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Substituent effects on the decomposition of chemiluminescent tricyclic aromatic dioxetanes

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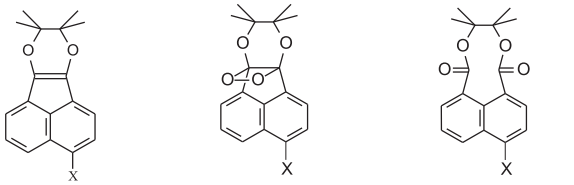
ABSTRACT: Three tricyclic 1,2-dioxetane derivatives, 1a, 2a and 3a were synthesized from their corresponding 1,4-dioxin acenaphthylene compounds, 1, 2 and 3, by reaction with singlet-oxygen ($^1O_2$) in dichloromethane. Evidence for the formation of the dioxetanes 1a, 2a and 3a is provided by the chemiluminescence (CL) that corresponds to the emission from the electronically excited diesters 1b*, 2b* and 3b*, which are decomposed thermally from the dioxetanes 1a, 2a and 3a, respectively. The highly strained 1,2-dioxetane ring decomposes from a twisted geometry by simultaneous cleavages of the O–O and C–C bonds, producing the electronically excited diester that emits CL. It was observed that the CL from compound 2a is red-shifted relative to that of compounds 1a and 3a suggesting a higher degree of stabilization for the excited state by the electron-donating methoxy group. Also, a study of the solvent effect on fluorescence shows a significant red-shift in compound 2b, indicating a more polar excited state. The kinetics of the thermal decomposition of the 1,2-dioxetanes clearly demonstrate that the CL characteristics of compound 2a are quite different from those of compounds, 1a and 3a. These results are consistent with the proposed intramolecular chemically initiated electron exchange luminescence (CIEEL) mechanism which is triggered by the electron-donating group of compound 2a. Copyright © 2013 John Wiley & Sons, Ltd.



Keywords: chemiluminescence; tricyclic dioxetane; chemically initiated electron exchange luminescence

Introduction

The phenomenon of firefly bioluminescence (1,2) has led to the theoretical (3,4) and practical (5–7) study of the chemiluminescence (CL) of 1,2-dioxetanes and has been of interest to chemists for a long time. High-energy 1,2-dioxetane molecules are the focus of many investigations because of their unique ability to decompose thermally into electronically excited carbonyl products. Although 1,2-dioxetanes have been postulated as reaction intermediates for over 100 years, charge transfer (CT)/electron transfer (ET) and electron back-transfer (EBT) have been suggested as a chemically initiated electron exchange luminescence (CIEEL) mechanism for CL, but the details of the mechanism have not yet been fully clarified (8). It is likely that the effect of structural changes will help to elucidate the still-debated mechanism of this reaction. In general [2 + 2] cycloaddition of singlet-oxygen with electron-rich alkenes is the most convenient method for the synthesis of 1,2-dioxetanes (9).

The key concept of the intramolecular CIEEL mechanism is that thermal decomposition of 1,2-dioxetane proceeds through a twisted diradical transition state that yields intramolecular radical ion intermediates. Subsequent exothermic EBT annihilation leads to an excited state and CL (10–15). For example, the intramolecular CIEEL mechanism of the dioxetane substituted with the electron-donating moiety [*p*-(dimethylamino)phenyl] is illustrated, where CT from the electron-donating moiety to

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the O–O bond of the dioxetane promotes decomposition of the dioxetane into the excited ester (see Scheme 1) (16).

The CL from ozonization and singlet-oxygen oxidation of the unsubstituted tricyclic 1,4-dioxin acenaphthylene compound **1** was reported several years ago from our laboratory (17). In continuation of this work, 5-methoxy-substituted 1,4-dioxin compound **2** and 5-chloro-substituted 1,4-dioxin compound **3** were synthesized to study the substituent effects on the decomposition of dioxetanes. We report herein the CL of the rigid tricyclic aromatic dioxetanes compounds, **1a**, **2a** and **3a**, with different functional groups (−H, $-OCH_3$ and –Cl) to assess the influence on the intramolecular CIEEL mechanism of 1,2-dioxetanes.

