Photochemical & Photobiological Sciences

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Journal Name

Photochemical & Photobiological Sciences

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Solvent Viscosity Influence on the Chemiexcitation Efficiency of Inter and Intramolecular Chemiluminescence Systems

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Abstract

The effect of medium viscosity on the chemiexcitation quantum yields of the induced decomposition of 1,2-dioxetanes (highly efficient intramolecular CIEEL system) and the catalyzed decomposition of diphenoyl peroxide and a 1,2-dioxetanone derivative (model systems for the intermolecular CIEEL mechanism, despite their low efficiency) are compared in this work. Quantum yields of the rubrene catalyzed decomposition of diphenoyl peroxide and *spiro*-adamantyl-1,2-dioxetanone as well as the fluoride induced decomposition of a phenoxy-substituted 1,2-dioxetane derivative are shown to depend on the composition of the binary solvent mixture toluene / diphenyl ether, which possess similar polarity parameters but different viscosity. Correlations of the quantum yield data with the medium viscosity using the diffusional and the frictional (free-volume) models indicate that the induced 1,2-dioxetane decomposition is indeed occurring by an entirely intramolecular process and the low efficiency of the intermolecular chemiluminescence systems (catalyzed decomposition of diphenoyl peroxide and 1,2-dioxetanone derivative) in not primarily due to cage escape of radical ion species.

Introduction

Chemiluminescence (CL) refers to the generation of visible light due to the occurrence of a chemical reaction. The relationship between the number of emitted photons during a certain chemical reaction and the number of moles of limiting reactant is known as the CL quantum yield (Φ_{CL}), whereas the singlet quantum yield (Φ_S) is the number of electronically excited singlet species formed per mol of limiting reactant.[1] Most of the efficient CL transformations involve cyclic peroxides as reagents or reactive intermediates, among them, 1,2-dioxetanes and 1,2-dioxetanones (α-peroxylactones) are the most important derivatives.

The unimolecular decomposition of these four-membered cyclic peroxides is known to produce mainly non emissive triplet excited carbonyl fragments,[2,3] however, the decomposition of 1,2-dioxetanones can be catalyzed by appropriate fluorescence activators, leading to the formation of the activator's singlet excited state.[4] The catalytic process was shown to involve an electron transfer from the activator (commonly polycondensed aromatic hydrocarbons with low oxidation potentials) to the peroxide and occurs with diphenoyl peroxide,[5] as well as 1,2-dioxetanones,[6-10] however does not occur with alkyl and aryl-substituted 1,2-dioxetanes.[1] Mechanistic studies on the catalyzed decomposition of these peroxides, mainly diphenoyl peroxide and 1,2-dioxetanones, led to the formulation of the Chemically Initiated Electron Exchange Luminescence (CIEEL) mechanism,[4,7] which was widely utilized to explain excited state formation in several CL transformations and also applied to rationalize the mechanism of firefly bioluminescence.[11,12]

However, more recently it has been shown that the quantum yields obtained in the catalyzed decomposition of diphenoyl peroxide and 1,2-dioxetanones are much lower than that initially reported,[13] therefore these model CIEEL systems proved to be inefficient CL transformations.[14] Contrarily, the decomposition of phenoxy-substituted 1,2-dioxetanes derivatives showed to be highly efficient chemiexcitation processes,[15-17] possessing singlet quantum yields of up to 100%.[18,19] The decomposition mechanism for these 1,2-dioxetane derivatives, which have found widespread utilization, most prominently as detection system in immunoassays,[20-24] has been formulated as the intramolecular version of the CIEEL mechanism;[1,16-19] however only quite recently, direct experimental evidence on the occurrence of an initial intramolecular electron transfer from a phenolate unit to the 1,2-dioxetane ring has been reported.[25] Additionally, mechanistic studies on the solvent viscosity dependence of the singlet quantum yields from this induced 1,2-dioxetane decomposition appeared to indicate the involvement of an intermolecular electron back-transfer (EBT) in this highly efficient chemiexcitation system.[26-29] However, a more recent study on the solvent viscosity influence on the singlet quantum yields in the induced decomposition of two phenoxy-substituted 1,2-dioxetane derivatives has revealed that the observed viscosity dependence of Φ_S is still in agreement with the occurrence of an intramolecular electron back-transfer and the necessity for a specific conformation for this process in order to lead to efficient formation of excited states.[30] In this work, the results obtained with the intramolecular CIEEL system induced 1,2-dioxetane decomposition were compared to the highly efficient peroxyoxalate reaction, which is believed to involve an intermolecular CIEEL mechanism in its chemiexcitation step.[1,14,31-33]

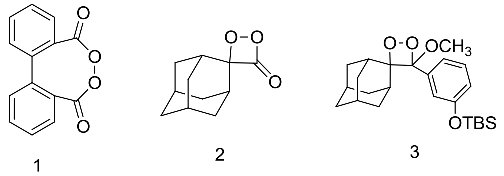
Finally, theoretical calculations appear to be in agreement with the occurrence of an intramolecular charge transfer during chemiexcitation in induced 1,2-dioxetane decomposition and might suggest a direct chemiexcitation pathway, however, also indicate the importance of conformational factor for both unimolecular and induced chemiexcitation of 1,2-dioxetanes.[34-43]

On the basis of the above discussion, we compare here the effect of medium viscosity on the chemiexcitation quantum yields of the induced decomposition of 1,2-dioxetanes (highly efficient intramolecular CIEEL system) and the catalyzed decomposition of diphenoyl peroxide and a 1,2-dioxetanone derivative (model systems for the intermolecular CIEEL mechanism, despite their low efficiency). The results indicate that the induced 1,2-dioxetane decomposition indeed involves an intramolecular electron back-transfer and the reason for the low efficiency of the intermolecular CIEEL systems appears not to be solvent cage escape of intermediate ion radicals.

