Studies on the Intramolecular Electron Transfer Catalyzed Thermolysis of 1,2-Dioxetanes

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Abstract—This work reports the synthesis and the chemiluminescence properties of the dioxetanes: 4-ethyl-4-methyl-3-(3-methoxy-phenyl)-1,2-dioxetane (I), 4-ethyl-4-methyl-3-(3-tert-butyldimethylsilyloxyphenyl)-1,2-dioxetane (II), 4,4-dimethyl-3-(3-methoxybenzyl)-1,2-dioxetane (III) and 4,4-dimethyl-3-(3-tert-butyldimethylsilyloxybenzyl)-1,2-dioxetane (IV). While in the thermal decomposition of I–IV preferential formation of triplet excited states is observed, in the presence of fluoride ions the decomposition rate constants of II and IV increase drastically and singlet excited states are formed with high quantum yields. These results are discussed based on the CIEEL ('Chemically Initiated Electron Exchange Luminescence') mechanism where the decomposition of the dioxetanes should be initiated by an intramolecular electron transfer from the phenolate ion (generated by fluoride catalyzed deprotection of the silyloxy group), either directly bound to the peroxicid ring (II) or separated from it by a methylene bridge (IV). © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

The phenomenon of luminescence generated either by living organisms (bioluminescence) or by chemical processes (chemiluminescence) has become an important analytical tool in recent years, in particular for biomedical applications. The chemiluminescent reaction most investigated over the past 30 years is the decomposition of 1,2-dioxetanes.1 Well before these were first prepared and isolated by Kopecky and Mumford in 1969,2 1,2-dioxetanes were proposed as key intermediates in several chemi- and bioluminescent reactions.3 The thermal cleavage of 1,2-dioxetanes generates two carbonyl fragments, one of which can be formed in an electronically excited state, predominantly in the triplet state.1,4–6 However, when these high-energy molecules bear an electron-rich substituent,5 singlet states are obtained predominantly. In these cases, such dioxetanes become labile and display 'chemically initiated electron exchange luminescence' (CIEEL), an electron transfer mechanism originally proposed by Schuster for the decomposition of diphenylperoxide7,8 and latter for α-peroxylactones9,10 and various other peroxides.11–15 The electron transfer may proceed either inter- or intramolecularly. An efficient intramolecular CIEEL is considered to take place in the firefly bioluminescence, where an α-peroxylactone (1) was proposed as intermediate.16 1,2-Dioxetanes containing substituents with low oxidation potentials,5 such as aryl-O–, aryl-RN– function-

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Most of the recent work in this field has been devoted to the synthesis of stable dioxetanes with triggering functionalities, in the search for efficient chemiluminescent systems useful in analytical applications. Recently, Matsumoto et al.28 have described the synthesis of dioxetanes containing a phenylethylgroup (3) or a phenylethynylgroup (4) as substituent, whose fluoride-catalyzed decomposition in

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DMSO yields red light with relatively high quantum yields.

Other work describes the synthesis and thermal decomposition of 1-alkoxy-1-aryl-2,2-diisopropylethylenes substituted dioxetanes (5), whose fluoride catalyzed decomposition leads to an intense blue light with chemiluminescence quantum yields higher than 0.2. ²⁷

However, although CIEEL remains a controversial proposition, mechanistic studies devoted to its features are rare. The decomposition mechanism of these dioxetanes has not yet been totally clarified, especially when the electron transfer occurs intramolecularly and these reactions are very fast. Recent discussions were directed to the odd/even relationship for the catalyzed decomposition of 3,3-diisopropyl-4-methoxy-4-(siloxy-2-naphthyl)-1,2-dioxetanes (6)²⁸ and to the solvent-cage effect on the decomposition of dioxetane ². ³¹ In the latter case, the authors propose that the back electron transfer process is the key step in chemiexcitation.

In a previous communication, ³² we report some of the chemiluminescence characteristics of dioxetanes II and IV upon unimolecular and fluoride catalyzed decomposition. In this work we report the synthesis and chemiluminescent properties of the 1,2-dioxetanes I to IV. Our studies include the determination of the activation parameters and quantum yields in the unimolecular decomposition of I–IV and of the fluoride-initiated decomposition of II and IV. Dioxetanes I and III were prepared to compare simple substituent effects on the thermolysis of 1,2-dioxetanes, thus a methoxy- or a sililoxy-substituent may exert similar effects on the decomposition of the peroxidic ring.

Compounds II and IV were treated with fluoride to generate the corresponding phenolate ion either directly bound to the peroxide ring (II) or separated from it by a methylene bridge (IV), in order to verify the occurrence of an intramolecular CIEEL mechanism. In this respect, the distinction between a ‘resonance’ (II) and a ‘through σ-bond’ (IV) electron transfer from the generated phenolate to the dioxetane moiety appeared of special interest to us, due to the fact that there is no example in the literature of an intramolecular CIEEL when the electron donor and the peroxide ring are separated. Our studies indicate that an intramolecular CIEEL occurs in both cases (II and IV) in the presence of fluoride, leading to the preferential formation of singlet excited states.