Experimental

Materials

1,4-Dioxin acenaphthylene, compounds 1–3. Acenaphthenequinone (ANQ) was obtained from Sigma-Aldrich Company(Taiwan agent). 5–Nitro ANQ was synthesized from ANQ and sodium nitrate in concentrated sulfuric acid by refluxing the reaction mixture for 2 h. 5-Methoxy ANQ was synthesized from purified 5-nitro ANQ and potassium hydroxide in methanol by refluxing the reaction mixture for 2 h (18). 5-Chloro ANQ was synthesized from ANQ and *N*-chlorosuccinimide (NCS) in concentrated sulfuric acid by refluxing the reaction mixture for 2 h (Scheme 2A). Compounds **1–3** were synthesized by the photo-cycloaddition reaction of ANQ with tetramethylethylene (TME) in benzene (Scheme 2B) (19).

Tricyclic 1,2-dioxetane compounds 1a–3a. Singlet-oxygen oxidation of the 1,4-dioxin compounds **1–3** to produce the tricyclic 1,2-dioxetane compounds **1a–3a** was carried out by using the ozone-triphenyl phosphite procedure (5). The triphenyl phosphite ozonide, $(PhO)_3PO_3$, was prepared by passing extra pure oxygen through a commercial Fischer Model 501 ozonizer and bubbling the effluent into a solution of the phosphite in the range of 195–223 K (dry ice/acetone bath). The solution was saturated with ozone for ~ 2 h, and the temperature was kept within the range of 238–253 K for ~ 30 min to undergo singlet-oxygen oxidation of the 1,4-dioxin compounds. Dioxetane adducts **1a–3a** were isolated by ice-chilled *n*-hexane extraction from low-temperature synthesis of ozonized triphenyl phosphite [Scheme 2C (1)].

Naphthalene diester compounds 1b–3b. Two methods were utilized for the synthesis of the naphthalene diester compounds **1b–3b**. The first method involved the thermal decomposition of the compounds **1a–3a** to the naphthalene diester compounds **1b–3b** [Scheme 2C (1)]. The second procedure was the irradiation of compounds **1–3** in dichloromethane solution in the presence of the photosensitizer (methylene blue) under an oxygen atmosphere [Scheme 2C (2)]. The ^{1}H-NMR, Infrared (IR) and Mass spectrometry (MS) spectral data for the naphthalene diester compounds **1b–3b** are shown below.

Compound **1b**: ^{1}H-NMR (200 MHz, $CDCl_3$): 7.99–7.95 (*d*, 2H, Ar–H, $J = 8$ Hz), 7.90–7.86 (*d*, 2H, Ar–H, $J = 8$ Hz), 7.56–7.48 (*t*, 2H, Ar–H, $J = 8$ Hz), 1.74 (*s*, 12H, $4CH_3$), FT-IR (KBr, cm^{-1}): 2922, 1725, 1693, 1579, 1280, SIMS *m/z* 298 [M].

Compound **2b**: ^{1}H-NMR (200 MHz, $CDCl_3$): 8.46–8.42 (*d*, 1H, Ar–H, $J = 8$ Hz), 7.95–7.91 (*d*, 1H, Ar–H, $J = 8$ Hz), 7.83–7.79 (*d*, 1H, Ar–H, $J = 8$ Hz), 7.52–7.44 (*t*, 1H, Ar–H, $J = 8$ Hz), 6.87–6.83 (*d*, 1H, Ar–H, $J = 8$ Hz), 4.03 (*s*, 3H, OCH_3), 1.75 (*s*, 6H, $2CH_3$), 1.68 (*s*, 6H, $2CH_3$), FT-IR (KBr, cm^{-1}): 2935, 1718, 1583, 1242, SIMS *m/z* 328 [M].

Compound **3b**: ^{1}H-NMR (200 MHz, $CDCl_3$): 8.51–8.47 (*d*, 1H, Ar–H, $J = 8$ Hz), 7.93–7.89 (*d*, 1H, Ar–H, $J = 8$ Hz), 7.81–7.77 (*d*, 1H, Ar–H, $J = 8$ Hz), 7.67–7.60 (*m*, 2H, Ar–H), 1.74 (*s*, 6H, $2CH_3$), 1.70 (*s*, 6H, $2CH_3$), FT-IR (KBr, cm^{-1}): 3005, 1734, 1687, 1570, 1283, SIMS *m/z* 332 [M].

