus, the dependency of $\Delta G^{\ddagger}$ on the substituent R apparently resembled that among TD, BID, and SPD for dioxetanes **3a−d**. Figure 5 shows the relationships between $\Delta G^{\ddagger}_{SPD}$ and $\Delta G^{\ddagger}_{BID}$ and between $\Delta G^{\ddagger}_{SPD}$ and $\Delta G^{\ddagger}_{TD}$ for **3a−d**. We can see from Figure 5 that SPD was linearly related to BID rather than to TD in terms of $\Delta G^{\ddagger}$. To better understand the thermodynamic aspects of these decompositions, we analyzed the substituent effect in these decompositions by the use of Taft's dual substituent parameter (DSP):

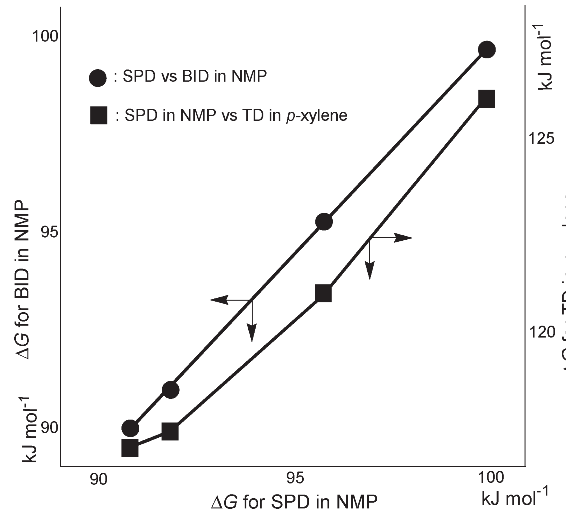


FIGURE 5. Relationship of $\Delta G^{\ddagger}_{SPD}$ to $\Delta G^{\ddagger}_{BID}$ and to $\Delta G^{\ddagger}_{TD}$ for dioxetanes **3a−d**.

$\log(k/k_0) = \rho^{*}\sigma^{*} + \delta E_s$, where σ^{*} is a polar substituent constant and E_s is a steric substituent constant.[22] DSP can be applied to $\Delta G^{\ddagger}$, since log *k* at a given temperature is proportional to the free energy of activation $\Delta G^{\ddagger}$. Thus, by using the values for $\Delta G^{\ddagger}$s, σ^{*}, and E_s in Table 3, we estimated that $\rho^{*} = -16 \pm 11$ kJ mol^{-1} and $\delta = -3.4 \pm 2.2$ kJ mol^{-1} for $\Delta G^{\ddagger}_{SPD}$ ($R^2 = 0.98$), and $\rho^{*} = -17 \pm 13$ kJ mol^{-1} and $\delta = -3.6 \pm 2.5$ kJ mol^{-1} for $\Delta G^{\ddagger}_{BID}$ ($R^2 = 0.98$). Although these values have rather large standard deviations, we can see that SPD and BID resembled each other and were sensitive to the polarity of the alkyl substituents R at the 5-position in terms of the response of $\Delta G^{\ddagger}$.

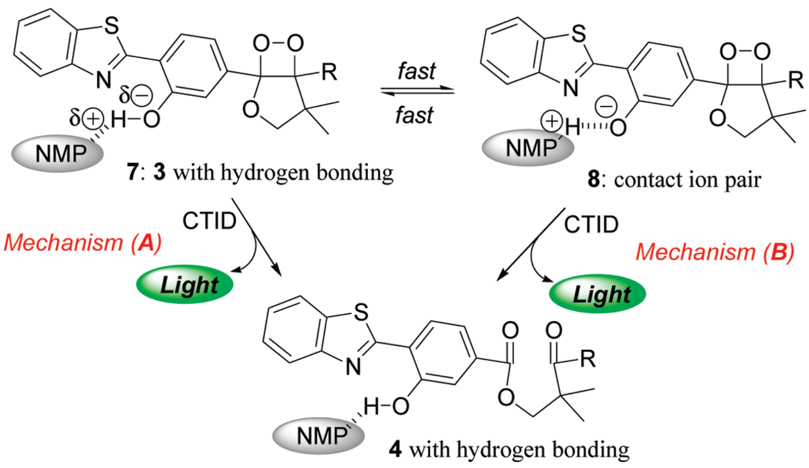
However, SPD showed features different from those of BID in terms of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Table 3). SPD proceeded with $\Delta H^{\ddagger}$ far smaller than that for BID: $\Delta H^{\ddagger}_{BID} - \Delta H^{\ddagger}_{SPD}$ = 14−21 kJ mol^{-1}, though both $\Delta H^{\ddagger}_{SPD}$ and $\Delta H^{\ddagger}_{BID}$ increased in the order **3a** < **3b** < **3c** < **3d**. The substituent effect on $\Delta H^{\ddagger}$ for SPD was more similar to that of TD than to that of BID. Thus, the difference in $\Delta H^{\ddagger}_{SPD}$, i.e. $\Delta\Delta H^{\ddagger}_{SPD}$, between **3d** and **3a**, which represents the extremes of bulkiness of the substituent R among **3**, was considerably smaller than $\Delta\Delta H^{\ddagger}_{BID}$ and was nearly equal to $\Delta\Delta H^{\ddagger}_{TD}$: $\Delta\Delta H^{\ddagger}$ = 9, 10, and 16 kJ mol^{-1} for $\Delta H^{\ddagger}_{TD}$, $\Delta H^{\ddagger}_{SPD}$, and $\Delta H^{\ddagger}_{BID}$, respectively.