Dioxetanes I to IV were prepared from the corresponding olefins by the Kopecky route.² Dioxetanes I and II were obtained through a four step sequence (Scheme 1) in...
approximately 10% yield as a mixture of the isomers Z and E, which were not separated. The compounds III and IV were obtained in lower yields, 1.0 and 0.1%, respectively (Scheme 2), probably due to the elimination of HBr in the reaction between the β-bromohydroperoxide and the base, generating the corresponding allylic hydroperoxide; a peroxidic compound was indeed detected as the major product of this reaction.

The dioxetanes were purified by low temperature (−35°C) silica gel chromatography column and unequivocally characterized on the basis of their spectral data (1H and 13C NMR) and decomposition products. The purity of the compounds I to IV, determined by 1H NMR, was greater than 95% in all cases, with the decomposition products being the only detectable impurities. Furthermore, it should be pointed out that the dioxetanes III and IV do not contain traces of I and II, respectively, as the synthetic routes for obtaining them are totally different (Schemes 1 and 2). A minor product derived from the allylic 1,3-substitution (S₂2') has been observed under certain experimental conditions. However, even when these monosubstituted olefins (3-methyl-1-(3-R-phenyl)-1-butene, 16a—R= OCH₃, 16b—R=OSi(Me)₃-But) were present as side products in the Grignard coupling reaction, the corresponding monosubstituted dioxetanes V and VI (3-(3-R-phenyl)-isopropyl-1,2-dioxetane, V—R=OCH₃, VI—R=OSi(Me)₃-But) could not be detected even in traces, in the preparations of III and IV, respectively, presumably due to the highly unstable nature of monosubstituted dioxetanes.33

Thermal decomposition of I to IV in toluene leads exclusively to the formation of the expected carbonyl cleavage products, as verified by NMR spectroscopy. Direct emission with a maximum at 412 nm is observed for I and II (Fig. 1), which should correspond to the emission of the singlet excited aromatic aldehydes as their singlet energies are lower than those of aliphatic ketones.34 In the case of III and IV excited state formation can only be detected in the presence of sensitizers: 9,10-dibromoanthracene (DBA) and 9,10-diphenylandanthracene (DPA).

For dioxetanes I and II the activation parameters were obtained from the temperature dependence of the decomposition rate constants by direct emission measurements, whereas for III and IV by sensitized emission (Table 1). The chemiluminescence activation parameters $\Delta H^\#_{13}$ were obtained by plotting the log of initial emission intensities as a function of $1/T$ instead of the rate constants in the Eyring plots.35 The chemiexcitation quantum yields were obtained by utilization of the sensitizers DPA for singlet and DBA for triplet state counting,36 using luminol as light standard.37,38 The emission profiles of dioxetane decomposition were measured at 80°C at different concentrations of DPA and DBA in toluene. The rate constants obtained for I to IV at this temperature were in the range of 3.0×10⁻³ to 4.3×10⁻³ s⁻¹ (see Experimental). The initial emission intensity ($I_0$) was determined for each sensitizer concentration.

<table>
<thead>
<tr>
<th>Dioxetane</th>
<th>$\Delta H^#$</th>
<th>$\Delta S^#$</th>
<th>$\Delta G^#$ (25°C)</th>
<th>$\Delta H^#_{13}$</th>
<th>$\Phi^1$ (×10⁻³)</th>
<th>$\Phi^5$ (×10⁻³)</th>
<th>$\Phi^1/\Phi^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>23.6±0.4</td>
<td>-3.8±0.10</td>
<td>24.7±0.6</td>
<td>22.2±0.3</td>
<td>5.2±0.8</td>
<td>2.3±0.06</td>
<td>23</td>
</tr>
<tr>
<td>II</td>
<td>24.9±0.6</td>
<td>-0.54±0.02</td>
<td>25.1±0.6</td>
<td>21.3±0.4</td>
<td>6.8±1.8</td>
<td>3.6±0.10</td>
<td>19</td>
</tr>
<tr>
<td>III</td>
<td>22.6±0.2</td>
<td>-6.1±0.1</td>
<td>24.4±0.2</td>
<td>26.2±0.4</td>
<td>4.5±0.8</td>
<td>0.16±0.002</td>
<td>280</td>
</tr>
<tr>
<td>IV</td>
<td>22.6±0.9</td>
<td>-5.8±0.7</td>
<td>24.1±1.1</td>
<td>24.5±1.0</td>
<td>6.6±0.6</td>
<td>0.22±0.009</td>
<td>307</td>
</tr>
</tbody>
</table>

\(^a\) In kcal mol⁻¹.
\(^b\) In cal mol⁻¹ K⁻¹.
\(^c\) [I] = (6.7±0.8)×10⁻³ M, [II] = (1.0±0.2)×10⁻⁴ M, 412 nm.
\(^d\) [III] = (8.3±0.33)×10⁻⁵ M, [IV] = (2.1±0.4)×10⁻⁵ M, DPA 10 mM, 438 nm.

