# Solvent Cage Effects: Basis of a General Mechanism for Efficient Chemiluminescence

Erick L. Bastos, Sandra M. da Silva,[†] and Wilhelm J. Baader*

Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, São Paulo, SP, Brazil

S *Supporting Information*

ABSTRACT: The induced decomposition of 1,2-dioxetanes results in the efficient formation of singlet-excited carbonyl compounds. This transformation has been assumed to involve two sequential electron-transfer steps, and the viscosity dependence of the chemiexcitation efficiency (solvent cage effect) has been considered as evidence for the occurrence of an intermolecular electron back-transfer, despite the very high chemiexcitation quantum yields observed. However, all other chemiluminescent reactions assumed to occur according to the entirely intermolecular mechanism, referred to as CIEEL, are inefficient, except for the peroxyoxalate system. Therefore, we have investigated the solvent cage effect on the singlet quantum yields in both the induced decomposition of 1,2-dioxetanes and the peroxyoxalate reaction. Analysis of the viscosity effect observed for both systems, using a collisional as well as a free-volume model, indicates a very distinct behavior, which was interpreted as the occurrence of intramolecular chemiexcitation in the induced 1,2-dioxetane decomposition. We propose a general mechanism for efficient chemiluminescence in which the required electron back-transfer and C−C bond cleavage are concerted and compete with conformational changes that compromise the chemiexcitation. This mechanism is in agreement with both experimental and theoretical data available on the induced 1,2-dioxetane decomposition as well as with the high quantum efficiency of this transformation.
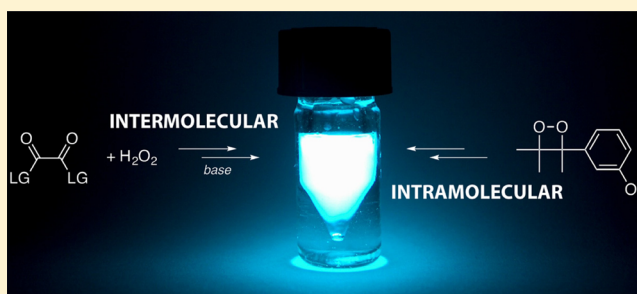
1. INTRODUCTION

Light is a common byproduct of chemical reactions that is usually produced with very low efficiency: i.e., chemiluminescence quantum yields are generally below 1% ($\Phi_{CL} < 10^{-2}$ E mol^{-1}).[1,2] An outstanding exception is the peroxyoxalate system (Φ_{CL} up to 0.6), for which chemiexcitation has been assumed to proceed via the chemically initiated electron-exchange luminescence (CIEEL) mechanism.[3,4] This mechanism was first proposed as an intermolecular series of events, starting with an electron transfer from a fluorescent oxidizable dye, called the activator (ACT), to a high-energy cyclic peroxide, resulting in the loss of a neutral fragment or rearrangement.[5] An intermolecular electron back-transfer (EBT) involving the resulting radical pair is able to release enough energy to produce the ACT in the electronically excited singlet state (Scheme 1).[3,4,6]

The *intramolecular* version of the CIEEL mechanism has been used to rationalize both firefly bioluminescence ($\Phi_{BL} \approx$ 0.4)[7] and the induced (or triggered) decomposition of electron-rich phenoxy-substituted 1,2-dioxetanes.[8−13] This mechanism includes an irreversible electron transfer in the rate-limiting step: i.e., the electron is transferred from the phenolate moiety to the antibonding σ^* orbital of the peroxide, resulting in O−O bond cleavage. This rate-limiting electron transfer process has been experimentally confirmed for phenoxy-substituted 1,2-dioxetanes by our group and is described in detail elsewhere.[14] For the following reaction steps, two main alternatives have been considered: (i) an entirely *intramolecular* chemiexcitation

pathway proceeding either in a stepwise manner (CIEEL) or via the charge transfer-induced luminescence (CTIL) mechanism and (ii) the annihilation of radical pairs in an *intermolecular* EBT step (Scheme 1).

In case an intermolecular EBT takes place, a solvent cage effect is expected, and therefore, the efficiency of the process depends on the ratio between the probability of annihilation resulting in singlet chemiexcitation and the sum of all other probabilities leading to ground-state products.[15] Adam and collaborators have studied the solvent cage effect on the chemiexcitation efficiency of the induced decomposition of phenoxy-substituted 1,2-dioxetanes through the solvent viscosity dependence of the singlet quantum yields.[15−18] Using a binary solvent system containing benzene and diphenylmethane (DPM) in different ratios, the medium viscosity was modulated without affecting significantly the solvent reorganization energy (λ_S). The chemiexcitation quantum yield (Φ_{S1}) for the catalyzed decomposition of the meta and para regioisomers of the 1,2-dioxetane **1** (Scheme 1) increases ca. 2.6 times as the reaction media changes from benzene to DPM (4-fold viscosity increase). This viscosity dependence was interpreted by means of a probabilistic model based on the conceptual distinction between a collision and an encounter of reacting species, hereafter called the *collisional model*.[15,18]

