INTRODUCTION

Photoluminescence is a type of optical spectroscopy in which a photoluminescent molecule is promoted to an electronically excited state by absorption of incident radiation. Chemiluminescence is a type of optical spectroscopy in which a chemiluminescent molecule is generated to an electronically excited state by chemiexcitation reactions. There are few reports about the room temperature chemiluminescent fluorescence and phosphorescence. For example, room temperature luminescence is rarely observed from the thermal decomposition of 1,2-dioxetanes which produce excited carbonyl compounds. The energy in the form of light is released from 1,2-dioxetanes due to a chemiexcitation reaction during thermal decomposition. A simple example is the thermal decomposition of tetramethyl dioxetane (TMDO). In the TMDO structure, the C-O-O-C is a twisted four-membered ring peroxide with high strain energy, which liberates much energy during thermal decomposition into two excited carbonyl fragments (singlet and triplet excited acetone) and then return to the ground state by chemiluminescence (Scheme-I)\textsuperscript{1-5}.

The molecular structure of TMDO was used as a base template to design and synthesize compounds (1a-3a). The structure of the 1,2-dioxetane tricyclic compounds (1a-3a) are comprised of three parts. These are the 1,2-dioxetane ring (main structure), the electron-donor dialkoxyl activator (tetramethyl 1,4-dioxin ring) on one side and the lumiphor (5-heavy atom substituted acenaphtho moiety) on the other side (Scheme-II). The chloro- and bromo- substituents on the lumiphor are incorporated to study the internal heavy atom effect, which is an important factor for the room temperature heavy atom effect.

Key Words: Chemiluminescence, Fluorescence, Phosphorescence, Dioxetane, Heavy atom effect.
chemiluminescent phosphorescence (RTCP) detection of chemiluminescent molecule by experimental measurements.

It is well known that the 1,2-dioxetane ring with its high strain energy undergoes simultaneous cleavage of both the O-O and C-C bonds during thermal decomposition into two excited intramolecular carbonyl fragments (singlet and triplet excited intramolecular naphthalene diester compounds \(1b^*\) \(3b^*\), which return to the ground state by chemiluminescent fluorescence (CF) and chemiluminescent phosphorescence (CP), respectively.\(^\text{6,9}\)

While it is difficult to detect the room temperature chemiluminescence from compounds \(1b-3b\) under nondegassed condition, because of quenching by triplet-oxygen \(^{\text{18O}}\), the room temperature chemiluminescence phosphorescence is detected more easily, because the room temperature chemiluminescence phosphorescence emission derives from the chemixcitation reactions of 1,2-dioxetanes. It is well known that the internal heavy atom effect can enhance the phosphorescence. This paper describes the room temperature chemiluminescent phosphorescence of 1,2-dioxetane tricyclic compound with a 5-heavy atom substituent in the acenaphtho moiety.

**EXPERIMENTAL**

1,4-Dioxin acenaphthylene, compounds (1-3): Acenaphthenequinone (ANQ) was obtained from Aldrich. The 5-chloro acenaphthenequinone was synthesized from acenaphthenequinone and N-chlorosuccinimide (NCS) in concentrated sulfuric acid. The reaction mixture was refluxed for 2 h. The 5-bromo acenaphthenequinone was synthesized from acenaphthenequinone and bromine liquid. The reaction mixture was refluxed for 2 h.\(^\text{10,11}\) (Scheme-III part A). The compounds (1-3) were synthesized by the photo-cycloaddition reaction of acenaphthenequinone (ANQ) with tetramethyl-ethylene (TME) in benzene.\(^\text{12}\) (Scheme-III part B).

1,2-Dioxetane tricyclic compounds (1a-3a): Singlet-oxygen oxidation of the 1,4-dioxin compounds (1-3) produces the 1,2-dioxetane tricyclic compounds (1a-3a) was carried out using the ozone-triphenyl phosphite procedure given in ref. \(^\text{13}\). Dioxetane adducts (1a-3a) were isolated by ice-chilled n-hexane extraction from the low temperature synthesis of ozonized triphenyl phosphite [Scheme-III part C(1)].

**Naphthalene diester compounds \(1b-3b\):** There are two methods to synthesize the naphthalene diester compounds \(1b-3b\). (1) The compounds (1a-3a) were decomposed thermally to the naphthalene diester compounds \(1b-3b\) (Scheme-III part C(1)). (2) The compounds (1-3) in benzene solution were irradiated in the presence of photosensitizer methylene blue and purged oxygen [Scheme-III part C(2)].