For quantum yield determinations: $\Phi^1$ = (6.0±0.7)×10⁻⁰ M, $\Phi^5$ = (4.7±1.0)×10⁻⁵ M, [III] = (8.3±0.3)×10⁻⁵ M. [IV] = (2.1±0.4)×10⁻⁵ M, 80°C, [DPA] and [DBA] from 1.7×10⁻³ to 1.0×10⁻² M, $\Phi^1$ and $\Phi^5$ in E mol⁻¹. All data were obtained in toluene.
and the emission intensity at infinite sensitizer concentration obtained by extrapolation of the double-reciprocal plot $1/I_0$ versus $1/[\text{sensitizer}]$. Singlet and triplet quantum yields were calculated according to literature procedures (see Discussion).\(^5\)

The treatment of II and IV with tetrabutylammonium fluoride (TBAF, 1.0 M solution in THF), causes deprotection of the silyloxy-substituted phenyl moiety, generating the corresponding phenolates. As a consequence, the decomposition rates increase drastically and a yellow flash of light is observed. The fluoride-initiated reactions are about $10^4$ times faster than the unimolecular ones and in both cases a strong direct emission with a maximum around 550 nm is observed (Fig. 2).

At low fluoride concentrations the observed rate constants ($k_{\text{obs}}$) show a linear dependence on the fluoride concentration ([F$^-\$]), indicating the deprotection as the rate limiting step. However, at high fluoride concentrations, the $k_{\text{obs}}$ values are independent of its concentration. Therefore, under these conditions $k_{\text{obs}}$ should correspond to the decomposition of the phenolate substituted dioxetane (Fig. 3).

The activation parameters for the initiated decomposition were determined by monitoring the direct light emission of the dioxetanes in the presence of fluoride at temperatures varying from 0 to 25°C, under identical reaction conditions. For the initiated decomposition of II, the activation parameters were obtained at three different fluoride concentrations: $1.3\times10^{-3}$, $1.3\times10^{-2}$ and $3.2\times10^{-2}$ M, in order to verify if a variation of the fluoride concentration would exert any effect on the activation parameters. The activation enthalpies ($\Delta H^\circ$) obtained at the saturation region of Fig. 3 ([F$^-$]=$1.3\times10^{-2}$ and $3.2\times10^{-2}$ M) are practically the same, while at lower fluoride concentration the $\Delta H^\circ$ are a little higher (ca. 1 kcal) (Table 2).

In contrast to the unimolecular decomposition, a strong, easily visible yellow emission is observed in the presence of fluoride. Due to the longer wavelength emission (Fig. 2), it was not possible in this case to use DPA and DBA for the determination of the chemiexcitation yields. No significant enhancement of the emission intensity was observed with rubrene. Thus, the singlet quantum yields were determined by measurements of the direct chemiluminescence. The chemiluminescence quantum yields ($\Phi_{\text{CL}}$) were obtained from the integral of the emission curves, using luminol\(^3\) as standard with correction for the photomultiplier sensitivity (Table 2). Singlet excitation yields can be obtained from $\Phi_{\text{CL}}$ values, if the fluorescence quantum yields of the emitting species are known. As the chemiluminescence spectra of II and IV (Fig. 2) match the fluorescence spectra of the respective substituted phenolate, the decomposition products, the aromatic aldehydes appear to be the emitting species. The fluorescence quantum yields of the emitting species were determined using standard procedures\(^3\) by

![Figure 2. Direct emission spectrum for the fluoride catalyzed decomposition of dioxetanes II and IV in THF ([F$^-$]=$3.2\times10^{-2}$ M, [II]=$2.0\pm0.4\times10^{-3}$ M at 25°C, [IV]=$4.2\pm0.8\times10^{-5}$ M at 7.5°C), emission intensities (I) in counts s$^{-1}$.](image)

![Figure 3. Dependence of the observed rate constant ($k_{\text{obs}}$) on [F$^-$] for the decomposition of II and IV in THF at 25°C ([II]=$2.0\pm0.4\times10^{-3}$ M, [IV]=$4.1\pm0.8\times10^{-5}$ M).](image)
reacting the silyloxy-substituted carbonyl compound with TBAF under the experimental conditions used for the kinetics measurements (Scheme 3). Fluorescein was chosen as standard as it shows an emission spectrum with maximum around 560 nm and its fluorescence quantum yield ($\Phi_{FL}$) is well established ($\Phi_{FL}$=0.91 in 0.1 M NaOH).39