The greatest difference in the thermodynamic aspects of SPD from those of BID and TD was in the entropy of activation $\Delta S^{\ddagger}$. For BID of **3a−d** in TBAF/NMP, $\Delta S^{\ddagger}$ varied

---

(22) (a) Taft, W., Jr. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; pp 556−675. (b) MacPhee, J. A.; Panaye, A.; Dubois, J.-E. *Tetrahedron* **1978**, *34*, 3553–3562.

SCHEME 4. Solvent-Promoted Decomposition of Dioxetane 3 through Hydrogen Bonding with a Solvent Molecule, NMP



from 0.5 to −22 J mol^{-1} K^{-1} as the substituent R became smaller. For TD of **3a**−**d**, $\Delta S^{\ddagger}$s did not show such a tendency. On the other hand, $\Delta S^{\ddagger}$ for SPD had a markedly large negative value (−69 to −74 J mol^{-1} K^{-1}) regardless of the substituent R for **3a**−**d**. These results show that (a) SPD for **3a**−**d** proceeded through a transition state that was far less disordered than that for BID and (b) the structure of the transition state was presumably controlled not by substituent R but rather was regulated by an external factor(s), i.e., hydrogen bonding with NMP molecule(s).

A plausible mechanism (Scheme 4, mechanism A) consistent with these results is that hydrogen bonding of **3** with the NMP molecule induces negative charge on phenolic oxygen as illustrated in **7** (Scheme 4), which undergoes chemiluminescent decomposition by CTID mechanism: CTID occurred with low enthalpy of activation as shown in Table 3, when a phenolic ring lies in a particular conformation (vide infra). Another candidate that we first thought is mechanism B in which SPD of **3** proceeds consecutively through rapid pre-equilbrium between **3** (with hydrogen bonding) and intermediary species such as a contact ion pair **8** between anionic dioxetane **5** and protonated NMP (Scheme 4). However, considering that pK_a values are 12−17 for phenols in NMP,[23] mechanism B would be less plausible except in the case that unknown factors cause predominant shift to **8** in pre-equilibrium between **3** in NMP.

For an oxidoaryl-substituted dioxetane, CTID has been suggested to proceed preferentially when the oxidoaryl group lies in a particular conformation(s).[3c,11] According to this idea, the result that SPD possessed low $\Delta H^{\ddagger}$ and large negative $\Delta S^{\ddagger}$ suggests that species **7** activated through hydrogen bonding with NMP could undergo CTID only when an aromatic ring lay in a conformation(s) that was far more regulated than in the case of BID: in contrast, for BID, the intermediary anion **5** should be slightly solvated or, as an extreme, naked in an aprotic polar solvent system such as TBAF/NMP.

Conclusion

Bicyclic dioxetanes **3a**−**d** were found to undergo SPD accompanied by the emission of bright light in an aprotic polar solvent that was a strong proton acceptor. SPD of **3** was an effective chemiluminescence reaction, in which dioxetane **3** was presumably activated through hydrogen bonding with aprotic polar solvent such as NMP so that it underwent CTID. The chemiluminescence properties for SPD resembled those for BID. Both free energies of activation, $\Delta G^{\ddagger}_{\mathrm{SPD}}$ and $\Delta G^{\ddagger}_{\mathrm{BID}}$, increased depending on the bulkiness of the substituent R in **3**, and were linearly correlated with each other. However, there were marked differences in $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ between SPD and BID. SPD had $\Delta S^{\ddagger}$ with a large negative value (−69 to −74 J mol^{-1} K^{-1}) regardless of the substituent R at the 5-position for **3a**−**d**, while for BID it changed from 0.5 to −22 J mol^{-1} K^{-1} as R became smaller. $\Delta H^{\ddagger}$ for SPD was 14−21 kJ mol^{-1} smaller than that for BID. These results suggest that SPD proceeded only when dioxetanes **3** with hydrogen bonding lay in a considerably restricted conformation(s) with respect to an aromatic electron donor.

