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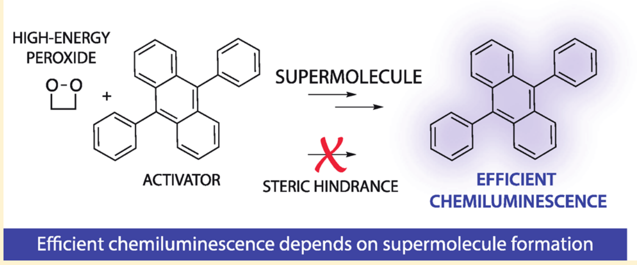
Chemiluminescence Efficiency of Catalyzed 1,2-Dioxetanone Decomposition Determined by Steric Effects

Fernando Heering Bartoloni,[†] Marcelo Almeida de Oliveira, Luiz Francisco Monteiro Leite Ciscato,[†] Felipe Alberto Augusto, Erick Leite Bastos,* and Wilhelm Josef Baader*

Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, 05508-000 São Paulo, Brazil

Supporting Information

ABSTRACT: The chemiluminescent decomposition of 1,2-dioxetanones (α-peroxylactones), catalyzed by an appropriate fluorescent activator, is an important simple model for efficient bioluminescent transformations. In this work, we report experimental data on the catalyzed decomposition of two spiro-substituted 1,2-dioxetanone derivatives, which support the occurrence of an intermolecular electron transfer from the activator to the peroxide. The low efficiency of the studied systems is associated with steric hindrance during the chemiexcitation sequence, rationalized using the concept of supermolecule formation between the peroxide and the catalyst. This approach explains the difference in the chemiexcitation efficiencies in the decomposition of four-membered cyclic peroxide derivatives: 1,2-dioxetanes, 1,2-dioxetanones, and 1,2-dioxetanedione (the intermediate in the peroxyoxalate reaction), which are the most important model compounds for excited-state formation in chemiluminescence and bioluminescence processes.



1. INTRODUCTION

Light is a coproduct of many chemical and biochemical reactions. Efficient processes show quantum efficiency up to unity and include firefly bioluminescence (Φ_{BL} = 0.4 E mol^{-1}),[1] the peroxyoxalate system (Φ_{CL} up to 0.7 E mol^{-1}), and the induced decomposition of 1,2-dioxetanes (Φ_{CL} up to 1.0 E mol^{-1}).[2,3] Cyclic peroxides have been frequently described as high-energy intermediates in chemical formation of products in the electronic excited state because their decomposition fulfills both energetic and geometric criteria required for chemiexcitation. However, the thermal decomposition of isolable four-membered ring peroxides, namely 1,2-dioxetanes and 1,2-dioxetanones, often results in inefficient chemiexcitation and the preferential formation of products in the triplet excited state ($\Phi_S < 10^{-4}$ E mol^{-1} vs $\Phi_T > 10^{-1}$ E mol^{-1}).[2,4,5]

Schuster and co-workers reported that fluorescent aromatic hydrocarbons (referred to as *activators*, ACT) are able to catalyze the decomposition of both 3,3-dimethyl-1,2-dioxetanone (**1**) and diphenoyl peroxide, resulting in a noticeable increase in light emission intensity and high (singlet) chemiexcitation quantum yields ($\Phi_S = 10^{-1}$ E mol^{-1}).[6] The bimolecular rate constant for the process (k_{CAT}) was shown to depend on the oxidation potential of the ACT; therefore, intermolecular electron transfer has been assumed to be involved. Although this process has never been observed for 1,2-dioxetanes, it was the milestone for the postulation of the chemically initiated electron-exchange luminescence (CIEEL) mechanism and subsequent proposition of a 1,2-dioxetanone as the key intermediate in firefly luciferin/luciferase bioluminescence.[7]

Since this seminal experiment, the following findings have contributed to a better understanding of the mechanism involved in the chemical formation of electronic excited states. (i) Catalani and Wilson remeasured the chemiexcitation quantum yield of the catalyzed decomposition of diphenoyl peroxide and found that the initially reported value was overestimated by at least 2 orders of magnitude; i.e., the correct Φ_S is lower than 10^{-3} E mol^{-1}.[8] (ii) Our group found that the Φ_S values for the catalyzed decomposition of 1,2-dioxetanones, the model intermediate in firefly bioluminescence, were also overestimated by 2 orders of magnitude.[9] (iii) Although these results can suggest that the generation of excited states by the intermolecular CIEEL mechanism is inefficient (raising questions on its use as a model for the firefly bioluminescence),[1,7,10] this conclusion is refuted by the high efficiency of the peroxyoxalate system, which involves the interaction of a peroxidic intermediate formed in situ with the activator, in agreement with an intermolecular CIEEL mechanism.[11−13] Furthermore, the induced decomposition of phenoxy-substituted 1,2-dioxetanes, which occurs by the intramolecular version of the CIEEL mechanism, leads to highly efficient singlet excited-state formation.[14−26]

In this work, we provide experimental support for the occurrence of an *intermolecular* electron-transfer step in the ACT-catalyzed chemiluminescent decomposition of the alkyl-spiro-1,2-dioxetanones **2** and **3** (Scheme 1). The results are discussed in terms of the data available for the decomposition