Table 2 shows that excited singlet state formation in the initiated decomposition of II is quantitative, although there is a large uncertainty attached to this value, due to the error progression from the original experimental data ([dioxetane] determination, photomultiplier calibration, $\Phi_{FL}$ determination). In spite of the fact that $\Phi_S$ for IV is two orders of magnitude lower, this yield is still very high when compared to values obtained for most intramolecular CIEEL systems.39

Finally, control experiments were performed to prove the intramolecular nature of the catalysis in the decomposition of II and IV. For this purpose, the methoxy-substituted 1,2-dioxetanes I ([II]=[0.7×10^{-3} M] and III ([III]=[1.0×10^{-3} M]) were treated with TBAF ([TBAF]=[0.10 M]) in the absence and the presence of the protected aldehydes 9b and 15 ([9b] and [15]=[1.0×10^{-3} M]), respectively, in THF at 25 and 60°C. At 25°C, no measurable light emission could be observed under any experimental condition. At 60°C, the unimolecular decomposition of the dioxetanes can be observed by the direct emission of I and the DPA sensitized emission of III. The observed rate constants are not modified by the addition of TBAF or aldehydes 9b and 15, as well as the addition of both.

**Discussion**

Upon unimolecular decomposition of I and II direct emission at around 412 nm was observed, whereas for III and IV it was necessary to use sensitizers (DBA and DPA) for detecting the electronically excited state products. Compounds I to IV show typical characteristics of simple trisubstituted 1,2-dioxetanes; they are relatively stable ($\Delta G^\circ$=25 kcal/mol) and show preferential formation of triplet excited species (Table 1). The fact that I and II were obtained as a mixture of Z and E isomers does not invalidate the discussion on the activation parameters and quantum yields, as it is known that the activation energy ($E_a$) and the $\Phi_T$ and $\Phi_S$ for a series of Z/E isomers are practically the same within the experimental error.33,40,41 The ratio $\Phi_T/\Phi_S$ for I and II, 23 and 19, respectively, are lower than those normally observed for this kind of dioxetanes. Since no experiment was performed to determine the value for the efficiency of the triplet–singlet energy transfer ($\Phi_T^S$) from the specific excited carbonyl products to DBA, $\Phi_T^S$ was taken as 0.2.36 $\Phi_T$ may be underestimated if $\Phi_T^S$<0.2, as it would be if the triplet excited state energy of the carbonyl cleavage products are lower than the $T_2$ of DBA. On the other hand, as the absolute values for triplet quantum yields of I to IV are very similar, the obtained ratios for I and II could simply be an intrinsic characteristic of these dioxetanes, due to the higher singlet quantum yields.

The comparison of the values for the pairs I/II and III/IV shows the similarity in the thermal stability of silyloxy and methoxy substituted derivatives. The values of $\Delta H_f^r$ are lower than those determined by isothermal kinetics ($\Delta H^r$) for I and II, as can be associated to a negative activation energy of the fluorescence from the excited products.35 The results obtained upon unimolecular decomposition of I to IV clearly demonstrate that these compounds show chemiluminescence characteristics expected for simple trisubstituted 1,2-dioxetanes and no differences are observed for the methoxy and silyloxy substituted derivatives.

In contrast to the unimolecular decomposition, where a weak and continuous emission over about 30 min is observed at 80°C in THF, in the presence of fluoride, at 25°C, the complete decomposition of II and IV occurs in a few seconds, accompanied by an intense flash of yellow light. The half-lives at 25°C for II and IV in the absence of fluoride, 81 and 24 h, respectively, are reduced to 11 and 16 s, respectively, in the presence of the trigger. The activation parameters obtained for fluoride initiated decomposition are considerably lower than for the unimolecular one (Table 3). Moreover, the chemiluminescence spectra of the catalyzed reactions match the fluorescence spectra of the corresponding phenolates. In both cases, the decomposition profiles show first order decay and the observed rate constants ($k_{obs}$) are independent of the fluoride concentrations for [F$^-$]>2.0×10^{-2} M, showing a linear dependence for [F$^-$]<5.0×10^{-3} M. These facts indicate that at lower fluoride concentrations, the decomposition rates are determined by the bimolecular reaction between the dioxetane and fluoride. As the deprotection reaction becomes faster with increasing fluoride concentration, the rate limiting step becomes the electron transfer from the generated phenolate moiety to the peroxoic ring.
The activation parameters determined for this step for II and IV (Table 2) are reasonably similar and the \( \Delta G^\ddagger \) values obtained at 25°C are identical, within the experimental error. The negative value for \( \Delta S^\ddagger \) of IV, which compensates the surprisingly low value of \( \Delta H^\ddagger \), may be due to the need of a specific conformation for the electron transfer from the phenolate to the dioxetane ring through the methylene bridge.\(^{42} \) The \( \Delta H^\ddagger \) and \( \Delta H^\ddagger_{\text{cal}} \) values for dioxetane IV are similar and indicate that there is no major contribution of a dark decomposition pathway. The fact that the \( \Delta H^\ddagger_{\text{cal}} \) is lower than the \( \Delta H^\ddagger \) for II should be caused by the negative activation energy of the phenolate fluorescence, in analogy to the observations made in the unimolecular decomposition of I and II. In a general way, the activation parameters obtained for II and IV show that the initial electron transfer from the phenolate to the dioxetane ring occurs with the same efficiency whether the electron donor is directly linked to the acceptor (‘resonance electron transfer’) or connected to it by a methylene bridge (‘through \( \sigma \)-bond electron-transfer’).