**Measurements:** The UV/visible 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. Luminescence lifetimes were measured by a microsecond flash lamp Luminescence Spectrofluorimeter (Cary Eclipse) in a temperature range of 313-353 K. For the temperature-dependent kinetic measurements, the temperature of the sample solution were controlled to within ± 0.5 K with an electronically thermostating single cell and monitored with thermocouples attached to the cell. The room temperature chemiluminescence fluorescence (RTCF) and the room temperature chemiluminescent phosphorescence thermal decay of the compounds (1a-3a) were determined using a photomultiplier tube.
RESULTS AND DISCUSSION

The isolated compounds (1a-3a) were formed by reacting compounds (1-3) with singlet-oxygen (¹O₂) in dichloromethane at 238 K. Thermal decomposition of the 1,2-dioxetanes produce the electronically excited diesters (1b*-3b*) that decay by chemiluminescent fluorescence or chemiluminescent phosphorescence to the ground state compounds (1b-3b). To avoid triplet-oxygen (³O₂) quenching of the triplet excited states, we used the freeze-pump-thaw method to degas solutions where the compounds (1b-3b) are dissolved. Experimental evidences show that the chemiluminescence spectral peaks of the compounds (1a-3a) are consistent with that of the photoluminescence spectral peaks of the photoexcited nondegassed and degassed compounds (1b-3b). These spectroscopic observations suggest that the compounds (1a-3a) thermally decomposed to the excited state of the compounds (1b*-3b*), with subsequent radiative decay to the ground state of the compounds (1b-3b). These processes are showed in [Scheme-IV].

As an example, the UV/visible absorption and photoluminescence spectra of the compound 3b and the chemiluminescence spectrum of the compound 3a in dichloromethane are shown in Fig. 1. To compare the three spectra (chemiluminescence, nondegassed and degassed photoluminescence), the chemiluminescent fluorescence or chemiluminescent phosphorescence spectra relative intensity between the ground state compounds (3a) at 343 K in dichloromethane are normalized to same relative intensity.

![Chemiluminescence](image)

We observed quite different room temperature chemiluminescent phosphorescence spectra relative intensity between the nondegassed compounds 1a(H)-2a(Cl)-3a(Br). It is known that the rate of a spin-forbidden process is enhanced by the presence of an atom of high atomic number. This factor is observed with the room temperature chemiluminescent phosphorescence. The 5-heavy atom substituted acenaphthomoiety of 1,2-dioxetanes shows enhanced nonradiative intersystem crossing from the lowest triplet state, resulting in an increase in the intensity of the phosphorescence. This increase of the room temperature chemiluminescent phosphorescence spectra relative intensity from triplet excited state due to the internal heavy atom substituted is H < Cl << Br (Fig. 2).

The photoluminescence spectral peaks of the photoexcited compounds (1b-3b) are little shifted toward longer wavelengths as the solvent is changed from the less polar dichloromethane to more polar acetonitrile. The room temperature chemiluminescent fluorescence and room temperature chemiluminescent phosphorescence derive from singlet and triplet *π→π* states. An external heavy atom effect was observed with compound 3b in going from benzene to dichloromethane (Fig. 3). The intensity of phosphorescence of compound 3b which dissolved in dichloromethane is higher than that dissolved in benzene.
benzene solvent is 0.10, while this ratio increases to 0.17 in dichloromethane solvent.

The rate constants for the decomposition of the compound 3a was obtained at 10 K increments between 313-353 K by measuring the decay of the chemiluminescence intensity at the maximum wavelength of the chemiluminescence in dichloromethane (λ_{max}: 378 nm; λ_{CPmax}: 560 nm). Fig. 4 shows the chemiluminescent fluorescence and chemiluminescent phosphorescence decays of compound 3a at 343 K, monitored at 378 and 560 nm, respectively.

The overall chemiluminescent mechanism of the 1,2-dioxetane tricyclic compound 3a can be presented as eqn. 1.

\[
B \rightarrow B^{*} \rightarrow \text{C}^{*} \rightarrow \text{C}
\]  

where B = 1,2-dioxetane tricyclic compound 3a; X^i = the activated complex; C* = excited intramolecular diester compound 3b*.