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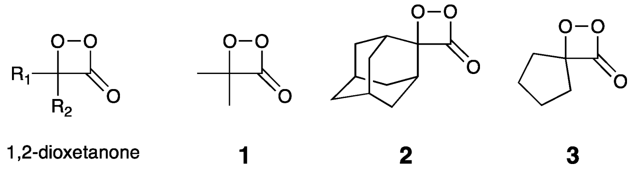
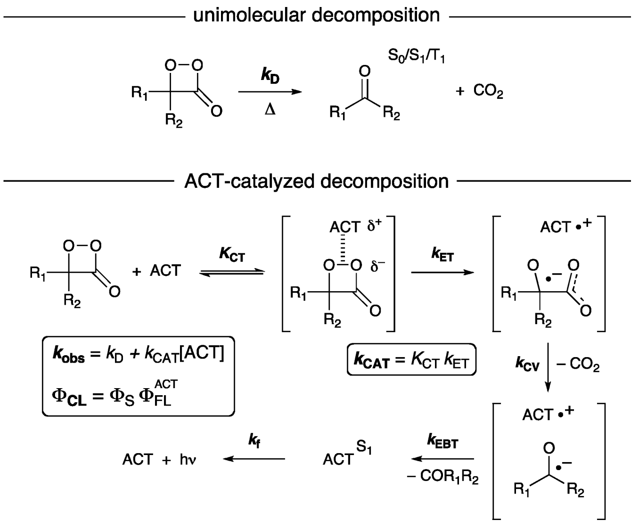
Scheme 1. Chemical Structures of the Studied 1,2-Dioxetanones



of 3,3-dimethyl-1,2-dioxetanone (**1**), the peroxide used by Schuster to propose the CIEEL mechanism (Scheme 2), and the peroxyoxalate system. Finally, a rationale for the effect of the structure of the cyclic peroxide on the chemiexcitation quantum yields is provided.

Scheme 2. Unimolecular and ACT-Catalyzed Decomposition of 1,2-Dioxetanones



2. RESULTS

The observed rate constant (k_{obs}) determined in the catalyzed decomposition of 1,2-dioxetanones has two main components: k_{CAT}[ACT] and the "dark" decomposition rate constant, k_D (Scheme 2). k_{obs} values for the decomposition of **2** and **3**, whose synthesis has been reported elsewhere,[27] were determined in toluene in the absence or presence of different ACTs. In both cases, k_{obs} does not depend on the ACT concentration. *Unimolecular decomposition* (without ACT): k_{obs}(unimolecular, **2**, 50 °C) = $(6 \pm 1) \times 10^{-3}$ s^{-1} and k_{obs}(unimolecular, **3**, 25 °C) = $(9 \pm 3) \times 10^{-4}$ s^{-1}. *Catalyzed decomposition* ([ACT] from 0.1 to 5.0 mmol L^{-1}): k_{obs}(ACT, **2**) = $(6.0 \pm 0.5) \times 10^{-3}$ s^{-1} and k_{obs}(ACT, **3**) = $(9 \pm 2) \times 10^{-4}$ s^{-1}. In contrast, the values of k_{obs} for the decomposition of 1,2-dioxetanone **1** under the same experimental conditions have been found to depend on the nature and the concentration of the ACT.[9] This discrepancy is probably a consequence of the lower contribution of the catalyzed pathway of **2** and **3**, compared to the unimolecular decomposition (Scheme 2). Therefore, the bimolecular rate constant (k_{CAT}) cannot be determined directly from the k_{obs} dependence on the ACT concentration. However, the k_{CAT}/k_D ratio (Table S2, Supporting Information) and the chemiexcitation quantum yield at the infinite ACT concentration (Φ_S^∞, Table 1) can be calculated from the double-reciprocal plots of the singlet quantum yields (Φ_S) versus the ACT concentrations ($1/\Phi_S$ vs 1/[ACT]) (eq 1, Figure 1).[11] Rubrene (5,6,11,12-tetraphenyltetracene, RUB), perylene (PER), 9,10-diphenylanthracene (DPA), and anthracene (ANT) were used as activators with both peroxides, while 2,5-diphenyloxazole (PPO) was used only with **2**, as the light emission intensity was too low to be detected when PPO was used with peroxide **3**. Therefore, 9,10-dibromoanthracene (DBA) was used as activator instead of PPO in the decomposition of **3**, since their oxidation potentials are similar.

$$\frac{1}{\Phi_S} = \frac{1}{\Phi_S^\infty} + \left(\frac{k_D}{k_{CAT}\Phi_S^\infty}\right)\frac{1}{[ACT]} \qquad (1)$$