Results

Diphenoyl peroxide (**1**), *spiro*-adamantyl-1,2-dioxetanone (**2**) and 4-(3-tert-butyldimethylsilyloxyphenyl)-4-methoxyspiro [1.2-dioxetane-3.2'-adamantane] (**3**) were prepared following literature procedures (Scheme 1).[44-48] The most difficult preparation is that of the 1,2-dioxetanone derivative **2**, which had only been synthesized by Adam's group before; we have recently lined out detailed procedures for the synthesis of unstable cyclic peroxide including this derivative **2**.[49] The cyclic peroxides were purified by low-temperature re-crystallization or low-temperature column chromatography and characterized by low-temperature ^{1}H and ^{13}C NMR spectroscopy in comparison with reported literature data.[46,48,49] It should be still mentioned here that only few research groups have been able to study the chemiluminescence properties of 1,2-dioxetanone derivatives due to their difficult preparation and extremely low stability.[1,14,50] Our research group has recently published a revision of chemiexcitation quantum yields of this class of cyclic peroxides, including the *spiro*-adamantyl derivative **2**.[13]

The influence of solvent viscosity on the chemiluminescence parameters of inter and intramolecular CIEEL systems was studied here using the binary mixture of toluene (TOL) and diphenyl ether (DPE). The decomposition of diphenoyl peroxide (**1**) and the *spiro*-adamantyl substituted α-peroxylactone derivative **2** with rubrene as an activator constitute intermolecular CIEEL systems and the induced decomposition of the spiroadamantyl-substituted 1,2-dioxetane **3** with tetrabutyl ammonium fluoride (TBAF) as deprotection agent is the classical intramolecular CIEEL system.



Scheme 1: Structure of cyclic peroxides studied, TBS = tert-butyldimethylsilyl group.

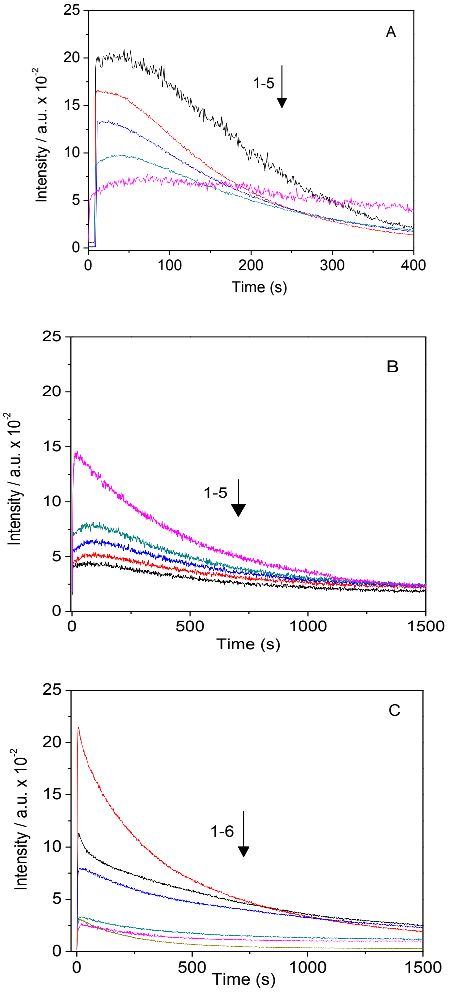


Figure 1: Emission intensity decay *versus* time curves for the reaction of diphenoyl peroxide (1.0 mmol L^{-1}) (A) and spiro-adamantyl-1,2-dioxetanone (0.075 mmol L^{-1}) (B) with rubrene and for the reaction of spiroadamantyl-substituted-1,2-dioxetane (0.01 mmol L^{-1}) with TBAF (2.5 mmol L^{-1}) (C) in mixtures of toluene and diphenyl ether at 36 °C.

A: toluene containing **1**: 95% DPE, **2**: 75% DPE, **3**: 50% DPE, **4**: 25% DPE, **5**: 0% DPE; **B**: **1**: 100% DPE, toluene containing **2**: 75% DPE, **3**: 50% DPE, **4**: 25% DPE, **5**: 0% DPE; **C**: **1**: 100% DPE, toluene containing **2**: 80% DPE, **3**: 60% DPE, **4**: 40% DPE, **5**: 20% DPE; **6**: 0% DPE.

