Thermal Stability and Chemiluminescence of 3-Alkoxy-3-aryl-4,4-diisopropyl-1,2-dioxetanes

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The singlet oxygenation of alkenes **1** gives the corresponding dioxetanes **2**, whose thermal stability and half-life of chemiluminescence induced by TBAF (NBu^n_4F) are significantly affected by the 3-alkoxyl group.

It has recently been reported that the reaction pathways of an alkene **1a** with singlet oxygen are affected by the reaction temperature, and the effect is likely due to the interaction, the so-called 'gear effect' of two geminal isopropyl groups.[1] We report here that an alkoxyl group adjacent to the 'gear' of two isopropyls affects significantly thermal stability and chemiluminescence of the dioxetanes **2** formed from **1** as well as the singlet oxygenation of alkenes **1**.

When a solution of an alkene **1b** (100 mg) and 5,10,15,20-tetraphenylporphyrin (5 mg) in CH_2Cl_2 (10 ml) was externally irradiated with a 940 W sodium vapour lamp under an oxygen atmosphere at −78 °C for 2 h, a dioxetane **2b** formed as an oil in a high yield together with a small amount of a hydroperoxide **3b** (**2b**:**3b** = 99:1) Scheme 1. Alkenes **1c, d** were similarly oxygenated at −78 °C to give the corresponding dioxetanes **2c, d** in >99% selectivities. For **1c** and **1d**, the 1,2-addition of singlet oxygen occurred in >98% selectivity even at 25 °C. On the other hand, the reaction modes of **1b** were affected by the reaction temperature (**2b**:**3b** = 90:10 at 0 °C, 80:20 at 25 °C), though the temperature dependence was far less significant than in the case of **1a**.[1] These results exhibit that the 1,2-addition of singlet oxygen occurs more preferentially even at high temperature as the alkoxyl group of **1** become bulkier. The facts may be in accord with that, for **2**, a bulky alkoxyl group such as *tert*-butoxyl interlocks the 'gear' of two isopropyls to prevent isopropyl methine hydrogen(s) from undergoing an 'ene' reaction with singlet oxygen.[2,†]

The dioxetanes **2b, d** were decomposed to the corresponding benzoates and diisopropyl ketone by a first-order process in hot C_6D_6 at 45–80 °C and their half-lives ($t_{1/2}$) at 25 °C were calculated from Arrhenius plots: $t_{1/2}$ = 1.28 for **2a**,[1] 1.45 for **2b**, 5.28 for **2c**, and 1.17 years for **2d**. These results indicated remarkable stability of **2a–d** and encouraged us to synthesize the dioxetanes **2e–h**, expected to be stable enough to examine their chemiluminescence. Thus, alkenes **1e–g** were similarly oxygenated at −78 °C to afford selectively (>95%) the corresponding dioxetanes **2e–h**. The activation parameters and half-lives of **2e–h** in thermolysis experiments in C_6D_6 are summarized in Table 1, which reveals that the thermal stabilities of **2e–g** are in the order similar to those of **2a–d**; MeO < EtO < Pr^iO ≫ Bu^tO.

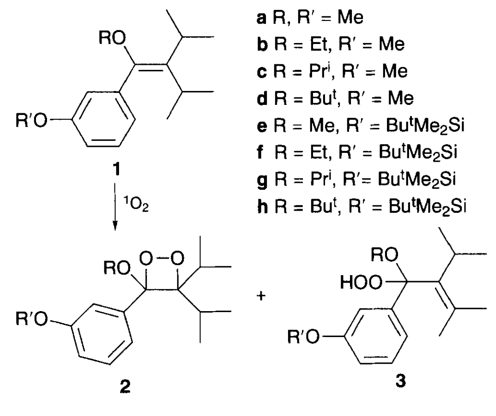
A dioxetane **4** has been reported to decay with luminescence in high quantum yield (Φ_{CL}) by removing the *tert*-butyldimethylsilyl group with tetrabutylammonium fluoride (TBAF) in Me_2SO[3] and the luminescence has been suggested to occur from an intermediary dioxetane **5** by the intramolecular CIEEL (chemically initiated electron exchange luminescence) mechanism.[3,4] The dioxetanes **2e–h** similarly emitted light (λ_{max} 463 nm) with Φ_{CL} and half-lives shown in Table 1, when solutions of **2e–h** in Me_2SO (1.0×10^{-5} mol dm^{-3} 1 ml) were added TBAF solutions in Me_2SO (1.0×10^{-2} mol dm^{-3}, 2 ml): under a N_2 atmosphere at 25 °C (Scheme 2). It should be noted that the half-life of the luminescence increases in the order of size of the alkoxyl group; **2h** has the longest half-life among **2e–h** in spite of its much lower thermal stability compared to **2e–g**.