The determination of k_{CAT} from the k_{CAT}/k_D ratio requires the assumption that the predominant pathway in the decomposition of **2** and **3** is the unimolecular reaction (i.e., $k_D \gg k_{CAT}[ACT]$); consequently, k_{obs} mainly reflects the unimolecular decomposition rate constant (i.e., $k_{obs} \approx k_D$, Table S2, Supporting Information). This assumption is supported by the observation that k_{obs} remains constant for a given 1,2-dioxetanone upon changing the ACT (Table S2, Supporting Information). Additionally, the mean rate constant values obtained in the peroxide decomposition in the presence of ACT are identical to those measured in the unimolecular decomposition of **2** and **3** (Tables S1 and S2, Supporting Information), whereas emission intensities are considerably higher in the ACT-catalyzed reactions, indicating higher quantum yields (Φ_{CL}) in the latter process. The values of k_{CAT} and Φ_S^∞ for the ACT-catalyzed decomposition of **2** and **3** are given in Table 1. The occurrence of *indirect* CL (i.e., energy transfer) was ruled out because the emission intensities (I_0) for the RUB-catalyzed decomposition of **2** and **3** are generally 1 order of magnitude higher than that with the same concentration of DPA (see Table S1, Supporting Information,

Table 1. Singlet Excited State Formation Quantum Yields at Infinite ACT Concentrations (Φ_S^∞) and Bimolecular Rate Constants (k_{CAT}) for the ACT-Catalyzed Decomposition of Peroxides 2 and 3[a]

	2		3	
ACT	$\Phi_S^{\infty b}$ (10^{-4} E mol^{-1})	k_{CAT}^{b} (L mol^{-1} s^{-1})	$\Phi_S^{\infty c}$ (10^{-4} E mol^{-1})	k_{CAT}^{c} (L mol^{-1} s^{-1})
RUB	100 ± 30	1.6 ± 0.5	3.9 ± 0.6	7.0 ± 1.0
PER	13.9 ± 0.7	1.81 ± 0.09	3.0 ± 0.4	1.26 ± 0.06
DPA	5.0 ± 2.0	0.8 ± 0.3	4.9 ± 0.1	0.264 ± 0.003
ANT	2.7 ± 0.6	0.8 ± 0.2	2.9 ± 0.4	0.9 ± 0.2
DBA			50 ± 30	0.23 ± 0.04
PPO	0.33 ± 0.03	0.5 ± 0.1		

[a] Obtained graphically from $1/\Phi_S$ vs 1/[ACT] linear plots. [b] In toluene at 50 °C. [c] In toluene at 25 °C.

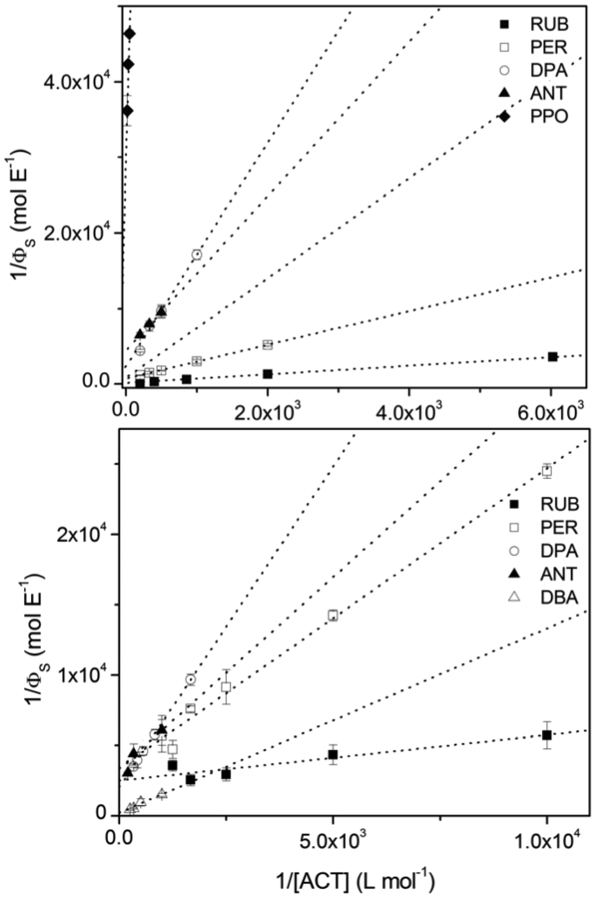


Figure 1. Double-reciprocal plots of the singlet quantum yields (Φ_S) and the activator concentration for the ACT-catalyzed decomposition in toluene of **2** (top graph, [**2**] = 0.25 mmol L^{-1}, 50 °C) and **3** (bottom graph, [**3**] = 3.0 μmol L^{-1}, 25 °C).

for an example in the decomposition of **3**). As both activators have similar Φ_{FL} values, this quantum yield difference indicates the importance of the oxidation potential ($E^{ox}_{1/2}$ = 0.61 V vs SCE and that for DPA is $E^{ox}_{1/2}$ = 1.06 V vs SCE) for the chemiexcitation efficiency, indicating the involvement of an electron-transfer step.[11]

The chemiexcitation quantum yields at infinite activator concentrations (Φ_S^∞) are independent of the [ACT], because Φ_S^∞ is determined in a hypothetical condition where all peroxide is consumed in the catalyzed path.[11] These Φ_S^∞ values, which span from 3.3 × 10^{-5} to 1.0 × 10^{-2} E mol^{-1} for **2** (in toluene at 50 °C) and from 2.9 × 10^{-4} to 7.0 × 10^{-3} E mol^{-1} for **3** (in toluene at 25 °C) (Table 1) are in agreement with the yields reported previously for the activated decomposition of **1**−**3** (<2 × 10^{-3} E mol^{-1}).[9]