The emission kinetics of the three CL systems were measured in mixtures of TOL and DPE, spanning a viscosity range from η = 0.5 - 2.2 cP, as determined with a Brookfield Rheometer for each mixture. The results indicate the influence of the medium viscosity on the emission intensity and emission kinetics for each system (Figure 1). Observed rate constants (k_{obs}) were obtained by fitting these curves employing a mono exponential decay function. The chemiluminescence quantum yields (Φ_{CL}) and the singlet chemiexcitation quantum yields (Φ_{S1}) for the decomposition of the peroxides were determined from the integration of the emission intensity time curves using appropriate intensity calibration, as described before (Tables 1 – 3).[1,13,31]

Table 1: Observed rate constants (k_{obs}), chemiluminescence quantum yields (Φ_{CL}) and singlet quantum yields (Φ_s) for the decomposition of diphenoyl peroxide (**1**) using rubrene as catalyst at 36°C in mixtures of toluene and diphenyl ether.

% DPE [a]	η (cP) [b]	k_{obs} (s^{-1}) x 10^3	Φ_{CL} (E mol^{-1}) x 10^4	Φ_s (E mol^{-1}) x 10^4
0	0.5	3.3 ± 0.6	1.04 ± 0.01	1.06 ± 0.01
25	0.74	4.9 ± 0.1	1.17 ± 0.02	1.19 ± 0.02
50	1.1	6.3 ± 0.2	1.24 ± 0.01	1.27 ± 0.01
75	1.6	7.3 ± 0.3	1.35 ± 0.06	1.38 ± 0.06
95	2.1	6.5 ± 0.5	2.21 ± 0.17	2.26 ± 0.18

[**1**] =1.0 mmol L^{-1}; [rubrene] = 1.0 mmol L^{-1}; at 36.0°C; mean values ± sd with triplicates. [a] Volume percentage of diphenyl ether (DPE) in toluene; [b] measured by a Brookfield LVD VII Rheometer.

Table 2: Observed rate constants (k_{obs}), chemiluminescence quantum yields (Φ_{CL}) and singlet quantum yields (Φ_s) for the decomposition of spiro-adamantyl-1,2-dioxetanone (**2**) using rubrene as catalyst at 36 ^{0}C in mixtures of toluene and diphenyl ether.

% DPE [a]	η (cP) [b]	k_{obs} (s^{-1}) x 10^3	Φ_{CL} (E mol^{-1}) x 10^4	Φ_s (E mol^{-1}) x 10^4
0	0.5	1.66 ± 0.01	5.6 ± 0.1	5.7 ± 0.1
25	0.74	1.69 ± 0.02	6.5 ± 0.2	6.6 ± 0.2
50	1.10	1.84 ± 0.01	7.3 ± 0.4	7.5 ± 0.4
75	1.6	2.0 ± 0.1	8.4 ± 0.1	8.6 ± 0.1
100	2.17	2.01 ± 0.05	10 ± 1	11 ± 1

[**2**] = 0.075 mmol L^{-1}; [rubrene] = 0.05 mmol L^{-1}; at 36.0 °C; mean values ± sd with triplicates. [a] Volume percentage of diphenyl ether (DPE) in toluene; [b] measured by a Brookfield LVD VII Rheometer.

Table 3: Observed rate constants (k_{obs}), chemiluminescence quantum yields (Φ_{CL}) and singlet quantum yields (Φ_s) for the decomposition of spiro-adamantyl-1,2-dioxetane **3** at 36^{o}C in mixtures of toluene and diphenyl ether.

% DPE [a]	η (cP) [b]	k_{obs} (s^{-1}) × 10^3	Φ_{CL} (E mol^{-1})	Φ_S (E mol^{-1})
0	0.50	3.1 ± 0.1	0.0087 ± 0.0001	0.0395 ± 0.0001
20	0.64	2.4 ± 0.1	0.0094 ± 0.0001	0.0433 ± 0.0001
40	0.92	2.20 ± 0.02	0.0154 ± 0.0006	0.072 ± 0.001
60	1.29	1.8 ± 0.3	0.0298 ± 0.0001	0.14 ± 0.01
80	1.80	2.0 ± 0.3	0.050 ± 0.001	0.227 ± 0.001
100	2.17	2.3 ± 0.2	0.077 ± 0.001	0.350 ± 0.001

[**3**] = 0.01 mmol L^{-1}; [TBAF] = 2.5 mmol L^{-1}; at 36.0 ^{0}C; mean values ± sd with triplicates. [a] Volume percentage of diphenyl ether (DPE) in toluene; [b] measured by a Brookfield LVD VII Rheometer.