Scheme 1. (A) Base-Catalyzed Chemiluminescent Oxidation of Oxalic Esters by Hydrogen Peroxide in the Presence of an ACT (Peroxyoxalate System), According to the Intermolecular CIEEL Mechanism, (B) Intramolecular (CTIL and Stepwise) and Intermolecular (via EBT) Chemiexcitation Pathways for the Induced Decomposition of Phenoxy-Substituted 1,2-Dioxetanes, and (C) Structure of 1,2-Dioxetanes

Within the same experimental conditions, the constrained bicyclic 1,2-dioxetane **3** has shown a much lower, but relevant, increase in Φ_{S1} (1.4 times).[16] However, as the cleavage fragments of this 1,2-dioxetane derivative cannot diffuse apart, a dependence of Φ_{S1} on medium viscosity is unexpected. This initially surprising result was explained by considering the *free-volume model*[19−21] and the assumption that, after the cleavage of the C−C bond of the 1,2-dioxetane ring, an decrease in medium viscosity will allow conformational changes in the biradical anionic intermediate formed and thereby decrease the efficiency of excited-state formation in the EBT process.[16]

However, the induced decomposition of many phenoxy-substituted 1,2-dioxetanes shows very high chemiexcitation quantum yields (Φ_{S1} up to 1.0):[22,23] e.g., the decomposition of both the 1,2-dioxetane **2** and the tricyclic dioxetane **4** by fluoride ion shows Φ_{S1}^{THF} = 1.0 ± 0.3 and Φ_{S1}^{DMSO} = 0.9, respectively.[22,24] This high chemiexcitation efficiency cannot be easily interpreted in terms of the intermolecular CIEEL mechanism, because the diffusion of radicals out of the solvent cage is reported to be very fast ($k_{diff} \approx 10^9 \ s^{-1}$).[25] In other words, if the intermolecular EBT actually occurs, it has to be much faster than radical diffusion to result in efficient chemiexcitation. This seems not to be the case, because the k_{EBT} value estimated by Burshtein from the data reported by Adam et al. for the 1,2-dioxetane **1** is $8.8 \times 10^8 \ L^{-1} \ mol^{-1} \ s^{-1}$.[15,26] Furthermore, the Φ_{S1} values determined for the catalyzed decomposition of both 1,2-dioxetanones and diphenoyl peroxide, the model systems for the intermolecular CIEEL, are lower than 0.1%, indicating very low chemiexcitation efficiency.[27] Finally, theoretical calculations have suggested that an intramolecular charge transfer may lead to

direct chemiexcitation, highlighting the importance of conformational changes for both unimolecular and induced chemiexcitation of 1,2-dioxetanes.[22,28−35]

Despite the above considerations, a question remains: why does the observed Φ_{S1} in the induced decomposition of 1,2-dioxetanes depend on the solvent viscosity? In an attempt to shed light on this matter, we compare here the effect of medium viscosity on the chemiexcitation quantum yields of the induced decomposition of 1,2-dioxetanes and the peroxyoxalate system, the latter being an unequivocally intermolecular and highly efficient CIEEL system. The results reported in the present work are used to propose a general mechanism for efficient chemiluminescence transformations.

2. RESULTS AND DISCUSSION

The use of binary solvent mixtures for the study of the viscosity dependence of singlet chemiexcitation quantum yields (Φ_{S1}) requires that solvents have similar physicochemical properties except for viscosity: i.e., the relative permittivity (ε_r) and refractive index (n_D) should be similar to keep the solvent reorganization energy (λ_S) nearly constant when solvents are mixed in any proportion. Although mixtures of benzene and diphenylmethane (DPM) are in agreement with these requirements,[15,16,18] we decided to replace benzene by the less toxic toluene (Tol) because the change in the λ_S value is negligible (Table S1, Supporting Information).[36] Addition of DPM to Tol in any proportion has no effect on the chemiluminescence spectra of **1** and **2** or on the fluorescence emission profile of the corresponding emitting phenolates (Figure S1 and Table S2, Supporting Information).