3. DISCUSSION

3.1. Value of k_{CAT}: Information on the Rate-Determining Step. According to the CIEEL mechanism, the rate-determining step for chemiexcitation is the electron transfer from the ACT to the peroxide, with a catalytic rate constant (k_{CAT}) (Scheme 2) which should depend on the oxidation potential (E^{ox}) of the ACT, the reduction potential (E^{red}) of the peroxide and a Coulombic term related to interaction of oppositely charged species (eq 2)[28−30]

$$k_{CAT} = A \exp\left[\frac{-\alpha}{RT}\left(E_D^{\,ox} - E_A^{\,red} - \frac{e^2}{\varepsilon R_0}\right)\right] \qquad (2)$$

where α is the electron transfer coefficient, R is the gas constant, T is the temperature; $E_D^{\,ox}$ is the oxidation potential of the activator, $E_A^{\,red}$ is the reduction potential of the high-energy intermediate; e is the electron charge; R_0 is the distance between radical ions in charge-transfer complex, and ε is the dielectric constant of the solvent.

Therefore, for a given peroxide (i.e., E^{red} constant), a linear correlation between the natural logarithm of k_{CAT} and the E^{ox} of the ACT is expected (eq 3). Such dependence has been observed for the catalyzed decomposition of diphenoyl peroxide, 1,2-dioxetanones, and the peroxyoxalate reaction[6,11,12]

$$\ln k_{CAT} = (\ln A + \alpha B) - \frac{\alpha}{RT}E_D^{\,ox} \qquad (3)$$

where A is the pre-exponential term of eq 2 and B is equal to $((E_A^{\,red}/RT) + (e^2/\varepsilon R_0 RT))$.

The ln k_{CAT} values determined for the ACT-catalyzed decomposition of 1,2-dioxetanones **2** and **3** show a linear correlation with the half-peak oxidation potential of the ACT ($E^{ox}_{1/2}$, Table S2 (Supporting Information), Figure 2) allowing

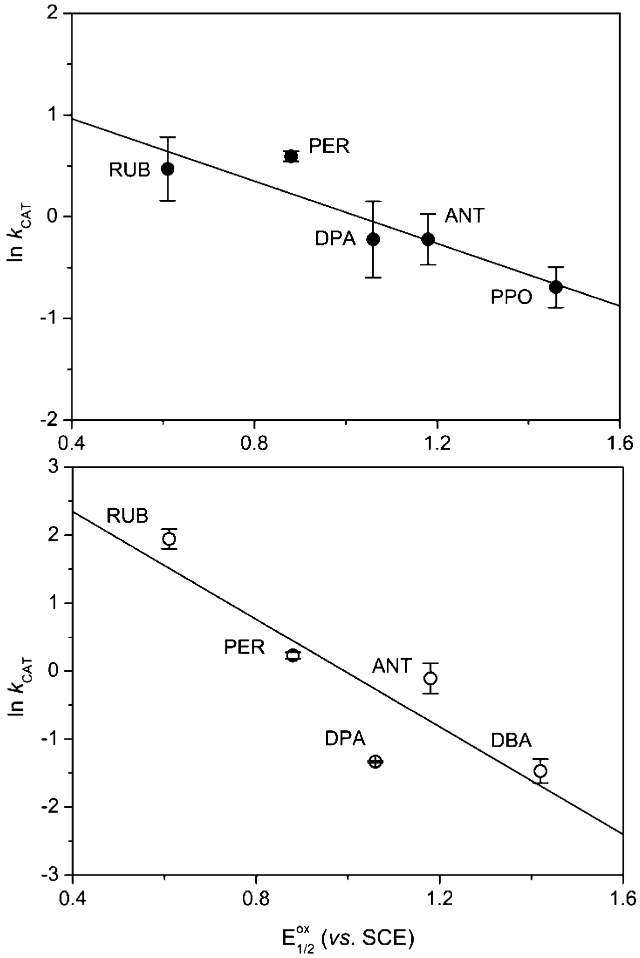


Figure 2. Linear correlation between the ln k_{CAT} values and the oxidation potentials ($E^{ox}_{1/2}$ vs SCE (saturated calomel electrode)) of the activator for the ACT-catalyzed decomposition of 1,2-dioxetanones **2** (●) and **3** (○).

the determination of the electron transfer coefficients $\alpha = 0.04 \pm 0.01$ and 0.10 ± 0.02 for **2** and **3**, respectively, using eq 3. Although these values are considerably low, they indicate the occurrence of an electron transfer from the ACT to the peroxide in the ACT-catalyzed decomposition of **2** and **3**, as predicted by the CIEEL mechanism (Scheme 2). The α values reported for several CIEEL systems are typically within the range of 0.1−0.3, including values for the peroxyoxalate reaction[11,12] and the decomposition of different isolated cyclic peroxides.[2,3,6,31−33] The α values of 0.04 and 0.10 obtained for **2** and **3** indicate an early transition state with respect to the electron transfer and presumably also to the O−O bond cleavage, as these two steps should be simultaneous.[2,12,28,29] Noteworthy, a value of $\alpha = 0.23 \pm 0.02$ was reported for the highly efficient peroxyoxalate reaction;[12] however, the α value reported for the (inefficient) catalyzed decomposition of 1,2-dioxetanone **1** was $\alpha = 0.3$.[6,34] These values might indicate that a high α value does not guarantee efficient chemiexcitation, and low α values only mean that an early transition state is involved in these cases.