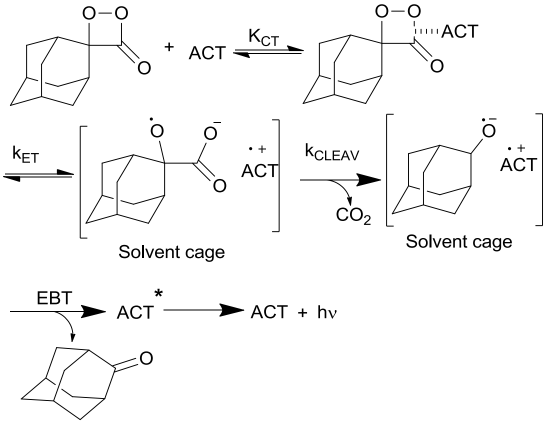
In general, the obtained results show that the observed rate constants (k_{obs}) do not change significantly and systematically with viscosity; for the diphenoyl peroxide system a slight increase of a factor of two is observed for higher viscosity mediums, however, k_{obs} is maintained almost constant for the rubrene catalyzed decomposition of **2**, increasing from 1.7 to 2.0 10^{-3} s^{-1} from pure toluene to pure DPE (Tables 1 and 2). Contrarily, the induced decomposition of 1,2-dioxetane **3** showed to be slightly faster in toluene, being approximately constant in mixtures with DPE and pure DPE (Table 3). Therefore it can be concluded that, as expected, the medium viscosity does not influence significantly the rate constants of the CL systems studied. The chemiluminescence (Φ_{CL}) and the singlet (Φ_S) quantum yields are much higher for the intramolecular CIEEL system (induced 1,2-dioxetane decomposition) than for the intermolecular systems, showing Φ_S values of up to 35% for the intramolecular system and values lower than 0.1% for the intermolecular systems (Tables 1 – 3).

For catalyzed diphenoyl peroxide decomposition, the singlet quantum yields (Φ_s) increased by a factor of only 1.3 from the pure toluene (η = 0.5 cP) to 75% diphenyl ether (η = 1.6 cP) and show a much higher increase for 95% of diphenyl ether (η = 2.1 cP) (Table 1). This might indicate the importance of the preferential solvatation of the radical ions in the chemiexcitation step for diphenoyl peroxide system. The singlet quantum yields (Φ_s) of the rubrene catalyzed decomposition of spiro-adamantyl-1,2-dioxetanone (**2**) increase by a factor of almost 2 from η = 0.5 cP (100% toluene) to η = 2.17 cP (100% diphenyl ether), similar to the increase observed for the diphenoyl peroxide system (Tables 1 and 2). However, the singlet quantum yields obtained for the induced 1,2-dioxetane decomposition show an increase of about 9 times for pure DPE as compared to toluene. The increase is only significant for mixtures with a DPE content of 60% or higher, also in this case indicating the importance of preferential solvatation.

Discussion

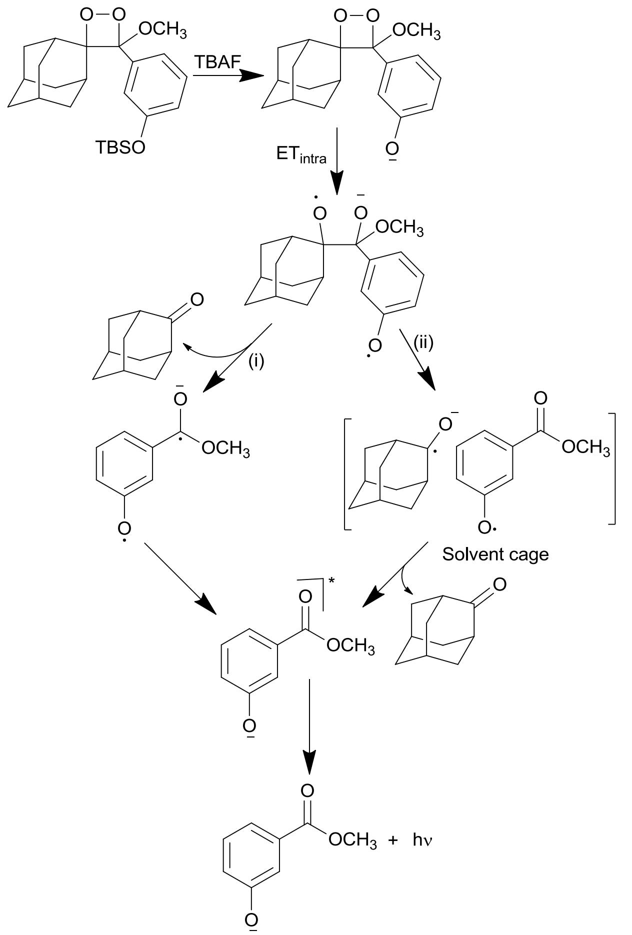
In order to clarify the mechanisms of excited state generation and to understand the drastic efficiency difference between inter and intramolecular systems, the solvent viscosity effect on the quantum efficiency in different CL systems involving intermolecular interactions between a peroxide and an ACT (catalyzed diphenoyl peroxide and 1,2-dioxetanone decomposition) and the induced 1,2-dioxetane decomposition involving an initial intramolecular electron or charge transfer has been studied in this work. The solvent viscosity effect on the efficiency of the induced 1,2-dioxetane decomposition has been studied before by two different research groups using the benzene (toluene) / diphenylmethane system and has initially been used to postulate the occurrence of an intermolecular electron back transfer (EBT) in this highly efficient CL transformation.[27-29] However, subsequent studies, including also the highly efficient intermolecular CIEEL based peroxyoxalate system, have shown that the observed solvent cage effect can also be compatible with an entirely intramolecular electron and electron back transfer.[30]

In this work the solvent cage effect on the low efficient catalyzed diphenoyl peroxide and 1,2-dioxetanone decomposition (Scheme 2) is compared to the effect observed on the highly efficient induced 1,2-dioxetane decomposition (Scheme 3).