The induced chemiluminescent decomposition of TBS-protected aryloxy-1,2-dioxetanes is usually triggered by tetrabutylammonium fluoride (TBAF). However, we have found that TBAF is only partially soluble in DPM: i.e., TBAF (added as a dry solid or in 1 mol L^{-1} THF solution) precipitates. The solubility of the fluoride source in the presence of DPM is increased by the use of a solution of TBAF in THF/DMSO (1/1 v/v).[15−18] The effect of DMSO on the medium microenvironment was investigated through $E_T(30)$ empirical polarity measurements.[37] Although the empirical polarities of Tol and DPM are similar ($E_T(30)$ = 33.9 and 34.4 kcal mol^{-1}, respectively), the addition of 2% v/v DMSO to a 1/1 Tol/DPM mixture is sufficient to change the medium microenvironment polarity,[38] evidenced by a 53 nm blue shift in the maximum absorption wavelength of the $E_T(30)$ probe (Figure S2, Supporting Information). Despite this effect, we continue to use TBAF in THF/DMSO in this study. The reason is 2-fold: (i) we were unable to obtain reproducible results in the absence of DMSO due to the precipitation of TBAF and (ii) this ternary solvent system allows us to compare the results obtained with those previously reported.[16]

We first repeated the study of the decomposition of 1 by TBAF using the Tol/DPM solvent system and compared the results with those obtained within the same experimental conditions using the smaller and less hindered 1,2-dioxetane 2 and the peroxyoxalate (PO) system. As the reference PO system, we chose the imidazole-catalyzed reaction of trichlorophenyloxalate (TCPO) with hydrogen peroxide in the presence of 9,10-diphenylanthracene (DPA).[4,39,40] The Φ_{S_1} determined for both the induced decomposition of 1,2-dioxetanes 1 and 2 by TBAF and the peroxyoxalate system increases nonlinearly with an increase of the medium viscosity (Figure 1). The addition of
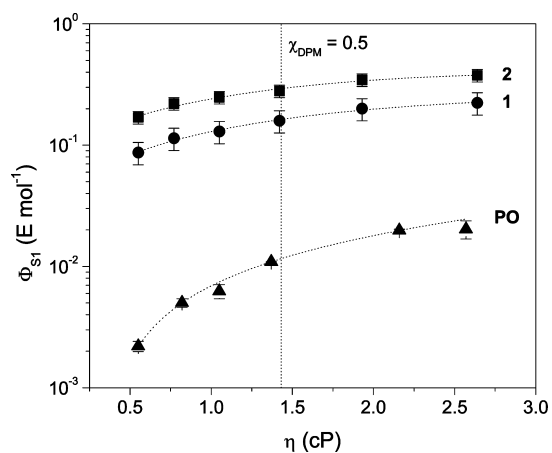
Figure 1. Viscosity dependence of Φ_{S_1} (log scale) in the TBAF-induced decomposition of 1 and 2 and of the PO system. The vertical dotted line indicates the viscosity at a molar fraction of DPM equal to 0.5. Final concentrations: [1] = 90 μmol L^{-1}, [2] = 0.7 μmol L^{-1}, [TBAF] = 2.5 mmol L^{-1}, [IMI-H] = 0.5 mmol L^{-1}, [H$_2$O$_2$] = 2.5 mmol L^{-1}, [DPA] = 1.0 mmol L^{-1}, and [TCPO] = 0.1 mmol L^{-1}.

DPM to Tol allows a 4.8 times variation in viscosity; within this range, the Φ_{S_1} increases 2.2 times for 1, 2.6 times for 2, and 9.4 times for the PO system.

Data analysis was carried out considering both collisional and free-volume models (Figure 2 and Table 1). Literature data for 1,2-dioxetanes 1 and 3 in benzene/DPM solvent mixtures were extracted from the original references and adjusted to both
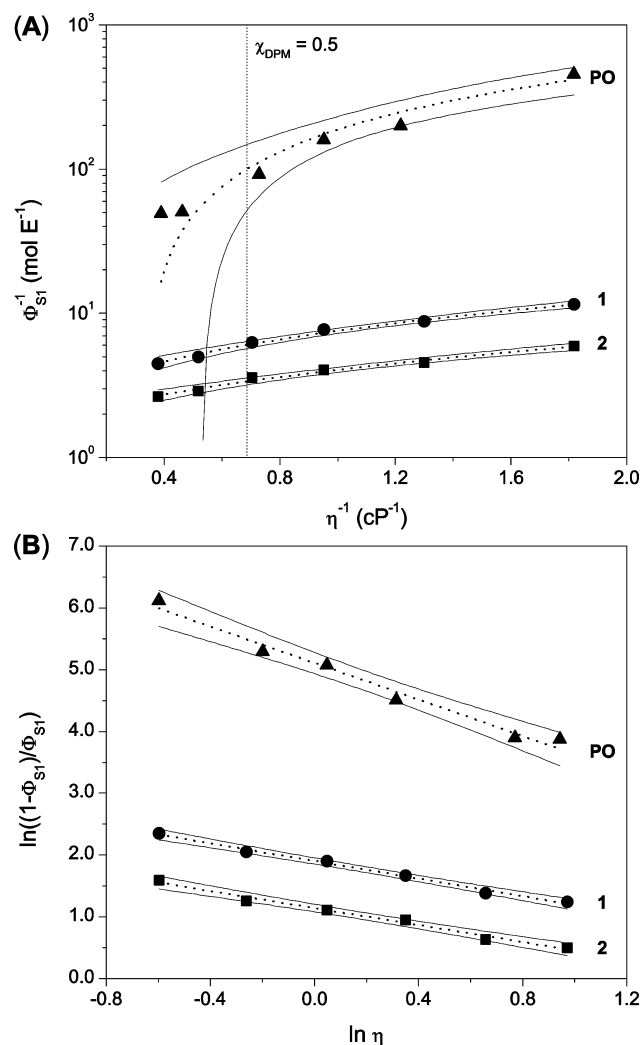
Figure 2. Correlation between (A) $1/\Phi_{S_1}$ and $1/\eta$ according to the collisional model and (B) $\ln((1 − \Phi_{S_1})/\Phi_{S_1})$ and $\ln \eta$ according to the free volume model. Dotted lines are the linear fittings, and the solid lines represent the 95% confidence intervals. Note that in (A) a log scale was used to represent all data.