Experimental Section

1-[4-(Benzothiazol-2-yl)-3-hydroxyphenyl]-5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptanes (3a−d) and 2,2-Dimethyl-3-oxobutyl 4-(benzothiazol-2-yl)-3-hydroxybenzenecarboxylates (4a−d). The bicyclic dioxetanes **3a**−**d** and keto esters **4a**−**d** used here were previously synthesized and fully 6characterized,[11] and were stored in a refrigerator. Their purities were checked by ^{1}H NMR before use in the present investigations.

Solvent-Promoted Decomposition of 1-[4-(Benzothiazol-2-yl)-3-hydroxyphenyl]-5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (3d): Typical Procedure. A solution of 1-[4-(benzothiazol-2-yl)-3-hydroxyphenyl]-5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (**3d**) (34.8 mg) in NMP (2 mL) was heated at 100 °C under a nitrogen atmosphere for 1 h. After being cooled the reaction mixture was poured into water and extracted with AcOEt. The AcOEt solution was dried over $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel and eluted with AcOEt−hexane (1:4) to give 2,2-dimethyl-3-oxobutyl 4-(benzothiazol-2-yl)-3-hydroxybenzenecarboxylate **4d** as a colorless solid (34.6 mg, 99% yield). The thus-obtained **4d** showed spectroscopic properties identical with those of authentic **4d**.[11] Solvent-promoted decomposition of dioxetanes **3a**−**c** was similarly carried out in NMP and the corresponding decomposition products **4a**−**c** were isolated in >99% yields.

---

[23] Izutsu, K. In *Acid-Base Dissociation Constants in Dipolar Aprotic Solvents*; Blackwell Sci.: Oxford, UK, 1990.

Measurement of Chemiluminescence and Time-Course of the Solvent-Promoted Decomposition of Dioxetanes 3: General Procedure. Chemiluminescence was measured with a JASCO FP-750, and/or FP-6500 spectrometer, and/or Hamamatsu Photonics PMA-11 multichannel detector.

NMP (2.90 mL) that had been preincubated at an appropriate temperature was transferred to a quartz cell ($10 \times 10 \times 50$ mm^3), which was placed in a spectrometer that was thermostated with stirring at an appropriate temperature range of 50−100 °C. After 3−5 min, a solution of the dioxetane **3** in *p*-xylene (1.0×10^{-3} mol/L, 0.10 mL) was added by means of a syringe, and measurement was started immediately. The time-course intensity of light emission was recorded and processed according to first-order kinetics. The total light emission was estimated by comparing it with that of an adamantylidene dioxetane, the chemiluminescent efficiency Φ^{CL} of which has been reported to be 0.29 and which was used here as a standard.[12,13] Similar experiments were carried out with DMF, DMPU, PPC, and EGM.

Measurement of Chemiluminescence and Time-Course of the Base-Induced Decomposition of Dioxetanes 3: General Procedure. Chemiluminescence was measured as in the case of solvent-promoted decomposition described above.

A freshly prepared solution (2.90 mL) of TBAF (1.0×10^{-2} mol/L) in NMP was transferred to a quartz cell ($10 \times 10 \times 50$ mm^3), which was placed in a spectrometer that was thermostated with stirring at an appropriate temperature range of 35−60 °C. After 3−5 min, a solution of dioxetane **3** in *p*-xylene (1.0×10^{-4} mol/L, 0.10 mL) was added by means of a syringe, and measurement was started immediately. The time-course of the intensity of light emission was recorded and processed according to first-order kinetics. The total light emission was estimated as in the case of solvent-promoted decomposition described above.

Acknowledgment. The authors gratefully acknowledge financial assistance provided by Grants-in-aid Nos. 17550050 and 21550052 for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supporting Information Available: General method for the Experimental Section, ^{1}H NMR/^{13}C NMR spectra of an epoxide **A** produced from **3d** and ORTEP view and crystallographic information file for epoxide **A**, as well as observed rate constants at various temperatures for SPD and BID, and Eyring plots for **3a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.