Scheme 2: Mechanism of the activator (ACT) catalyzed decomposition of 1,2-dioxetanone **2**, according to the intermolecular CIEEL mechanism.

After charge-transfer complex formation, the catalyzed decomposition of **2**, as well as the analogous reaction of diphenoyl peroxide **1** (not shown), is initiated by an intermolecular electron transfer from the ACT to the peroxide, accompanied by O-O bond cleavage. The electron back transfer, occurring after the C-C bond cleavage, is also necessarily intermolecular and can lead to the ACTs excited state formation and consequent light emission (Scheme 2).[1,4,5,7] Escape of the radical ions from the solvent cage will lead to a lower chemiexcitation efficiency, as these cage-escaped radicals will be annihilated by unspecific dark reactions. Therefore, a solvent viscosity effect is expected for the rubrene catalyzed decomposition of peroxides **1** and **2**.



Scheme 3: Mechanism of the induced decomposition of the *spiro*-adamantyl-substituted 1,2-dioxetane **3**, according to intramolecular CIEEL, indicating the possible occurrence of an (i) intramolecular and (ii) intermolecular electron back transfer.

Contrarily, the induced decomposition of 1,2-dioxetane **3** is initiated, after deprotection of the silyl ether moiety, by an intramolecular electron transfer, leading to a diradical anion (Scheme 3). Subsequent C-C bond cleavage can occur in two distinct manners: (i) an intramolecular pathway, where the excited phenolate is formed directly by an intramolecular electron back transfer, a pathway expected to lead to highly efficient chemiexcitation;[1,17-19,25] alternatively, (ii) a pair of radicals is formed within the solvent cage; the now intermolecular electron back transfer can lead to phenolate excited state formation, however this process might not be highly efficient, eventually due to possible radical cage escape leading to ground state product formation (Scheme 3).[1,13,14]

The solvent system toluene diphenyl ether was chosen for these studies as the reagents of all systems are perfectly soluble in both solvents (which is not the case for TBAF in diphenylmethane used in the former studies as the high viscous solvent). Additionally, these two solvents also possess very similar solvent polarity parameters and nearly identical solvent reorganization energies (λ_S), as calculated by the Marcus equation (eq. 1 and 2).[51-54]

$$\Delta G^*_{BET} = \Delta G^*_0\left(1+\frac{\Delta G^0}{4\Delta G^*_0}\right)^2 \qquad \textbf{eq. 1}$$

$$\Delta G^*_0 = \frac{e^2}{4}\left(\frac{1}{2r_D}+\frac{1}{2r_A}-\frac{1}{r_{DA}}\right)\left(\frac{1}{n^2}-\frac{1}{\varepsilon}\right) \qquad \textbf{eq. 2}$$

Where: r_D and $r_{A:}$ dimension of the electron donor and acceptor;
$r_{DA:}$ distance between electron donor and acceptor;
n: refractive index;
ε: relative permittivity (dielectric constant).