models for comparison.[15,16] Correlation of the chemiexcitation quantum yields with medium viscosities according to the collisional model shows poor linear dependence for both compound 3 and the PO system (Table 1). However, fitting of data using the free volume model resulted in improved adjusted coefficients of determination (adj-R^2 > 0.97) for all reactions.

The results will be discussed in three main topics for clarity.

(1) *The collisional model fails to explain the viscosity dependence of Φ_{S_1} determined for both 1,2-dioxetane 3 and the PO system.*

The model used by Adam and collaborators[15−18] to rationalize the viscosity dependence of the chemiexcitation yield Φ_{S_1} of the meta and para regioisomers of 1,2-dioxetane 1 was based on a stochastic model of discrete collisions.[41,42] However, the validly of the double-reciprocal relation that predicts the linear dependence between viscosity and the experimental singlet chemiexcitation yield of 1 and 2 has been questioned because the bulk recombination of radicals was not considered.[26] In other words, this model accounts only for the recombination of geminate radicals and ignores bimolecular events that may lead to chemiexcitation. Although this limitation may be irrelevant

Table 1. Fitting Parameters Calculated for the Induced Decomposition of 1 and 2 and the PO System Using Two Different Models

system	collisional model, $1/\Phi_{S_1} = B + A/\eta$			free volume model, $\ln((1 - \Phi_{S_1})/\Phi_{S_1}) = C - \alpha \ln \eta$		
	B	A	adj-R^2	C	$-\alpha$	adj-R^2
1	1.8 ± 0.1	2.2 ± 0.1	0.985	1.9 ± 0.1	0.7 ± 0.1	0.989
1[a,15]	1.9	5.8	0.99	1.9	0.9	0.99
2	2.7 ± 0.2	4.8 ± 0.2	0.990	1.1 ± 0.1	0.7 ± 0.1	0.984
3[a,16]	7.8	4.1	0.93	2.4	0.3	0.98
PO	-92 ± 33	279 ± 32	0.913	5.1 ± 0.1	1.5 ± 0.2	0.974

[a]Calculated with data extracted from the reference cited.

for the study of 1,2-dioxetanes **1** and **2**, it might explain the lack of fit of data (adj-R^2 < 0.93) obtained with the PO system, in which chemiexcitation, although clearly intermolecular, is highly efficient and bimolecular events might be thought to contribute to this high efficiency. Furthermore, this model leads to pronouncedly different fitting parameters for the PO system as compared to those for the 1,2-dioxetanes **1**−**3** (Table 1), indicating a clearly distinct behavior of the PO system in comparison to the induced decomposition of 1,2-dioxetanes.

(2) *The use of the free-volume model fits the data for all reactions studied.*

The free-volume model (also referred to as the frictional model[16]) was proposed to rationalize the viscosity dependence of photoisomerization quantum yields and is based on the representation of the viscosity of fluids proposed by Doolittle, Cohen, and Turnbull.[19−21] The basic assumption of this empirical model is that the rate constant of a given free-volume dependent process, k, will be related to the medium viscosity (η) according to eq 1,[21] where k_0 is the free-volume

$$\ln k = \ln k_0 + \alpha \ln A - \alpha \ln \eta \qquad (1)$$

independent rate constant, A is a constant, and α is the fraction of the critical free volume required for translation necessary to allow the rearrangement of the solute.

Loutfy and co-workers used this assumption of a power-law microfriction behavior (eq 2, where $C = \ln k_r - \ln k_{nr}^0$) to

$$\ln \Phi_{FL} = C + \alpha \ln \eta \qquad (2)$$

explain the dependence of the fluorescence quantum yields of molecular rotors able to form twisted intramolecular charge transfer complexes on the bulk medium viscosity. Interestingly,[43] the same relationship between quantum yield and bulk viscosity was derived under the assumption that the twisting molecular segments experience microfriction that is linked to the bulk viscosity through the Debye−Stokes−Einstein model of viscosity (eq 3). However, in the Förster−Hoffmann derivation α is equal to $2/3$ as the result of an integration step, whereas in the empirical model α can vary with the solvent and the solute.