Measurements

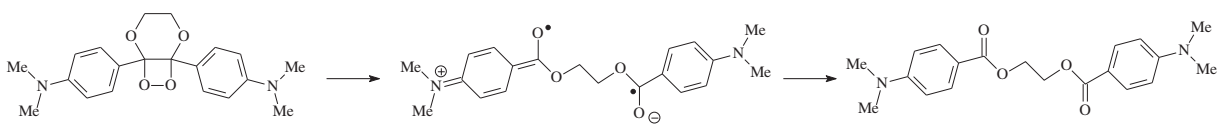
The absorption spectra were measured on a Hewlett-Packard diode array spectrophotometer. The steady-state emission spectra were obtained using a Cary Eclipsed Spectrofluorimeter equipped with a temperature controller. The absorption and emission experiments were performed with prepared solutions containing 1.0×10^{-4} M of diesters in dichloromethane. For the temperature-dependent kinetic measurements, the temperature of the sample solution was controlled to within ± 0.5 K using an electronically thermostatting single cell and monitored with thermocouples attached to the cell.

Results and discussion

The isolated dioxetane compounds **1a**, **2a** and **3a** were formed by reacting compounds **1**, **2** and **3**, respectively, with singlet-oxygen ($^1O_2$) in dichloromethane at 238 K and decomposed thermally into electronically excited diesters **1b***, **2b*** and **3b***, which then fluoresced to their corresponding ground state configurations **1b**, **2b** and **3b**. Experimental evidence shows that the CL spectral peaks of compounds **1a–3a** are consistent with that of the photoluminescence spectral peaks of the photoexcited compounds **1b–3b**. Figure 1 shows the UV/Vis absorption and photoluminescence spectra of compounds **1b–3b**, and the CL spectra of compounds **1a–3a** in dichloromethane. Therein, the CL and photoluminescence peaking at λ_{max} are normalized with the same relative intensity. It shows that the CL spectral peaks of the dioxetanes are consistent with those of the photoluminescence spectral peaks of the photoexcited diesters, respectively.

The CL peak of dioxetane compound **2a** at 430 nm shows an obvious red-shift in comparison with compounds **1a** (375 nm) and **3a** (378 nm). Presumably, the methoxy group of compound **2a** can donate electrons to the naphthalene ring and extend the conjugation of electrons, causing the obvious red-shift of CL.

Additional experimental evidence was obtained by examining the solvent effect on the photoluminescence of diesters **1b–3b**. Normalized fluorescence spectra of diesters **1b–3b** in different polar solvents are shown in Fig. 2. All the emissions from (π, π^*) excited states are seen in the three diesters, however,



Scheme 1. The intramolecular CIEEL mechanism of the dioxetane.

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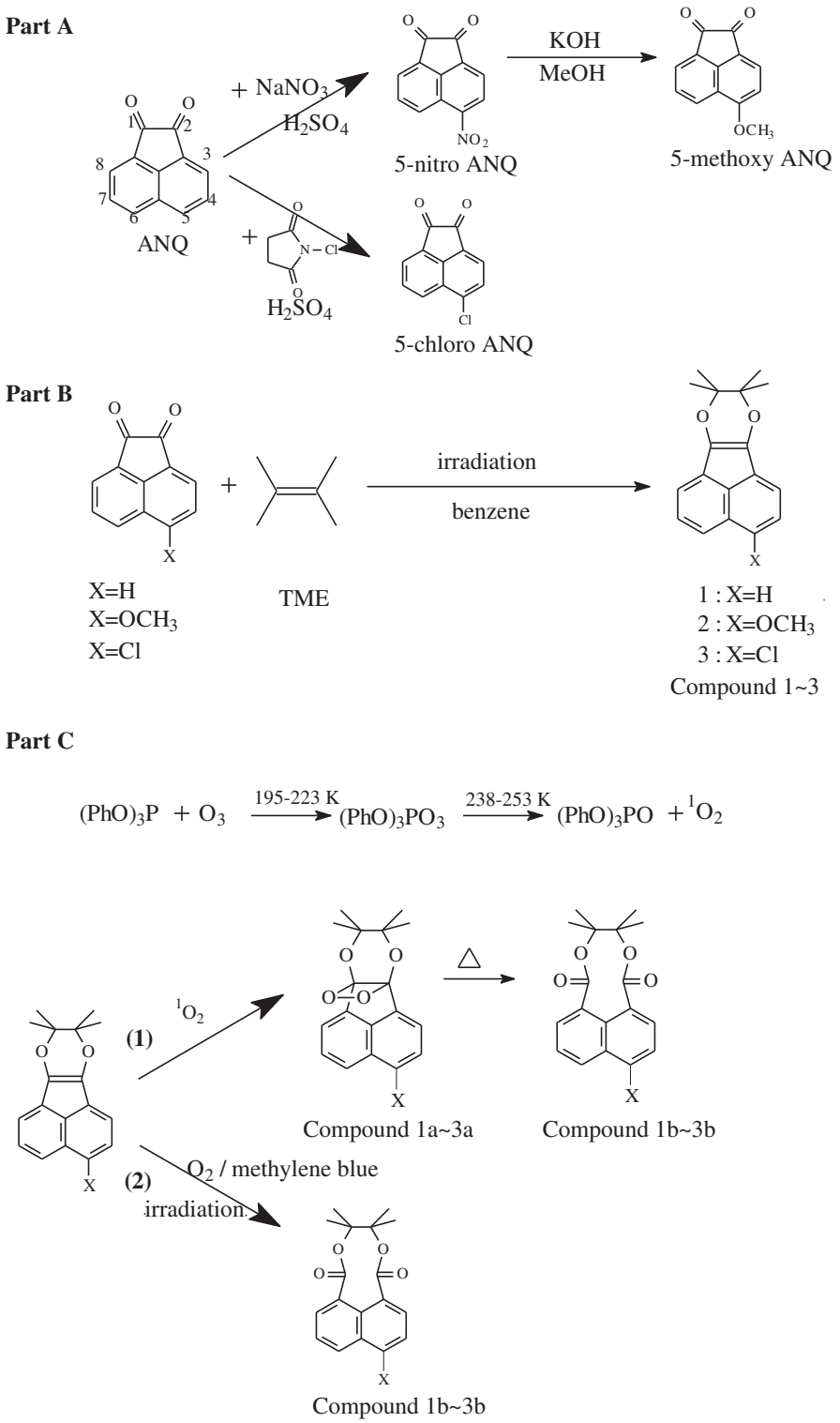