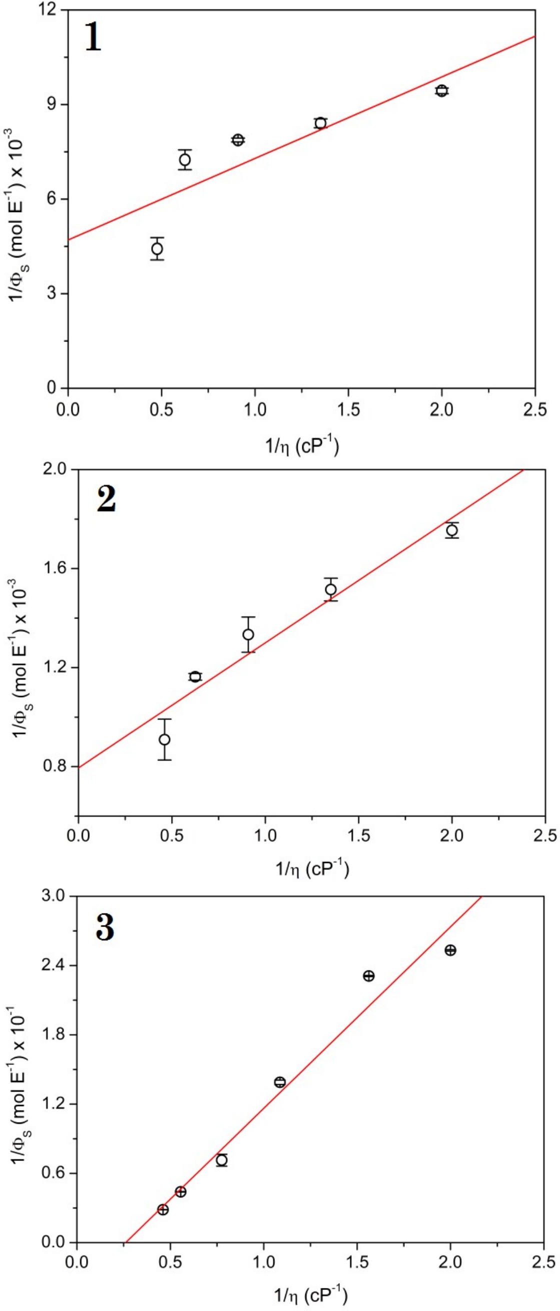


Figure 2: Correlation of the singlet quantum yields (Φ_S) measured in the rubrene catalyzed decomposition of diphenoyl peroxide (**1**) and 1,2-dioxetanone **2**, as well as the induced decomposition of phenoxy-substituted 1,2-dioxetane **3**, according to the collisional model ($1/\Phi_{S1} = B + A/\eta$).

The results obtained in our studies show that, in the intermolecular systems, an increase in the medium viscosity of a factor of around 4, from 0.5 to 2.2 cP, leads to a quantum yield increase of a factor of 2. Contrarily and surprisingly, the viscosity influence is much higher on the quantum yields obtained from the intramolecular system with an increase of almost 9 times of the yields obtained in DPE as compared to toluene (Tables 1-3).

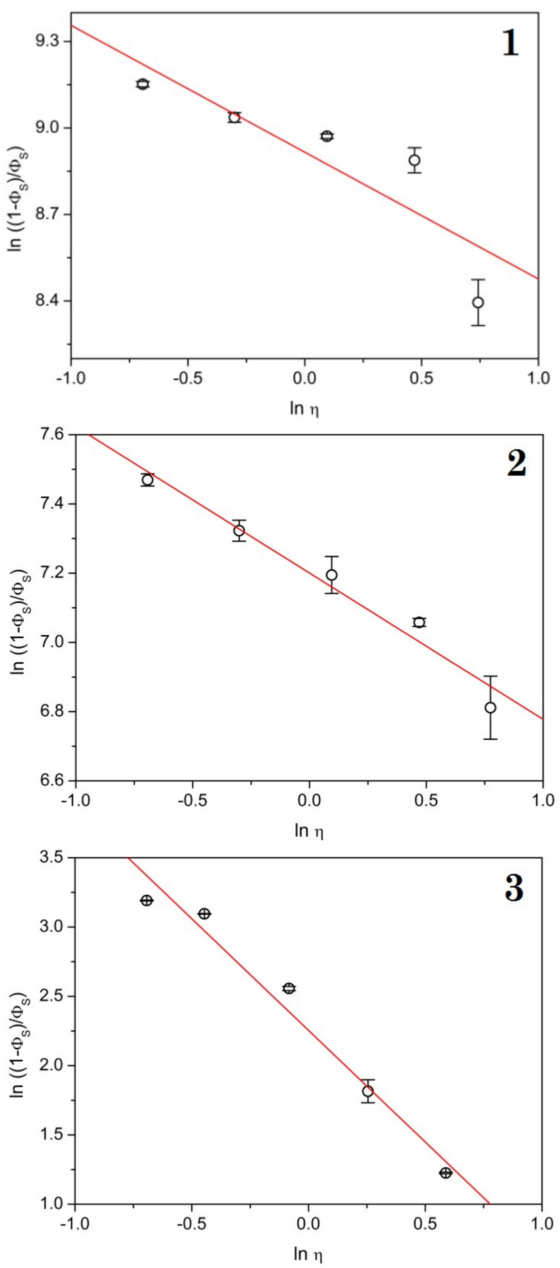


Figure 3: Correlation of the singlet quantum yields (Φ_S) measured in the rubrene catalyzed decomposition of diphenoyl peroxide (**1**) and 1,2-dioxetanone **2**, as well as the induced decomposition of phenoxy-substituted 1,2-dioxetane **3**, according to the free-volume (frictional) model ($\ln((1 - \Phi_{S1})/\Phi_{S1}) = C - \alpha \ln \eta$).

The behaviour of rate constants upon medium viscosity changes has been described in the literature by two distinct models, the free-volume’[55-57] as well as the collisional model;[58] and these models have been utilized to rationalize the solvent viscosity dependence of the singlet quantum yields in CL transformations.[26-30] The correlations of the quantum yields obtained in the three systems studied according to the free-volume and the collisional model show, in a first glance, that these models are not adequate for the description of the viscosity dependence of these quantum yields (Figure 2).

Table 4: Fitting parameters for the rubrene catalyzed decomposition of diphenoyl peroxide (**1**) and 1,2-dioxetanone **2**, as well as the induced decomposition of phenoxy-substituted 1,2-dioxetane **3**, using the diffusional and free-volume model.

	Collisional model			**Free-volume model**		
	$\frac{1}{\Phi_S} = B + \frac{A}{\eta}$			$ln\frac{1-\ \Phi_S}{\Phi_S} = C-\ \alpha \ln \eta$		
	B	**A**	**R^2**	**C**	**−α**	**R^2**
1	6300 ± 130	1600 ± 100	0.823	8.985 ± 0.006	0.24 ± 0.01	0.899
2	880 ± 20	440 ± 20	0.984	7.22 ± 0.01	0.36 ± 0.02	0.994
3	−4.60 ± 0.02	16.20 ± 0.03	0.986	2.278 ± 0.002	1.516 ± 0.005	0.932

Correlations were performed with all the data points shown in the figures and without using the error weighting option of the fitting program.