The model was also adapted to describe the viscosity dependence of the chemiexcitation in the induced decomposition of 1,2-dioxetanes (eq 3, where $C = \ln k_0 - \ln k_{S_1}^{BET} + \alpha \ln A$).[16]

The variable α depends on the nature of both the solvent and solute and was found to be lower than unity because the

$$\ln \frac{1 - \Phi_{S_1}}{\Phi_{S_1}} = C - \alpha \ln \eta \qquad (3)$$

isomerization volume is less than that needed for translation of the whole molecule.[44] The value of α cannot be easily related to measurable physical quantities[44] and only indicates the fraction of the free volume necessary for the occurrence of the molecular rearrangement essential for chemiexcitation.

The values of α determined for the decomposition of **1** and **2** are below unity and are very similar to that observed for the intramolecular photoisomerization of many compounds and in a number of different transformations, which have been interpreted in a variety of ways.[19−21,44,45] The value of $\alpha = 0.3$ determined for the decomposition of the bicyclic derivative **3**[16] corroborates this analysis, since this compound is constrained and does not produce two fragments on cleavage of the C−C bond of the 1,2-dioxetane ring. The α value determined for the peroxyoxalate system ($\alpha = 1.46$) is also in agreement with this interpretation, because chemiexcitation certainly involves a bimolecular process and the occurrence of solvent rearrangement (and change in free volume) has to occur in order to allow radical annihilation leading to effective chemiexcitation.

(3) *The Φ_{S_1} values determined for the induced 1,2-dioxetane decomposition as well as for the PO system in Tol/DPM are lower than those in more polar solvents.*

Quantum yields for the induced decomposition of 1,2-dioxetanes **1** and **2** are about 5 times lower in toluene (Table S2, Supporting Information) than those reported in THF.[9] This fact may be related to a better stabilization of charged intermediate species in the chemiexcitation sequence (Scheme 1). However, the Φ_{S_1} values obtained here for the PO system in toluene are almost 2 orders of magnitude lower than those determined in more polar solvents, such as ethyl acetate (Table S3, Supporting Information).[4] This great difference is probably due to solvent effects on the nucleophilic substitution reactions leading to the formation of the high-energy intermediate.[39,46,47] Furthermore, the cage recombination efficiency of polar radicals has been found to be insensitive to solvent polarity.[48]

General Chemiexcitation Mechanism. On the basis of the results and arguments outlined above, we propose here a general chemiluminescence mechanism that connects two highly efficient reactions: the induced decomposition of 1,2-dioxetanes and the PO system. This mechanism accounts for both the viscosity dependence of the chemiexcitation efficiency of these transformations and their remarkably high efficiency in comparison to that of similar chemiluminescent reactions, such as the catalyzed 1,2-dioxetanone decomposition.[9,27,46]

Scheme 2 depicts a two-dimensional reaction coordinate diagram that shows the chemiexcitation in the PO system and in the induced decomposition of 1,2-dioxetanes according to the CIEEL mechanism. This model proposes that the first step in the chemiluminescent decomposition of phenoxyl-substituted 1,2-dioxetanes is an irreversible electron transfer