According to eq 3, k_{CAT} is expected to increase the higher the difference in the redox potentials of the ACT/peroxide pair as well as the lower the steric hindering during their interaction. The weak dependence of the k_{CAT} values on the $E^{ox}{}_{1/2}$ observed for the ACT-catalyzed decomposition of **2** ($\alpha = 0.04$) might be related to the steric hindrance caused by the bulky spiro-adamantyl group, preventing the approximation between the ACT and the peroxide, resulting in a low CT complex formation equilibrium constant and consequently low catalytic rate constant values.

3.2. Value of $\Phi_S{}^\infty$: Information on the CL Efficiency.

The CIEEL mechanism (Scheme 2) does not imply, a priori, dependence between chemiexcitation quantum yields and the oxidation potential of the ACT, although the experimental results indicate this relation (Table 1). The quantum yields at infinite ACT concentrations should be determined only by the efficiency for excited-state formation of the electron back transfer (EBT) between the radical anion of the carbonyl compound and the radical cation of the ACT, as these hypothetical conditions imply in the reaction of all of the peroxide with the ACT.[2,11] In a first analysis, this efficiency might be related to the energy released in the EBT step leading to excited singlet-state formation ($\Delta G^*{}_{EBT}$) for the ACT, which was calculated from the free energy balance for the formation of ground-state products (ΔG_{EBT}), determined by the redox potentials of the electron-donor and -acceptor pair as well as the singlet excited-state energies (E_S) of the ACT (eq 4, Table S3, Supporting Information)[11]

$$\Delta G^*{}_{EBT} = -F[E_{1/2}{}^{ox}(\mathrm{ACT}) - E_{1/2}{}^{red}(\mathrm{ketone})] + E_S \tag{4}$$

where F is the Faraday constant and E_S is the singlet energy of the ACT.

The values of $\Phi_S{}^\infty$ obtained in the ACT-catalyzed decomposition of **2** are correlated with the calculated $\Delta G^*{}_{EBT}$ (Figure 3), showing that the chemiexcitation efficiency increases with increasing energy deliverance in the EBT step (Figure 3). However, in the decomposition of **3**, no such correlation can be observed (Figure 3), obviously due to the fact that the quantum yields were determined to be very similar for all the ACTs studied, except DBA (Table 1). However, the dependence of the quantum yields with the energy released in the EBT process for the reaction of **2** is in agreement with the observation that a more exothermic transformation leads to a higher probability of excited state formation; this has been shown by our group for the highly efficient peroxyoxalate reaction.[2,12]

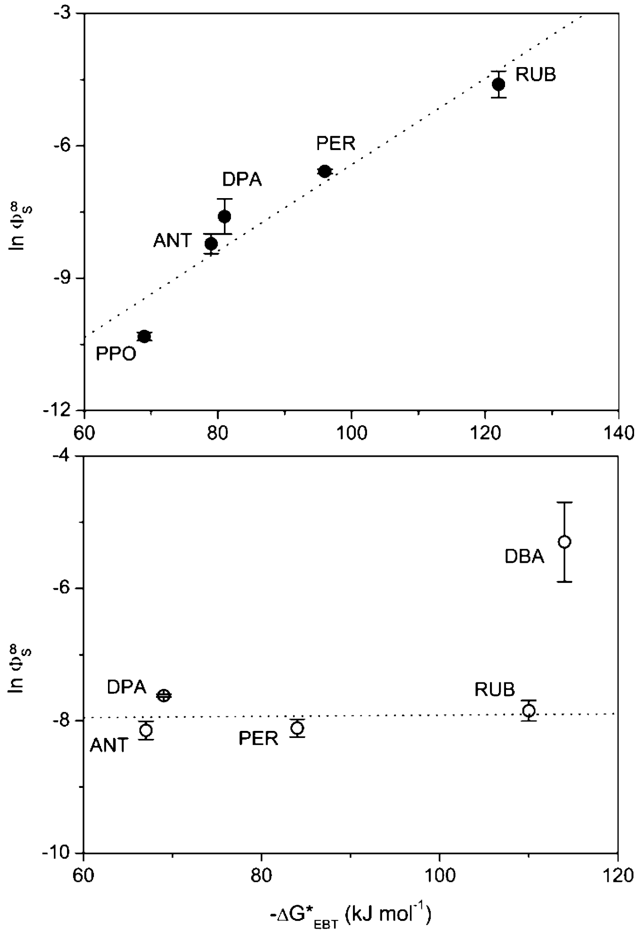


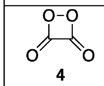
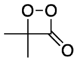
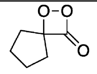
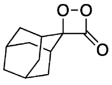
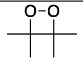
Figure 3. Correlation of the infinite singlet excitation quantum yields ($\Phi_S{}^\infty$) with the free energy released by the EBT process leading to excited-state formation ($\Delta G^*{}_{EBT}$) in the ACT-catalyzed decomposition of 1,2-dioxetanones **2** (●) and **3** (○). Linear regression was carried out excluding DBA as this ACT can act as a triplet energy acceptor.[35] The amount of light obtained using PPO to catalyze the decomposition of **3** is too small to be quantified.