Based on the above outlined facts, we have proposed a mechanism which is consistent with the CIEEL sequence. In the first step, the generation of the free phenolate occurs, which acts as an internal electron donor to the dioxetane moiety. Following this intramolecular electron transfer, the breakdown of the peroxidic ring generates two carbonyl fragments. In the last step, the formal back electron transfer is responsible for the generation of electronically excited states (Scheme 4).

Although the quantum yields in the initiated decomposition of II and IV, 100 and 1.0%, respectively, are very different, their magnitude is in agreement with occurrence of an intramolecular CIEEL mechanism in both cases. Control experiments using I and III in the presence of phenolates clearly exclude an intermolecular catalysis in the initiated dioxetane decomposition. Furthermore, the purity of IV and the fact that it cannot contain any traces of II (see Results) exclude the possibility that the observed emission in the initiated decomposition of IV might be due to impurities. It must be stated here again that the observed \( \Phi^S \) for IV, although two orders of magnitude lower than for II, is still a reasonably high quantum yield if compared to intermolecular\(^{7–10,43} \) and some intramolecular CIEEL systems.\(^{20,30} \) The observed difference of two orders of magnitude of \( \Phi^S \) for II and IV should be related to the efficiency of the excited state formation in the back electron transfer step \((k_{\text{BET}})\). In the case of II, the carbonyl radical anion, generated after the peroxide cleavage, represents an excited state. This hypothesis is supported by the so-called meta-effect, which predicts that the excited species generated in the case of II can be stabilized by ‘resonance structures’ (Scheme 5).\(^{44–46} \)

In the case of IV this stabilization is not possible and,
therefore, excited state formation by back electron transfer becomes less efficient. Moreover, in this case two pathways are possible: A and B in Scheme 4. In route A, an anion-radical derived from a non-conjugated carbonyl fragment would be formed. Although in this case the back electron transfer would be intramolecular too, it should be less efficient for excited state generation than for II, due to the impossibility of electronic conjugation between the electron donor and electron receptor species. In route B, an anion-radical derived from acetone could be formed, which means that the back electron transfer, responsible for generation of the excited states would proceed intermolecularly, resulting in reduced quantum yields. Escape from the solvent cage would cause a decrease in the singlet chemiexcitation yield, as previously described for the catalyzed decomposition of a spiroadamantyl-substituted dioxetane.31

In summary, the fluoride initiated decomposition of IV constitutes the first example of an intramolecular CIEEL mechanism, initiated by electron transfer from a donor which is not directly bound or conjugated to the peroxide ring. A comparison of the results obtained with II and IV shows that the initial electron transfer occurs with similar efficiency whether the donor is directly linked to the dioxetane ring or separated by a methylene bridge, indicating that efficient electron transfer can occur through the σ-bond.42 The intramolecular nature of this electron transfer has been unequivocally demonstrated by control experiments with the methoxy-substituted dioxetanes I and III in the presence of external phenolate ions. Two alternative interpretations are given for the much lower singlet quantum yields in the initiated decomposition of IV as compared to II. Whereas the reaction sequence is completely intramolecular for II and the excited state of the aromatic cleavage product is formed directly, in agreement with the unit singlet quantum yield (ΦS =1.0 E mol⁻¹), the back-electron transfer for IV can be an intramolecular (Scheme 4, route A) or an intermolecular (Scheme 4, route B) process. The lower ΦS for IV is caused by the lack of conjugation of the carbonyl anion radical with the aromatic ring in the intramolecular back-electron transfer, showing that in this case the methylene group considerably slows down the electron transfer process (or the electron transfer leads mainly to formation of the ground state product). In the intermolecular back-electron transfer, radical ion pair escape from the solvent cage may considerably lower ΦS.