Scheme 2. Synthesis of compounds 1-3, 1a-3a and 1b-3b.

the fluorescence spectrum of compound **2b** shows a noticeable dependence on the solvent polarity. By increasing solvent polarity from benzene to acetonitrile, the fluorescence peak of compound **2b** is red-shifted from 420 to 455 nm. Diesters **1b** and **3b** show emission peaks at 375 and 378 nm in benzene, and do not display a substantial shift with increasing solvent polarity. We can conclude, therefore, that this long-wavelength fluorescence band of compound **2b** has a prominent characteristics CT which is stabilized in polar solvent.

From Figs 1 and 2, it can be concluded that the CL as well as the photoluminescence originate from the singlet excited state, which should be a $^1(\pi^* \rightarrow \pi)$ state. In addition, the experimental results indicate that the electron-donating methoxy group

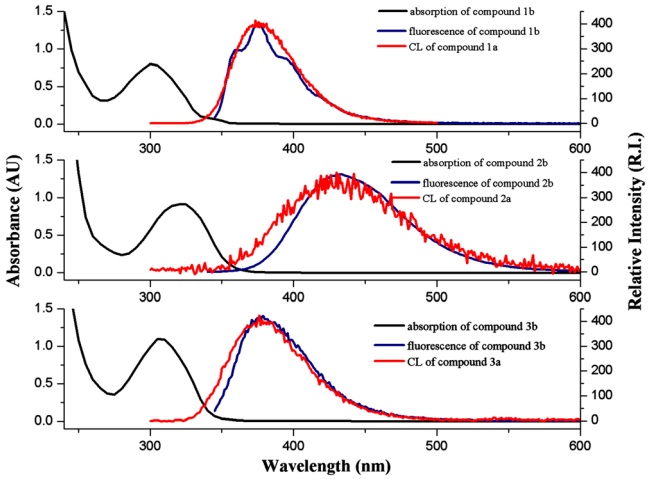

Figure 1. UV/Vis absorption, photoluminescence spectra of compounds **1b–3b**, and CL spectra of compounds **1a–3a** in dichloromethane.

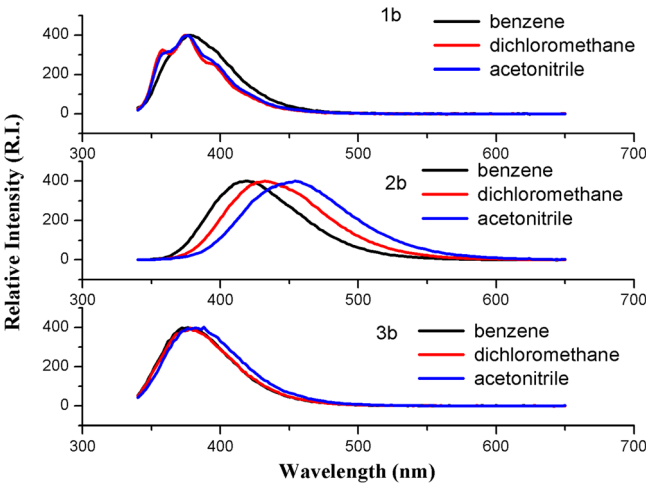

Figure 2. Photoluminescence spectral peaks of compounds **1b–3b** in going from nonpolar to polar solvents.