3.3. Structure−Reactivity Relationships in the Catalyzed Intermolecular CIEEL.

In order to rationalize the chemiluminescence properties of 1,2-dioxetanones **1**−**3** and 1,2-dioxetanedione (**4**), the thermal stability of these cyclic peroxides ($t_{1/2}$), their singlet excited-state quantum yields in the RUB-activated decomposition (Φ_S), and the bimolecular decomposition rate constants (k_{CAT}) are compiled (Table 2). The presence and the size increase of the alkyl group cause a rise in the thermal stability of these peroxides, as shown by their half-lifetimes. A similar influence of crowded alkyl groups on the thermal stability of 1,2-dioxetane derivatives has been observed.[2−4,36]

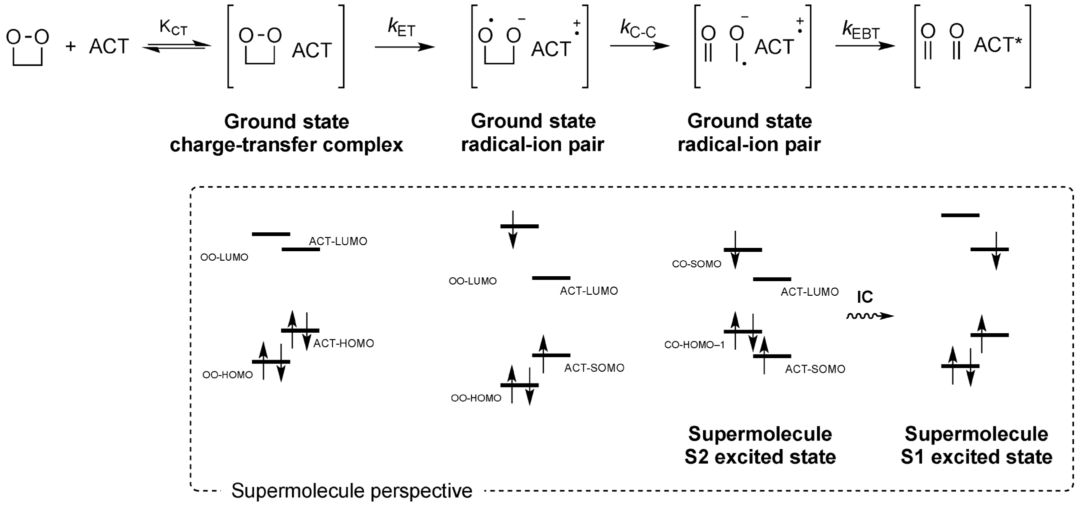
The highest k_{CAT} value is observed for the only efficient intermolecular CIEEL system, the ACT-catalyzed decomposition of the peroxyoxalate high-energy intermediate (HEI), 1,2-dioxetanedione (**4**). Its k_{CAT} value is more than 3 orders of magnitude higher than the one for **1**, the most reactive 1,2-dioxetanone derivative (Table 2). Additionally, an increase in the size of the alkyl substituent causes an evident decrease in

Table 2. Thermal Persistence and Chemiluminescence Parameters for the Rubrene-Catalyzed Decomposition of 1,2-Dioxetanones 1−3, 1,2-Dioxetanedione (4), and Tetramethyl-1,2-dioxetane (5)

Peroxide	k_{CAT} [a] (L mol^{-1} s^{-1})	Cavity volume (Å^3)	$t_{1/2}$ [b] (min)	Φ_S [a] (E mol^{-1})
 4	$(1.7 \pm 0.1) \times 10^{5}$ ref. 12	141.267	0.04 ref. 12	0.68 ± 0.05 ref. 11
 1	43 ± 1 ref. 9	149.191	12 ref. 37	$(1.0 \pm 0.2) \times 10^{-3}$ ref. 9
 3	7.0 ± 1.0	173.699	11.6 [c]	$(3.9 \pm 0.6) \times 10^{-4}$
 2	0.19 ± 0.01 [d]	233.438	48 [d]	$(1.0 \pm 0.3) \times 10^{-2}$
 5	e	156.504	1.4×10^{4} ref. 2,3	e

[a] With RUB in toluene for **1**−**3** or EtOAc for **4** at 25 °C. [b] For the unimolecular decomposition at 25 °C. [c] From unimolecular decomposition kinetics. [d] Calculated from the activation parameters for the unimolecular and RUB-catalyzed decomposition at 25 °C (data not shown). [e] Not susceptible to the catalyzed decomposition by RUB.[2,3]

Scheme 3. ACT-Catalyzed Decomposition of Cyclic Peroxides Showing the Qualitative Molecular Orbital Diagram of Hypothetical Supermolecular Species



k_{CAT}, which indicates a pronounced steric effect on the interaction of the peroxide with the activator, caused by the alkyl substituent attached to the peroxidic ring (Table 2). The value of k_{CAT} is related to the first oxidation step; therefore, the value of k_{CAT} should depend roughly on the energy to reduce the peroxide in one electron and on the donor−acceptor distance; consequently, it is expected that, under identical reaction conditions, the value of k_{CAT} will decrease if the distance between the peroxide and the ACT increase.