From the Boltzmann distribution eqn. 2

\[
k = \frac{k_{B}T}{h} e^{-\frac{-\Delta G^f}{RT}}
\]

\[\Delta G^f = \Delta H^f - T\Delta S^f\]

where \(k_{B}\) is the Boltzmann constant; \(h\) is Planck’s constant, \(\Delta G^f\) is the activation free energy of the transition state; \(R\) is the gas constant and the Gibbs free energy eqn. 3

\[
\ln \frac{k}{T} = \left(\ln \frac{R}{N_{A}h}\right) + \frac{\Delta S^f}{R} - \frac{\Delta H^f}{RT}
\]

where \(N_{A}\) is Avogadro’s constant; \(h = Planck’s constant.\)

A plot of \(\ln (k/T)\) and \((1/T)\) as a linear function. A plot of \(\ln (k/T)\) versus \((1/T)\) gives a straight line with slope (\(-\Delta H^f/R\)) from which the activation enthalpy of the transition state may be derived. The chemiluminescent fluorescence and chemiluminescent phosphorescence decays from 1,2-dioxetane 3a was analyzed by eqn. 4. There are two slopes

\[
\frac{\Delta H^f_{Singlet}}{R} \quad \frac{\Delta H^f_{Triplet}}{R}
\]

of the Eyring plots corresponding to the chemiluminescent fluorescence decay of compound 3a at 378 nm and the chemiluminescent phosphorescence decay of compound 3a at 560 nm, respectively, as shown in Fig. 5.

The activation parameters and rates of decomposition for compound 3a calculated with eqn. 2 are listed in Table-1.

### Table-1

<table>
<thead>
<tr>
<th>λ_{max} (nm)</th>
<th>(\Delta H^f) (kcal/mol)</th>
<th>(\Delta S^f) (cal/mol K)</th>
<th>(\Delta G^f (25\degree C)) (kcal/mol)</th>
<th>(k_{B}T^*) (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>378 (75.7)</td>
<td>22.2</td>
<td>-5.1</td>
<td>23.7</td>
<td>2.44×10^3</td>
</tr>
<tr>
<td>560 (51.1)</td>
<td>15.2</td>
<td>-26.5</td>
<td>23.1</td>
<td>7.6×10^3</td>
</tr>
</tbody>
</table>

The results show that there are two transition excited energy states in the chemiluminescence processes: (1) The transition singlet excited state activation enthalpy \(\Delta H^f_{Singlet}\). (2) The transition triplet excited state activation enthalpy \(\Delta H^f_{Triplet}\).
The singlet excited state activation enthalpy ($\Delta H_{\text{Singlet}}^o$) of compound 3a has been determined experimentally to be 22.2 kcal/mol. The different activation enthalpies and different rate constants seem to be a reasonable explanation that the triplet state is not formed by way of the singlet state and the chemiluminescent phosphorescence favours the pathway for the formation of the chemiluminescent phosphorescence.

The rate of a spin-forbidden process is enhanced by the internal presence of bromo-substituent, result the increase of the relative intensity of the room temperature chemiluminescent phosphorescence of compound 3a. The enhancement of the phosphorescence of compound 3b is also observed by the external heavy atom solvent. The calculations of the room temperature chemiluminescent decay time at variable temperature obtain the activation parameters for compound 3a. The enthalpy ($\Delta H^o_2$) of reaction for thermal decompositions of typical dioxetanes have been estimated from thermal calculations from 69 to 90 kcal/mol. The energy relationship diagram of the compound 3a thermal decomposed to compound 3b can be sketched, if we postulate the enthalpy of reaction for thermal decomposition of compound 3a symbol for “$\Delta H^e_2$”. The energy relationship diagram is showed in Scheme-V.

Conclusion

The unique feature of this work lies in the observed room temperature chemiluminescent phosphorescence of the 5-heavy atom substituted acenaphtho lumiphor. In the 1,2-dioxetane ring of compound 3a which has high strain energy due to the twisted four-membered ring peroxide structure (C-O-O-C), both the O-O and C-C bonds are cleaved almost simultaneously during thermal decomposition into two excited pathways: (1) singlet chemiexcitation processes, (2) triplet chemiexcitation processes. The internal heavy atom effect of 5-heavy atom substitutent is Br >> Cl > H. The transition triplet excited state activation enthalpy ($\Delta H_{\text{Singlet}}^o$) is lower than the transition singlet excited state activation enthalpy ($\Delta H_{\text{Singlet}}^o$) ca. 7 kcal/mol ($\Delta H_{\text{Singlet}}^o$ < $\Delta H_{\text{Singlet}}^o$). We have shown that the 1,2-dioxetane tricyclic compound-based chemiluminiscence especially chemiluminescent phosphorescence of compound 3a. We continue to investigate these and other aspects, example as 5-iodo substituted 1,2-dioxetane tricyclic compound.

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REFERENCES