present at the 5-position is able to stabilize the singlet excited state of the 1,2-dioxetane decomposition products. In the chemiexcitation processes, when both the O–O and C–C bonds are cleaved simultaneously, the electron-donating group ($-OCH_3$) at the 5-position can interact through the π electrons of the naphthalene ring to stabilize the singlet excited state $^1(\pi^* \rightarrow \pi)$. Hence, the CL emission of this tricyclic aromatic dioxetane highly depends on substitution on the 5-position of the naphthalene structure or polarity of solvent system. These observations, together with the CL spectra are consistent with an intramolecular CIEEL decomposition initiated by CT from the electron-donating group of compound **2a**, followed by EBT to produce the excited diester. Compounds **1a** and **3a** indicate that the CIEEL mechanism is not operating prominently and they are decomposed thermally without involvement of CT or ET.

The rate constants for the decomposition of compounds **1a–3a** were obtained at 313–353 K by measuring the decay of the CL intensity. The CL decay of compounds **1a–3a** was monitored at the maximum value of the CL in dichloromethane (compound **1a**-$\lambda_{CL,max}$, 375 nm; compound **2a**-$\lambda_{CL,max}$, 430 nm; compound **3a**-$\lambda_{CL,max}$, 378 nm). Figure 3 shows the time course

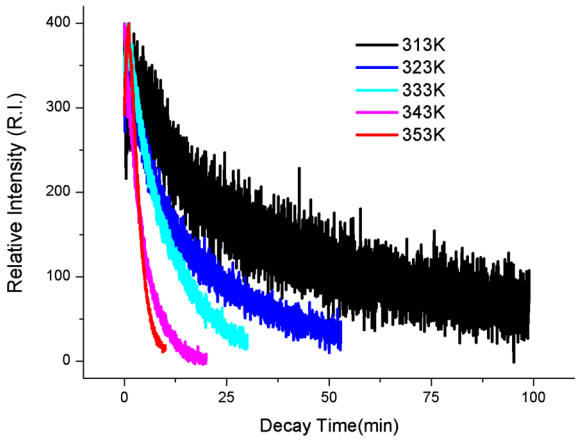

Figure 3. CL thermal decay of compound **2a** at different temperatures, monitored at 430 nm.

of the CL emission intensity at 430 nm upon thermal decomposition of compound **2a**, measured at different temperatures (313–353 K).

According to the transition state theory, the overall mechanism for the decomposition of the tricyclic 1,2-dioxetane compound can be presented as eqn (1).

$$B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X^{\ddagger} \rightarrow C^{*} \rightarrow C \qquad (1)$$

where B = tricyclic 1,2-dioxetane compound, $X^{\ddagger}$ = the activated complex and C* = excited intramolecular naphthalene diester compound. The Eyring equation (eqn 2) can be obtained by transition state theory (20).

$$\ln\frac{k}{T} = \left(\ln\frac{R}{N_A h} + \frac{\Delta S^{\ddagger}}{R}\right) - \frac{\Delta H^{\ddagger}}{RT} \qquad (2)$$

where N_A = Avogadro's constant and h = Planck's constant

The activation parameters of dioxetanes **1a–3a** were obtained from the temperature dependence of the CL decomposition rate constants. The CL activation parameters were obtained by plotting ln(k/T) vs 1/T in the Eyring plots, as shown in Fig. 4. The kinetics of the thermal decomposition of the 1,2-dioxetanes studied at 313–353 K reveal a significantly lower value for the activation enthalpy ($\Delta H^{\ddagger}$) of **2a**.