The value of Φ_S^{∞}, on the other hand, is related to the efficiency of electron back transfer (EBT) from the carbonyl radical anion to the $ACT^{\bullet+}$; this process can lead to excited-state formation and is too fast to be measured by conventional kinetic techniques. For a given ACT, Φ_S^{∞} is related to the EBT process and, consequently, to the energy released in the oxidation of the carbonyl radical anion and to the distance between the $carbonyl^{\bullet-}$ and the $ACT^{\bullet+}$. However, efficient chemiluminescence requires that both energetic and geometric conditions are fulfilled. In other words, even if the difference in the redox potential of the ACT and peroxide is higher than the singlet energy of the ACT, the process will be inefficient if the radical ion pair is separated. The opposite is also true; even intimate radical ion pairs will not promote efficient chemiluminescence if the amount of energy released by electron back transfer is not enough to excite the ACT.

On the basis of these considerations, we formulate a hypothesis to explain the differences in the values of k_{CAT} and Φ_S^{∞} determined for the activated decomposition of peroxides **1**−**4** (Scheme 3). In this model, the interaction of the ACT with the peroxide leads to a ground-state charge-transfer complex. The initial endergonic electron transfer from the ACT to the peroxide yields a short-lived intimate radical-ion pair, which can be considered a supermolecule.[38,39] The cleavage of the C−C bond takes the resulting supermolecule to the second singlet excited state (S2). The EBT can be considered as a simple internal conversion,[40−42] resulting in a supermolecule in the first singlet excited state (S1), corresponding to the singlet excited state of the ACT after its separation from the carbonyl fragment (Scheme 3).

A steric hindrance effect is probably acting mainly on the equilibrium constant for charge-transfer complex formation (K_{CT}) between the peroxide and the ACT (Scheme 3). Because k_{CAT} is composed by both K_{CT} and k_{ET}, a decrease in K_{CT} will also lead to a decrease in the experimentally determined k_{CAT} value. This consideration can explain the considerably lower k_{CAT} values for the peroxides **2** and **3**, making the reasonable assumption that the electron transfer rate constant (k_{ET}) should be similar for all the 1,2-dioxetanone derivatives studied. Therefore, these considerations allow, for the first time, a comparative *quantitative* analysis for rationalizing the efficiency of similar intermolecular CIEEL systems. The reactivity of the 1,2-dioxetanone derivatives **1**−**3** can be rationalized on the basis of the steric effect of the alkyl groups on the charge transfer complex formation constant K_{CT} (Table 2, Scheme 3). However, the huge difference of 4 orders of magnitude for **4**, the HEI in the peroxyoxalate reaction, cannot be due to steric effects alone. It appears that this difference should be mainly due to a more favorable reduction potential of this cyclic peroxide. Although redox potentials for this kind of cyclic peroxides have never been experimentally determined, this assumption appears reasonable due do the dicarbonyl structure of this derivative. Additionally, the same argumentation can be utilized to rationalize the fact that simple 1,2-dioxetanes are unreactive toward ACT-catalyzed decomposition,[2,3] where the steric effect should be much more pronounced due to two sp^3 carbon centers at the four-membered peroxidic ring; additionally, the absence of any carbonyl group would make these compounds much poorer electron acceptors.

The extremely high quantum yields measured for the peroxyoxalate reaction, as compared to the very low yields determined for the catalyzed decomposition of the 1,2-dioxetanone derivatives (Table 2), are more difficult to rationalize. In this context, one should keep in mind that the singlet excitation quantum yields at infinite activator concentration (a theoretical condition where all the peroxide molecules present or formed during the course of the reaction interact with the ACT) are determined mainly by the energetic of the EBT (see also the discussion above on the chemiexcitation efficiency with different ACTs).[11] As the oxidation potential of carbon dioxide is lower than that of carbonyl compounds like acetone, adamantanone, and cyclopentanone,[43] the annihilation of these carbonyl anion radicals with the ACT radical cation will release more energy than the analogous annihilation with the carbon dioxide radical anion. Therefore, considering energetic reasons only, it would be expected that the EBT from ketone radical anions to the ACT radical cation should lead to a higher singlet excitation quantum yields than the same transformation involving the carbon dioxide radical anion. Of course, the experimental results with 1,2-dioxetanones and the 1,2-dioxetanedione are exactly the opposite.

However, considering the hypothesis of the involvement of a supermolecule (Scheme 3), it can be understood that a more efficient supermolecule formation should favor excited state generation. Therefore, the distance between the molecules in the pairs formed by the ACT and the cyclic peroxide and, during the course of the transformation, its different cleavage products should be crucial for chemiexcitation efficiency. Consequently, it appears that in the case of 1,2-dioxetanedione (**4**) not only the better initial complex formation will increase the k_{CAT} values but also the more intimate complexation between the cleavage products (carbon dioxide in the final stage) and the ACT also allows more efficient chemiexcitation.