This mechanistic model adequately explains the chemiluminescence parameters and the quantum yields obtained in the initiated decomposition of II and IV and therefore supplies additional evidence for the validity of the intramolecular CIEEL mechanism. However, this model is not in full agreement with the conclusions of a study on the viscosity dependence of the quantum yields obtained in the initiated decomposition of a spiroadamantyl-substituted dioxetane, where an intermolecular back-electron transfer is proposed in the excitation step.31 Nevertheless, this latter mechanism cannot account for the high ΦS generally obtained in the intramolecular initiated dioxetane decomposition,18,19,25–28,32 as compared to the inefficient intermolecular CIEEL systems.7–10,43 These discrepancies clearly demonstrate that more mechanistic studies, using different model compounds, are necessary.

### Experimental

Solvents and commercially available reagents were purified by usual procedures.47 Tetrahydrofuran and diethylether were freshly distilled from sodium and benzophenone under nitrogen. The dichloromethane and hexane, used for chromatographic purification of the dioxetanes were dried over CaH₂, distilled, left overnight over EDTA, filtered and distilled again.

The formation of products and consumption of reagents were followed on a Shimadzu CG14A gas chromatography coupled to a flame ionisation detector, using a megabore column CBP1W25 100 (id: 0.53 mm, film thickness; 1.0 μm, L: 25 m). The ¹H and ¹³C NMR spectra were obtained in CDCl₃ on a Brucker AC-200F and the mass spectrum on a CG–MS Hewlett-Packard: 5890 (Chromatography) and 5988 (mass).

### Dioxetanes I–IV

2-Butytriphenylphosphoniumbromide (8).²⁸ 2-bromo-butane (7, 0.05 mol) and triphenylphosphine (0.05 mol), in 20 mL anhydrous xylene were heated in a sealed flask for 90 h at 160°C. The white crystals obtained were washed with cold xylene and dried under vacuum for 4 h (100°C/2 mmHg), yielding 80% of product with 198–203°C melting point.

To an emulsion of 0.040 mol of 8 in THF, 0.040 mol of n-BuLi in THF (stock solution 2.5 M) was added under nitrogen. Immediately after addition, the reaction mixture became red. After 2 h under magnetic stirring, 0.040 mol of aldehyde 9 was added. The reaction mixture was stirred for 1 h at room temperature and then allowed to stand overnight. The pale yellow solid was separated by filtration.
The organic layer was washed with cold water, dried over anhydrous MgSO₄, filtered and the solvent evaporated. The yellow product was distilled under vacuum (10a, 130°C/2 mmHg, 10b, 130°C/3 mmHg) and the fractions containing the products were purified by column chromatography on silica gel using CH₂Cl₂ and C₆H₁₄ (2:1) as eluent. A mixture of isomers Z and E was obtained (10a: 59%, 10b: 47%).

10a: LRMS m/z (% intensity) 176 (M⁺; 94.3), 161 (M⁺−15; 100), 145 (M⁺−CH₂CH₃; 53.3), 131 (CH₂OPh- C≡C; 20.1), 121 (CH₃OPhCH₂; 38.6), ¹H NMR δ (ppm) 7.15 (m, 4H); 6.16 (s, 1H); 3.73 (s, 3H); 2.12 (m, 2H); 1.79 (s, 3H); 1.05 (m, 2H).

10b: LRMS m/z (% intensity) 276 (M⁺; 21), 219 (M⁺−57; 100); 163 (219−(C(CH₃)CH₂)₂(C₂H₆); 34), 145 (M⁺−OSi(Me)₂−Bu; 3), ¹H NMR δ (ppm) 6.9 (m, 4H); 6.2 (s, 2H); 2.19 (m, 2H); 1.86 (s, 3H); 1.85 (s, 3H), 1.12 (m, 3H), 0.94 (s, 9H); 0.21 (s, 6H).

General procedure for preparation of bromohydroperoxides 13a and 13b

To 0.15 mol of Mg and 1 mL of bromoethane, 0.05 mol of 12 in 10 mL anhydrous THF was added dropwise under heating and stirring. The mixture was refluxed for 2 h. The excess of Mg was rapidly filtered through glass wool under nitrogen and 0.05 mol of dimethylallylbromide in 10 mL THF was added at 0°C. The solution was allowed to warm to room temperature, refluxed for 3 h and cooled to room temperature again. The precipitation of white needle was observed. The solution was poured into 20 mL of cold water and extracted with ethyl acetate (2×50 mL). The extracts were dried over MgSO₄ and concentrated (60°C/30 mmHg). The yellow oil was distilled under vacuum (13a: 125°C/3 mmHg, 13b: 130°C/3 mmHg). Chromatography on silica gel with hexane/methylene chloride (20:1 for 13a and 1:1 for 13b) as eluent was performed for further purification (13a: 52%, 13b: 38%).