The parameters obtained from the correlations for the catalyzed decomposition of **1** show a generally poor fitting with both models, as indicated by the low R^2 values. The correlation of data from the catalyzed decomposition of **2** and the induced 1,2-dioxetane **3** decomposition proved to be better described by both models. However, there is no difference in the quality of fitting with both models for the inter and intramolecular systems. Additionally, the α values obtained for the correlations of the intermolecular systems (catalyzed decomposition of **1** and **2**) by the free-volume model are significantly below 1.0, indicating that in these cases only a part of the molecule is experiencing the solvent viscosity effect (Table 4). Contrarily, for the intramolecular system, induced decomposition of 1,2-dioxetane **3**, the α value is considerably higher than 1.0, which would indicate the involvement of diffusion of “whole” molecules. Of course, these observations are completely contrary to that expected from the reaction sequences involved (Schemes 2 and 3).

Although the lack of correlation by the two models may in part be rationalized by the occurrence of preferential solvatation, this effect cannot explain the unexpected and dramatic difference for the inter and intramolecular systems; pointing out again that the viscosity influence is low for both intermolecular systems and much higher for the intramolecular system, contrarily to the expectation. These facts can now be utilized to withdraw the following mechanistic information with respect to chemiexcitation efficiency in these classical inter and intramolecular CIEEL systems (Scheme 2 and 3):

(i) In the case of the induced 1,2-dioxetane decomposition the surprisingly high viscosity influence on the quantum yields can be understood on the basis of an intramolecular electron back transfer step (Scheme 3, pathway(i)), considering that a specific conformation is necessary for efficient chemiexcitation, as suggested before by our group.[30] The results obtained in the present work, utilizing a different binary solvent system, confirm the former results, although in the present case the solvent viscosity effect is considerably higher than in the toluene / diphenylmethane system. This is partially due to lower quantum yields determined in the present work in toluene, however, the difference of a factor of two can still be accepted in the case of CL quantum yields obtained from two independent determinations, due to the possibility of various factors leading to deviations.[1] The most important result which corroborates the conclusion outlined above on the mechanism of induced 1,2-dioxetane decomposition is the fact that the obviously intermolecular systems (catalyzed diphenoyl peroxide and 1,2-dioxetanone decomposition) show much lower viscosity dependence.

(ii) The low efficient intermolecular CIEEL systems, catalyzed diphenoyl peroxide and 1,2-dioxetanone decomposition, cannot be made much more efficient by increasing the solvent viscosity, as a viscosity increase of a factor of 4 (from 0.5 to 2.2 cP) leads only to a twofold quantum yield increase in both systems. Consequently, these facts indicate that the low efficiency of these systems is not mainly due to cage escape of the radical pairs. There must be another reason for the lack of efficiency in these classical CIEEL systems, which should be investigated and clarified for a general understanding of chemiexcitation mechanism. One reason for this low efficiency may be steric effects on charge-transfer complex formation by these peroxides with the ACT, as outlined in a most recent publication from our group.[59]

(iii) The surprisingly different behaviour, contrary to simple expectation, of the inter and intramolecular systems points out the importance to try to understand the exact reasons for these facts in both cases. Only the comprehension of this mystery can lead to the formulation of a general chemiexcitation mechanism for efficient CL systems occurring with the involvement of electron or charge transfer processes during the decomposition of highly energetic cyclic peroxides. This understanding might lead to the rational discovery of new, highly efficient, chemiexcitation systems.

Experimental

Toluene was treated overnight with EDTA (50 g/L), distilled after filtration (bp 111 °C (760 mmHg) redistilled over sodium wire, and stored under an inert atmosphere. Diphenyl ether was stirred in the presence of $MgSO_4$ for 6 hours, after filtration it was distilled under reduced pressure and stored over 4 Å molecular sieves. The viscosities of pure solvents toluene/diphenyl ether and their binary mixtures were measured at 36.0 ± 0.5 °C with a Brookfield LVD VII Rheometer (CP40 cone, 0.8° angle, 0.5 mL final volume, 3.4 cm radius). Solvent mixtures were prepared immediately prior to the viscosity measurements. Rubrene (RUB) was used as received. The preparation and characterization of diphenoyl peroxide (**1**), *spiro*-adamantyl-1,2-dioxetanone (**2**), and the phenoxy-substituted *spiro*-adamantyl-1,2-dioxetane **3** as well as their precursors were reported elsewhere.[46,48,49] The peroxide stock solutions were stored at low temperature (−80 °C) and kept at −78 °C during the experiments. All glassware i.e., pipettes and micro syringes, were washed with EDTA solutions in order to remove traces of metal ions, followed by extensive washing with deionized water.