The discrepancy of the order between thermal stabilities and half-lives of chemiluminescence for **2e–h** is likely due to ease (rate) of the electron transfer from the phenoxide to the σ* orbital of the O–O in intermediary dioxetanes **6e–h**, considering that the order of thermal stabilities of **6e–h** should reflect those of the parent dioxetanes **2e–h**. On the other hand, an NMR study on the temperature dependence of signals due to the aromatic protons of **2e–h** (−50 to 30 °C) showed the existence of energy

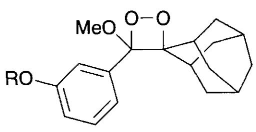
Table 1 Thermal stability and chemiluminescence of dioxetanes **2e–h**

	Thermal stability[a]			Chemiluminescence[b]	
	E_a/kcal mol^{-1} [c]	log *A*	$t_{1/2}$/y at 25 °C[d]	$t_{1/2}$/s	Φ_{CL}[e]
2e	25.5	14.9	0.53	6.3	0.21
f	25.9	15.2	0.59	11.5	0.23
g	26.7	15.5	0.91	20.5	0.35
h	22.5	13.2	0.17	37.5	0.31

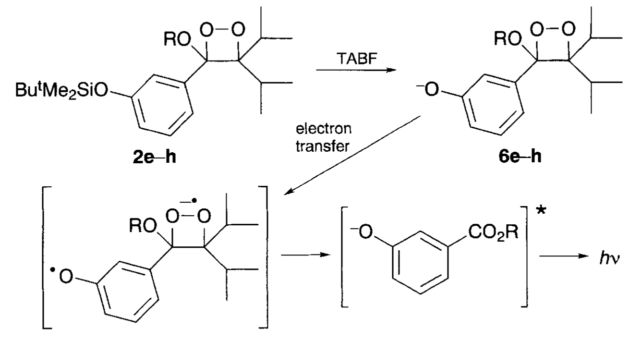
[a] First order rates of decomposition were measured in C_6D_6 at 45–80 °C by ^{1}H-NMR spectroscopy. [b] Solutions of **2e–h** in Me_2SO (1.0×10^{-5} mol dm^{-3}, 1 ml) were added to TBAF solutions in Me_2SO (1.0×10^{-2} mol dm^{-3}, 2 ml) under N_2 atmosphere at 25 °C. [c] 1 cal = 4.184 J. [d] Calculated values. [e] Relative quantum yields based on the value for **4** (ref. 3): λ_{max} = 470 nm (463 nm), Φ_{CL} = 0.25, $t_{1/2}$ = 5 (4.7 s); values in parentheses were obtained in the present work.



Scheme 1



4 R = OSiBu^{t}Me$_2$
5 R = O$^-$



Scheme 2

barrier(s) (**2h** ≫ **2e–g**) for the rotation of the aromatic ring in **2e–g**.§ These facts suggest that the phenoxide ring in **6h** can not rotate freely to the conformation¶ favourable for the intramolecular electron transfer|| from the phenoxide to the O–O.

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Footnotes

† The 'ene' reaction of singlet oxygen occurs preferentially for alkenes possessing an allylic hydrogen which sometimes lies perpendicular to the plane of the double bond.[2] For the present alkenes, especially **1c**, **d**, isopropyl methine protons are likely far from being at a 90° dihedral angle with respect to the plane of the double bond even at 25 °C.

‡ The luminescence occurred by a pseudo-first order process at concentrations of TBAF $> 5 \times 10^{-3}$ mol dm^{-3}.

§ Although a detailed variable-temperature NMR study is required to calculate energies of the rotational barriers, the preliminary study showed that **2e** exists as a 1 : 1 mixture of rotational isomers at below −30 °C, whereas **2h** exists as a 1 : 1 mixture of rotamers even at 30 °C, whose isolation is now in progress.

¶ For the *tert*-butoxy dioxetanes, the aromatic ring plane was suggested by a MM-2 calculation to be nearly on the plane comprising of an oxygen at the 2-position, a carbon at the 3-position, and an aromatic carbon attached to the dioxetane ring.

|| The rates of intramolecular electron transfer are known to be influenced by the donor–acceptor attachment geometry, though it is obscure for the present case whether the electron transfer occurs through space or through bonds.[5]

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