13a: LRMS m/z (% intensity) 176 (M⁺; 100), 161 (M⁺−15, 93.2), 147 (OPhCH₂CH(CH₂CH₃); 10.3), 131 (PhCH₂CH₂CH(CH₃); 9.9), 121 (MeOPhCH₂; 22.4), 107 (MeOPh; 8.14), 91 (C₆H₅; 53.1), 77 (C₆H₅; 22.4), ¹H NMR δ (ppm) 6.99–6.46 (m, 4H); 5.12–5.04 (m, 1H); 3.54 (s, 3H); 3.07 (d, 2H, J=7.35 Hz); 1.50 (s, 3H); 1.47 (s, 3H), ¹³C NMR δ (ppm) 17.19, 25.73, 132.62, 122.97, 34.35, 143.47, 114.10, 159.65, 110.86, 129.26, 120.72, 55.08.

13b: LRMS m/z (% intensity) 276 (M⁺−t-Bu; 96.4), 219 (M⁺−t-Bu; 84.9), 204 (M⁺−t-Bu(Me); 30.9), 161 (M⁺−t-Bu(Me)); 84.7), ¹H NMR δ (ppm) 6.96–6.43 (m, 4H); 5.13–5.12 (m, 1H); 3.09 (d, 2H, J=7.75 Hz); 1.56 (s, 3H); 1.52 (s, 3H); 0.82 (s, 9H); 0.06 (s, 6H), ¹³C NMR δ (ppm) 17.9, 25.7, 132.4, 123.1, 34.2, 143.3, 120.1, 155.6, 117.2, 129.1, 121.3, −4.4, 18.2, 25.8.

General procedure for preparation of bromohydroperoxides 11 and 14

Anhydrous H₂O₂ in ether. 20 mL of 60% aqueous H₂O₂ were extracted with ether (3×15 mL). The ether phase was dried over MgSO₄ at 4°C during about 24 h. The peroxide concentration, as determined spectrophotometrically, gives a concentration of the H₂O₂ solution close to 8 M.

Preparation of bromohydroperoxides. To a cooled solution (−20°C) of 0.02 mol of olefin was added 50 mL of an ether H₂O₂ solution ([H₂O₂]≈8 M, 0.4 mol). The mixture was cooled to −40°C and 0.01 mol of 1,3-dibromo-5,5-dimethylhydantoin (DBH) was added in small portions. The initially clear mixture became turbid at each addition of DBH and after some time under stirring became clear again, indicating that DBH has reacted and a new addition can be performed. The total reaction occurs in approximately 1.5 h. The mixture was then allowed to reach 0°C under stirring. The workup of the reaction was performed by washing the cold mixture with cold saturated solutions of Na₂CO₃ (2×30 mL), NaHCO₃ (2×30 mL), (NH₄)₂SO₄ (2×50 mL) and water (1×30 mL), respectively. The ether layer was dried over MgSO₄ during 1 h at 4°C. The solvent was evaporated at 0°C (30 mmHg) on a rotary evaporator. Due to its instability the product was not purified (row material: 11a: 77%, 11b: 67%, 14a: 69%, 14b: 80%).

In the case of 14b a small portion was reserved for chromatographic purification on a silica gel column at −30°C using dichloromethane/hexane (5:1) as eluent. The decomposition of the product was clearly observed during the purification process (just 13% of the row product was obtained as pure product).

14b: ¹H NMR δ (ppm) 7.81 (s, 1H); 7.20–6.53 (m, 4H); 4.23 (dd, 1H); 3.23–3.14 (m, 1H); 2.62–2.49 (m, 1H); 1.29 (s, 3H); 1.27 (s, 3H); 0.78 (s, 9H); 0.00 (s, 6H).

General procedure for preparation of dioxygenes I to IV

In a three necked round bottomed flask, equipped with a reflux condenser and an addition funnel, containing 0.0015 mol of β-bromohydroperoxide (11 or 14) in 15 mL CH₂Cl₂ and 18-crown-6 (ca. 50 mg), 38 mL of a 2 M KOH solution (0.76 mol) were added dropwise under stirring at 0°C, in the dark. After addition the mixture became pale yellow. The progress of the reaction was monitored by thin layer chromatography on silica gel using CH₂Cl₂/ C₆H₁₄ (2:1). After about 1.5 h TLC analysis indicated the total consumption of the corresponding β-bromohydroperoxide. In the case of III and IV another peroxidic compound, with a Rf similar to that of the β-bromohydroperoxide, was formed as the major product. The mixture was washed with cold solutions of NaCl (2×20 mL) and water (2×10 mL). The organic layer was dried over MgSO₄ during 10 min at 0°C, filtered and the solvent evaporated on a rotary evaporator at 0°C. The purification was performed on a silica gel column at −30°C using a mixture of CH₂Cl₂ and C₆H₁₄ as eluent: 2:1, 1:1, 5:1 and 2:1 for I, II, III and IV, respectively (I: 28%, II: 19%, III: 3.5%, IV: 0.30%).