UV-Vis spectroscopy

UV-visible spectra were obtained on a Varian Cary 50 Bio-spectrophotometer which possesses a cell holder for 18 quartz cells, thermostated by a Varian Cary PCB 150 bath at 25.0 ± 0.5°C. The peroxide content of the stock solutions was determined by a spectrophotometric iodometric assay with 3 mL of KI (0.05 mol L^{-1}) in acetate buffer (0.1 mol L^{-1}, pH = 3.8) and 10 µL of a horseradish peroxidase (HRP) solution (1 mg mL^{-1}), where 10 µL of an appropriately diluted (typically 10 times with methanol) peroxide stock solution were added. Peroxide concentration was calculated from the absorbance of the I_3^- formed at 353 nm ($\boldsymbol{\varepsilon}_{353}$ = 25,500 mol L^{-1} cm^{-1}).

Chemiluminescence emission measurements

Kinetic emission intensity experiments were performed on a Hitachi F-4500, fluorescence spectrophotometer equipped with a magnetic stirring system and thermostated at 36 ± 0.5 °C by a Lauda Brinkmann bath E100, in quartz cells of 3.0 mL capacity containing final volume of 2.0 mL. The sensitivity of the apparatus was regulated by varying the parameters of the photomultiplier voltage and emission slit.

Kinetics of the catalyzed decomposition of peroxides 1 and 2

The peroxide stock solution was added by means of a micro syringe to the activator solution contained in the quartz cell placed in the thermostated cell holder of the fluorimeter and data acquisition initiated. The peroxide stock solution was maintained at 0 °C in an ice chamber in order to avoid thermal peroxide decomposition. After an initial period of mixing and reaction temperature adjustment, the emission intensity showed a monoexponential decay, which was followed during at least 4 half-lives. The equipment baseline was discounted for all kinetic assays. The observed rate constants (k_{obs}) were obtained by fitting the intensity versus time curves using a mono exponential decay function.

Kinetics of the induced decomposition of 1,2-dioxetane 3

The 1,2-dioxetane **3** stock solution was added by means of a micro syringe to the solvent contained in the quartz cell placed in the thermostated cell holder of the fluorimeter. Data acquisition was initiated and the TBAF stock solution (in THF) added. After an initial period of mixing and reaction temperature adjustment, the emission intensity showed a monoexponential decay, which was followed during at least 4 half-lives. The equipment baseline was discounted for all kinetic assays. The observed rate constants (k_{obs}) were obtained by fitting the intensity versus time curves using a mono exponential decay function.

Determination of quantum yields

The CL quantum yield (Φ_{CL}) is defined as the relation between the number of photons emitted by a certain chemical reaction (in Einstein, E) per number of moles of limiting reactant (eq. 3). Whereas, the singlet quantum yield is the number of excited state products formed per number of moles of limiting reactant. The CL quantum yields have been obtained experimentally from the integral under the emission intensity kinetic curves, using the luminol standard for photomultiplier calibration.[31] Absolute singlet quantum yields (Φ_S) have been determined from the calibrated chemiluminescence quantum yields (Φ_{CL} in E mol^{-1}) and fluorescence quantum yields (Φ_{FL}) of rubrene (Φ_{FL} = 0.98)[31] and the emitter of 1,2-dioxetane **3** (Φ_{FL} = 0.22)[30] (eq. 4). These quantum yields do not change significantly for the solvents toluene and diphenyl ether.

$$\Phi_{CL} = \frac{\text{number of photons emitted}}{\text{mols of limiting reagent}} \qquad \textbf{(eq. 3)}$$

$$\Phi_S = \frac{\Phi_{CL}}{\Phi_{Fl}} \qquad \textbf{(eq. 4)}$$

Conclusions

The viscosity influence on the chemiluminescence quantum yields is low for both intermolecular systems, however much higher for the intramolecular system, contrarily to the expectation. The dependence observed for the induced 1,2-dioxetane decomposition can be understood, also on the basis of former literature reports, with the necessity of a specific molecular conformation upon electron back-transfer for a highly efficient excited state formation. The fact that the quantum yields for the intermolecular system show a much lower dependence on the medium viscosity clearly indicates that solvent cage effects are not of crucial importance for high quantum efficiencies. For the very low efficient intermolecular systems the observation of no significant solvent viscosity effect indicates that cage escape of radical ions is not the main reason for this low efficiency. Further studies have to be performed for the attempted understanding of the factors which rule the efficiency of chemiexcitation in electron transfer catalyzed peroxide decomposition and to clarify the exact reason for the huge efficiency difference of intra and intermolecular transformations.

Acknowledgments

The authors thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, WJB 2006/03420-7, FHB 2005/58320-4, LFMLC 2012/02428-5), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, PhD fellowship for SPSJ) and Coordenadoria de Aperfeiçoamento de Pessoal de Ensino Superior (CAPES, PhD fellowship for MK) for financial support. Additionally, the donation of a concentrated hydrogen peroxide solution by Solvay – Peróxidos do Brasil is gratefully acknowledged. We thank Prof. Dr. Omar A. El Seoud for providing the rheometer to measure the viscosity of binary mixture of solvents. We thank Felipe A. Augusto for a careful reading of the manuscript.

Notes and references

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