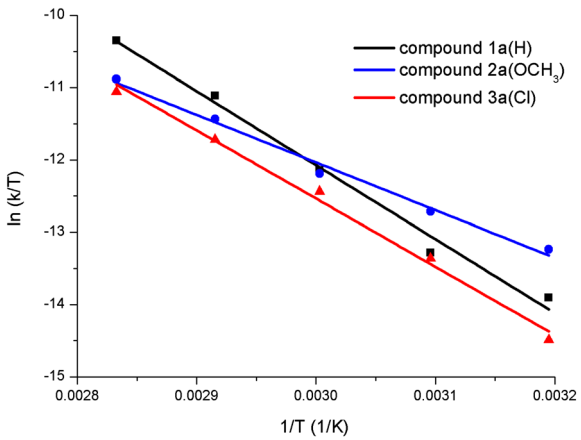

Figure 4. Eyring plots of the CL kinetics of compounds **1a–3a**.

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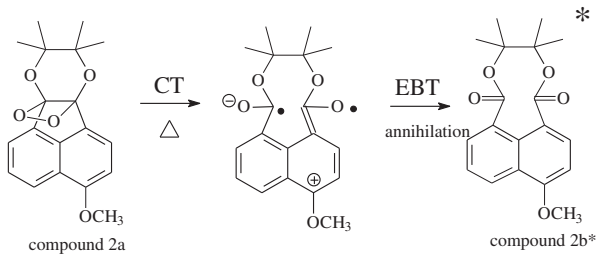
Table 1. Activation parameters and rates of decomposition for 1,2-dioxetanes 1a–3a

Compound	λ_{max} (nm) kcal/mol	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ cal/mol/K	$\Delta G^{\ddagger}$ (25°C) kcal/mol	$k_{25°C}$ s^{-1}	$\tau_{1/2}$ (25°C) h
1a (H)	375 (76.3)	20.3	−10.2	23.4	4.54×10^{-5}	4.24
2a (OCH_3)	430 (66.5)	13.1	−31.8	22.6	17.1×10^{-5}	1.13
3a (Cl)	378 (75.7)	18.8	−15.8	23.5	3.79×10^{-5}	5.08



Scheme 3. The intramolecular CIEEL mechanism of the compound 2a.

Table 1 shows the activation parameters and rates of decomposition for 1,2-dioxetanes **1a–3a**. The$\Delta H^{\ddagger}$ value of compound **2a** is significantly lower than those values for compounds **1a** and **3a**. The rate constants obtained for compound **2a** is ~ 4–5 times faster than that of **1a**, and **3a** at 298 K. The activation parameters of the unsubstituted compound **1a** and the chloro-substituted compound **3a** show similar thermal stability at room temperature, with a Gibbs' activation energy ($\Delta G^{\ddagger}$) that differed by only ~ 0.1 kcal/mol. However, the methoxy-substituted compound **2a** has a $\Delta G^{\ddagger}$value of 22.6 kcal/mol at 25°C corresponding to a $\tau_{1/2}$ value of ~ 1.13 h, and shows a much lower thermal stability than compounds **1a** and **3a**. These results obtained upon intramolecular decomposition of dioxtanes clearly demonstrate that the CL characteristics of compound **2a** are quite different from those of compounds **1a** and **3a**. The more negative activation entropy ($\Delta S^{\ddagger}$) for compound **2a**, which compensates for the surprisingly low value of $\Delta H^{\ddagger}$, can be understood by the need for a specific conformation for the CT from the methoxy group of the naphthalene ring to the O–O bond of the dioxetane, which promotes decomposition of the dioxetane into two radicals confined within a solvent cage. Subsequent EBT annihilation between the radicals releases enough energy to excite the naphthalene emitter to its singlet excited state. These results are consistent with the intramolecular CIEEL mechanism in which the electron-donating methoxy group promotes O–O bond cleavage by resonance interaction through the π electrons of the naphthalene moiety. The intramolecular CIEEL mechanism is triggered by the increasing electron-donating ability, with subsequent EBT annihilation leading to an excited state diester and luminescence to the ground state (Scheme 3).

Conclusions

We have shown that the 1,2-dioxetane-based CL color is modulated by a dioxetane bearing a substituted-naphthalene group. The color of the CL emission from compound **2a** is just different due to the different fluorescence spectrum of the thermodynamic decomposition product **2b**, caused by the stabilization effect of the methoxy group. The change of substituent on the naphthalene emitter causes a change in the color of the dioxetane-based CL, and also affects the decomposition reaction activation enthalpies of the dioxetanes. The chemiexcitation process of the intramolecular CIEEL decay was rationalized and described as being mainly due to a particular form of electron-donating substituent at the 5-position of acenaphtho moiety. Further investigation of present and the other aspects of the intramolecular CIEEL mechanism are underway in our laboratory.

Acknowledgements

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