Scheme 2. Two-Dimensional Reaction Diagram for Intra- and Intermolecular Chemiexcitation in the Induced 1,2-Dioxetane Decomposition and for the Intermolecular Chemiexcitation in the PO System (Gray Background)
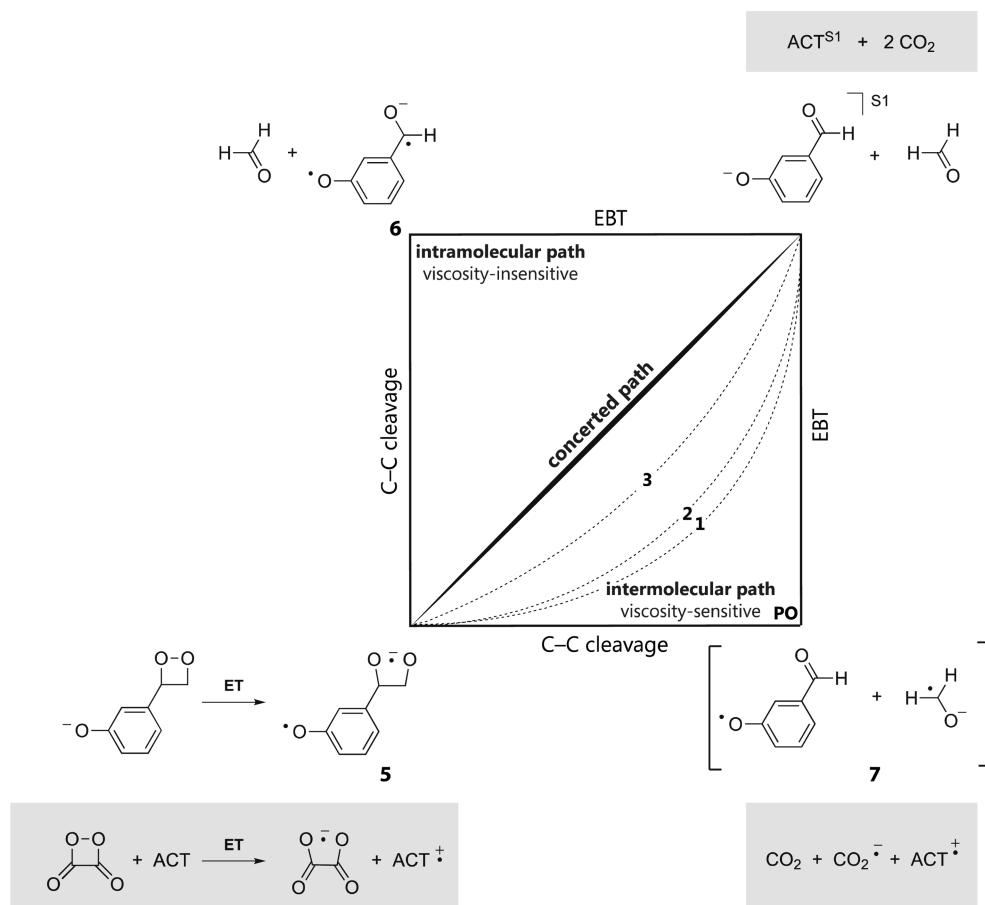
that gives the diradical anion **5** (Scheme 2).[9] Although the occurrence of an electron transfer or charge transfer in this step is controversial,[23,29,49−53] our group provided clear-cut experimental evidence of the formation of a full negative charge already in the transition state in the induced decomposition of a series of acridinium-substituted 1,2-dioxetanes.[14]

Further reactions of radical anion **5** involve C−C bond cleavage followed by EBT and may be assumed to occur by two distinct stepwise pathways. In the intramolecular chemiexcitation pathway, the step in which the diradical anion ion **6** is converted to the excited product is unimolecular and should be instantaneous and not expected to be subject to solvent cage effects (Scheme 2). Consequently, although this path would explain the high efficiency of chemiexcitation (Φ_{S_1} up to 1.0),[22−24,54] it is, apparently, not supported by the viscosity dependency of Φ_{S_1} observed experimentally. On the other hand, the intermolecular pathway assumes the formation of a radical pair **7**, leading to a lower Φ_{S_1} value, except the EBT step is much faster than solute reorientation or diffusion, which is not the case according to Burshtein.[26] Therefore, both extreme stepwise decomposition pathways are not compatible with all experimental results.

A mechanism involving concerted C−C bond cleavage and EBT would explain both the high chemiexcitation efficiency and medium viscosity dependence of Φ_{S_1} (Scheme 2, diagonal line). Considering the α parameter obtained with the free volume model (Table 1) as a measure for the influence of the medium viscosity on Φ_{S_1}, one can infer that the higher the value of α, the

closer the chemiexcitation mechanism will be to the stepwise intermolecular CIEEL mechanism (i.e., poor synchronization between C−C bond cleavage and EBT). Thus, considering the value of α, the chemiexcitation of 1,2-dioxetanes **1** and **2** is likely to be less concerted than the decomposition of **3**, probably due to conformational constraints resulting from the bicyclic structure of **3** (Scheme 2).

Furthermore, after the cleavage of the O−O bond of the 1,2-dioxetane two different electronic configurations for the biradical anion **5** are possible (Scheme 3; **5a,b**). The EBT from **5a** or **5b** before the cleavage of the C−C bond results is the formation of a glycol diradical (Scheme 3), which may give triplet-excited carbonyls in low yields and, eventually, singlet-excited products in still much lower yields in analogy to the unimolecular 1,2-dioxetane decomposition.[55] However, homolytic C−C bond cleavage before EBT can lead to intramolecular or intermolecular donor−acceptor pairs, i.e., a diradical anion or radical pair, respectively, depending on the charge distribution in biradical anion **5** (Scheme 3A). In contrast, if C−C bond cleavage and electron transfer are concerted (i.e., the C−C bond of either **5a** or **5b** is not completely broken before the electron is considerably transferred), the polar transition state will always have the same charge distribution, which depends on the synchronicity of C−C bond cleavage and electron transfer as well as the stabilization of the resonance structures **8** (Scheme 3B). However, in this concerted mechanism (Scheme 3B), excited state formation will be entirely unimolecular and, a priori, no viscosity effect on the efficiency of excited state formation would be expected.