I: ¹H NMR δ (ppm) Z isomer: 7.68–7.08 (m, 4H); 6.38 (s, 1H); 4.05 (s, 3H); 2.01–1.93 (m, 1H); 1.71–1.67 (m, 1H); 1.94 (s, 3H); 0.85 (t, 3H, J=7.75 Hz), E isomer: 7.68–7.08 (m, 4H); 6.53 (s, 1H); 4.05 (s, 3H); 2.36–2.28 (m, 2H);
... and the lamp off. The dioxetane concentration ([I]) was calculated by measuring the absorbance (A) at 353 nm, using [I]=(6.7±0.8)×10^{-5} M, [II]=(1.0±0.2)×10^{-5} M, [III]=(8.3±0.3)×10^{-5} M and [IV]=(2.1±0.4)×10^{-5} M.

Quantum yields.\(^5\) The dioxetane stock solution (10–20 μL in toluene) was added to a cuvette, containing 3 mL of the sensitizer solution in toluene pre-heated to 80°C, and the kinetic profiles were recorded using [I]=(6.0±0.7)×10^{-6} M, [II]=(4.7±1.0)×10^{-5} M, [III]=(8.3±0.3)×10^{-5} M, [IV]=(2.1±0.4)×10^{-5} M, [DBA] and [DPA]: 1.7×10^{-3}–1.0×10^{-2} M.

Fluoride initiated decomposition of II and IV

The emission spectra from the initiated dioxetane decomposition were obtained by adding 100 μL of a 1.0 M TBAF solution to a cuvette containing dioxetane in 3 mL of THF. The experiments were performed at 25°C for II and 75°C for IV, using [F\(^-\)]=(3.2±1.0)×10^{-2} M, [II]=(2.0±0.4)×10^{-5} M and [IV]=(4.2±0.8)×10^{-5} M.

The kinetic experiments were performed with the grating set at the mirror position by treating II and IV with TBAF (1.0 M solution in THF) in anhydrous THF. All glassware was carefully dried, THF and TBAF solution were handled under nitrogen and the experiment was performed in a cuvette closed with a rubber septum to avoid humidity in the system. As the decomposition kinetics is very fast, the addition of TBAF solution was done very quickly in a dark room.

Fluoride concentration dependence. To a 3 mL cuvette, containing dioxetane in anhydrous THF at 25°C, TBAF was added and the kinetic profiles were measured at different fluoride concentrations, using [II]=(2.0±0.4)×10^{-5} M,
were determined according to the following equation:

\[ [\text{IV}] = (4.1 \pm 0.8) \times 10^{-3} \, \text{M} \quad \text{and} \quad [\text{F}] = 6.6 \times 10^{-3} \text{ to } 6.2 \times 10^{-2} \, \text{M}. \]

**Activation parameters for the initiated decomposition.**

These experiments were performed as those for the unimolecular decomposition. The dioxetane was added to a cuvette, containing 3 mL THF at the desired temperature, followed by addition of 100 µL of TBAF (1.0 M solution in THF) and the kinetic profiles measured, using \([\text{II}]= (2.0 \pm 0.4) \times 10^{-5} \, \text{M}, \quad [\text{IV}]= (4.1 \pm 0.8) \times 10^{-5} \, \text{M}, \quad [\text{F}] = 3.2 \times 10^{-2} \, \text{M}, \text{ at } 0-25^\circ\text{C}.\]

**Fluorescent quantum yields.**

The fluorescence quantum yields of the cleavage products of II and IV were determined by deprotection of the corresponding silylated aldehydes 9b and 15 by TBAF ([TBAF] = 3.2 \times 10^{-2} \, \text{M}), in THF, using fluorescein as standard (\(\Phi_{\text{FL}} = 0.91\) in aqueous 0.1 M NaOH).\(^{39}\) The fluorescence spectra of both solutions, fluorescein and the deprotected cleavage products, were measured by exciting the samples at 430 nm under identical experimental conditions.

**Chemiluminescence and singlet quantum yields.**

In a 3 mL cuvette, containing anhydrous THF and the dioxetane, 100 µL of the fluoride solution (TBAF 1.0 M solution in THF) were added at 25°C. The kinetic profiles for the decomposition were measured and the integral of the curves calculated. The chemiluminescence quantum yield (\(\Phi_{\text{CHL}}\)) corresponds to the total light emission (area under the curve) divided by the number of moles of dioxetane (n) using \([\text{II}]= (2.3 \pm 0.5) \times 10^{-5} \, \text{M} \quad \text{and} \quad [\text{IV}]= (4.3 \pm 0.7) \times 10^{-5} \, \text{M}.\) After calculation of \(\Phi_{\text{CHL}}\), the singlet quantum yields (\(\Phi_s\)) were determined according to the following equation: \(\Phi_s = \Phi_{\text{CHL}}/\Phi_{\text{FL}}.\)

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**References**