4. CONCLUSION

Despite of the low efficiency, both 1,2-dioxetanones **2** and **3** are susceptible to catalyzed decomposition by suitable activators. Experimental evidence suggests that this activated decomposition involves an electron or charge transfer ($\alpha = 0.04$ and 0.10, for **2** and **3**), as predicted by the intermolecular CIEEL mechanism. The chemiexcitation yields involved in these chemiluminescence reactions are low ($<10^{-3}$ E mol^{-1}), confirming the status of the peroxyoxalate reaction as the only intermolecular CIEEL system with proven high quantum yields. A comparative analysis of the rate constants for the rubrene-catalyzed decomposition of four cyclic peroxide derivatives, using a hypothetical supermolecule formation between the cyclic peroxides and the activator, clearly demonstrates that a steric effect is determinant for the initial rate-limiting electron-transfer step of the CIEEL sequence. Additionally, the different chemiexcitation efficiency in the catalyzed 1,2-dioxetanone decomposition and the peroxyoxalate reaction can be rationalized on the basis of excitation efficiency in the supermolecule formed by the cyclic peroxides and the chemiluminescence activators.

5. EXPERIMENTAL SECTION

Materials and Peroxides Handling. Toluene for the kinetic CL assays was stirred overnight over EDTA, filtered, distilled, and then redistilled from metallic sodium; ethyl acetate (EtOAc) for kinetic assays was kept over $CaCl_2$ during 24 h, filtered, mechanically stirred with NaOH pellets (40 g NaOH per liter of EtOAc), filtered, and distilled from P_2O_5 under inert atmosphere. Activators: RUB = rubrene, PER = perylene, DPA = 9,10-diphenylanthracene, ANT = anthracene, DBA = 9,10-dibromoanthracene, and PPO = 2,5-diphenyloxazole are commercial and were used as received. Spiro-adamantyl-1,2-dioxetanone (**2**) and spiro-cyclopentyl-1,2-dioxetanone (**3**) were prepared and handled as described elsewhere.[27] Peroxide solutions for the kinetic CL assays were stored in vials and kept at −78 °C during the experiments; their concentration was determined by an iodometric assay, as reported elsewhere. All glassware, including pipettes and microsyringes, was treated with EDTA solutions to remove traces of metal ions.

Kinetic Chemiluminescence Assays. Light emission time profiles were recorded on a fluorescence spectrophotometer or, for low intensity assays with **3**, on a tube luminometer. For the low intensity kinetic unimolecular decomposition assays of peroxide **2**, a photon counter system was used.

A quartz cuvette or luminometer glass tube containing the solvent or ACT solution is allowed to equilibrate thermally and the reaction initiated by addition of a small amount (typically 10−30 μL for a total volume of 2.00 mL) of peroxide stock solution, the CL emission intensity decay being registered for at least 3 half-lives. The equipment baseline emission intensity was discounted for all kinetic assays. The light emission intensity, registered in arbitrary units (a.u. s^{-1}), was converted to absolute light units (einstein s^{-1}) through calibration of the photomultiplier tube (PMT) using a modified version[11] of the luminol standard method[44−47] and considering the PMT wavelength sensibility. Light emission time profiles were fitted with a first-order exponential decay equation to determine the initial emission intensities (I_0, in E s^{-1}) and the observed rate constants (k_{obs}, in s^{-1}). This procedure is described in detail elsewhere.[9,11]

Determination of k_{CAT} and k_D. The k_{CAT}/k_D ratio was obtained from the double-reciprocal plots of Φ_S and the ACT concentration (eq 1). The chemiexcitation quantum yield at an *infinite* concentration of the ACT (Φ_S^{∞}, eq 1), a hypothetical condition where all the peroxide is decomposed by the activated pathway, can be determined from the intercept of the double-reciprocal plots.[9]

Chemiluminescence Quantum Yields (Φ_{CL}) and Singlet Excited-State Formation Quantum Yields (Φ_S). As described in detail elsewhere,[11] the chemiluminescence quantum yields (Φ_{CL}), in E mol^{-1}, were obtained from the total amount of light emitted by a sample, in absolute units (einstein, E), divided by the number of moles of organic peroxide used (limiting reagent). The singlet excited-state formation quantum yields (Φ_S), also in E mol^{-1}, were obtained from Φ_{CL} by normalizing them by the fluorescence quantum yield of the ACT (Φ_{FL}) (Scheme 1).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Kinetic data for the decomposition of 1,2-dioxetanone **3** catalyzed by different ACTs, photophysical data of ACTs, and results of double-reciprocal plots for 1,2-dioxetanones **2** and **3**, as well as the energy balance of the electron back-transfer for different ACTs (Tables S1−3). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: elbastos@iq.usp.br.
*E-mail: wjbaader@iq.usp.br.

Present Address

[†](F.H.B. and L.F.M.L.C.) Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André, SP, Brazil.

Notes

The authors declare no competing financial interest.

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