Scheme 3. Detailed Description of the Stepwise (A) and Concerted (B) C−C Bond Cleavage/Electron Back-Transfer (EBT) Step during Chemiexcitation in the Induced Decomposition of 1,2-Dioxetanes[a]
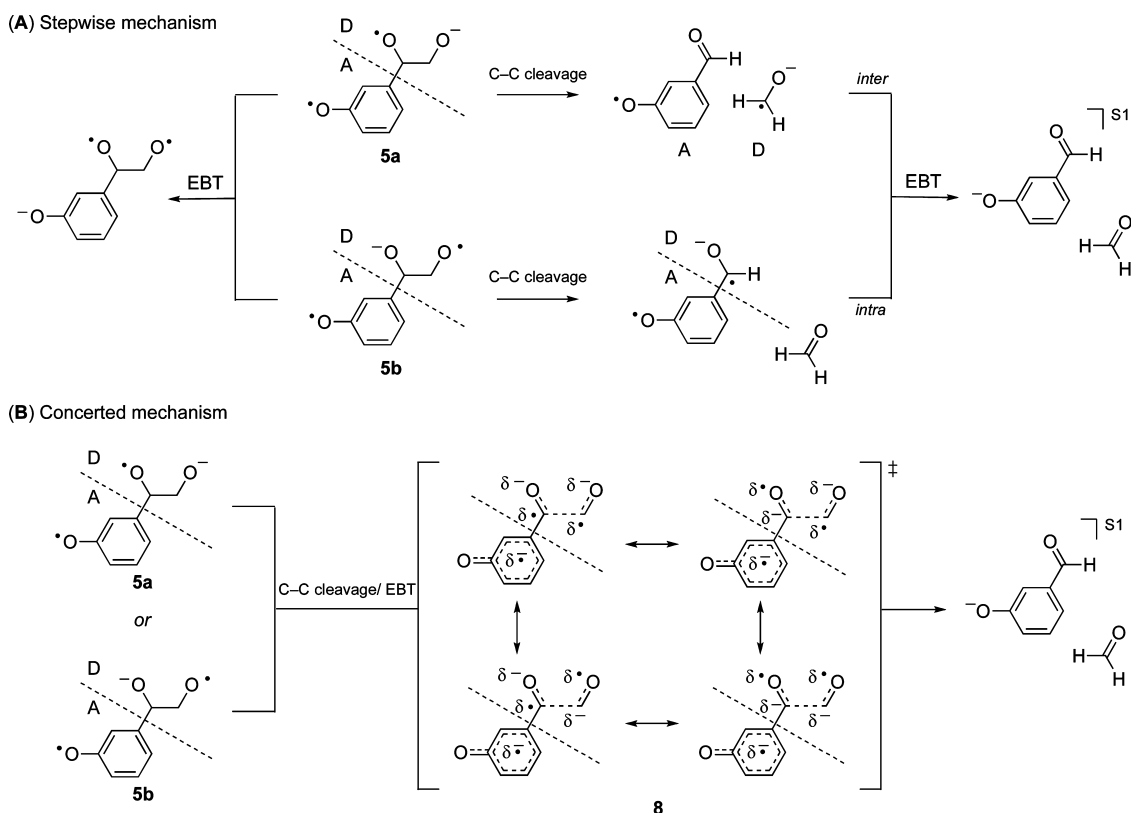

[a]Dotted lines indicate the separation of donor (D) and acceptor (A) portions.

The solvent cage effect can be rationalized by this general chemiexcitation mechanism, considering the effect of conformational changes involving the OC−CO dihedral angle of **5** on the synchronicity of the C−C bond cleavage and EBT. This model assumes that, after O−O bond cleavage, EBT and C−C bond cleavage are concerted and slow enough to compete with the C−C bond rotation around the OC−CO dihedral angle.

Conformational changes after the cleavage of both O−O and C−C bonds have been evoked by Adam and co-workers to explain the viscosity dependence observed for the bicyclic 1,2-dioxetane derivative **3** according to the intermolecular CIEEL mechanism.[16] They concluded that, after the C−C bond was completely broken, high medium viscosity favors the carbonyl alignment required for efficient chemiexcitation. Accordingly, it has been pointed out that molecular radicals generally require a certain mutual orientation in order to react with each other, and because geminate radicals are formed from homolysis of a bond in a parent molecule, they are initially aligned for recombination.[48] Therefore, any process that changes the mutual orientation of the radicals and prevents realignment will compromise the efficiency of the electron transfer. On the other hand, an increase in solvent viscosity will maintain the alignment of the radical species favoring the electron transfer, which in the specific case of the induced 1,2-dioxetane decomposition results in the increase of Φ_{S_1}. Adam, Matsumoto, and Trofimov rationalized the viscosity dependence of **3** as the concurrence of an effective electron back-transfer in the aligned conformation and the lower efficiency of the EBT to the phenoxide radical after bond rotation of the biradical anion formed by C−C bond cleavage.[16]

On the basis of these considerations, we propose a three-dimensional reaction diagram in which the x and z axes correspond to the C−C bond cleavage and the EBT, respectively, and the y axis corresponds to the 180° rotation of the OC−CO dihedral angle (Scheme 4). The diagonal line in the top

Scheme 4. Three-Dimensional Reaction Diagram for the Chemiexcitation Step in the Induced Decomposition of 1,2-Dioxetanes
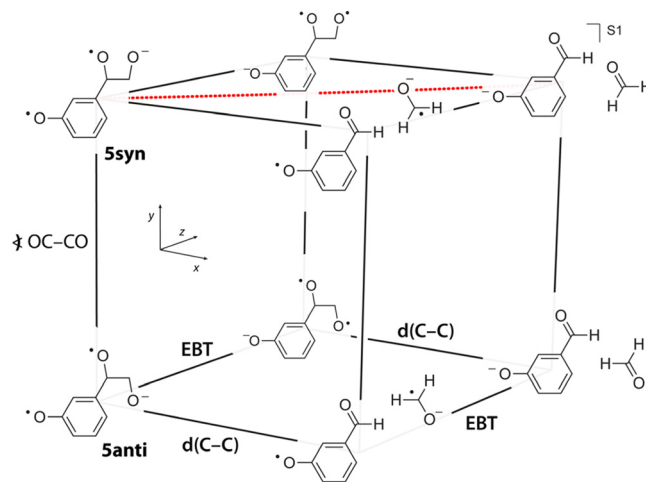
horizontal plane indicates the synchronized concerted limit of the chemiexcitation mechanism. Basically, after the O−O bond cleavage, the OC−CO dihedral angle in **5syn** is close to 0° and

the concerted mechanism leads to efficient chemiexcitation. Rotation around the C−C bond of **5syn** leads to **5anti** and consequently to ground-state products after C−C bond cleavage (i.e., low Φ_{S_1}). Therefore, the chemiexcitation yield from the decomposition of the biradical anion **5syn** depends on the competition between the rotation of the OC−CO dihedron and the concerted C−C bond cleavage/EBT. Furthermore, in the adiabatic and solvent-controlled electron-transfer regimes, the reaction rate is controlled by nuclear motion(s) of the system through the transition-state region.[56] Therefore, the solvent viscosity will influence the rate of dihedral angle change as well as the rate of electron transfer leading to chemiexcitation. Finally, this chemiexcitation mechanism could also explain the marked dependence of the chemiexcitation efficiency on the syn/anti conformation of the aromatic electron donor observed in the induced decomposition of bicyclic 1,2-dioxetanes bearing oxidaryl groups.[57]

In conclusion, the viscosity dependence of the chemiexcitation efficiency in induced 1,2-dioxetane decomposition is compatible with an entirely intramolecular transformation, providing C−C bond cleavage and EBT are concerted. Furthermore, according to the concerted mechanism introduced here efficient chemiexcitation depends on (i) the rate of electron back-transfer, which depends on the redox properties of the donor and acceptor, (ii) the conformational equilibrium constant of the initially formed biradical anion **5**, which depends on the structural features of the 1,2-dioxetane as well as medium viscosity, and (iii) the polarity of the medium, which may stabilize the partial charges formed during C−C bond cleavage and electron transfer.

3. MATERIALS AND METHODS

Solvent Mixtures. Toluene (Tol) and diphenylmethane (DPM) were treated overnight with EDTA (50 g/L), distilled after filtration (bp 111 °C (760 mmHg) and 86 °C (1 mmHg), respectively), redistilled over sodium wire, and stored under an inert atmosphere. The viscosities of pure solvents and Tol/DPM mixtures were measured at 25.0 ± 0.5 °C with a Brookfield LVD VII Rheometer (CP40 cone, 0.8° angle, 0.5 mL final volume, 3.4 cm radius). Determination of the $E_T(30)$ empirical polarity parameter was carried out using the relation $E_T(30)$ (kcal mol^{-1}) = 28591.5/λ_{max} (nm), as described elsewhere.[58−60] Solvent mixtures were prepared immediately before the execution of all experiments. Relevant physicochemical parameters of solvents cited in this work are presented in Table S1 (Supporting Information).

Chemiluminescence Emission Measurements. Experiments were carried out at 25.0 ± 0.5 °C under intense magnetic stirring to ensure complete mixing of the components in a Varian Eclipse spectrofluorimeter (photomultiplier tension, 750 V; bandpass, 5 nm; CL/BL mode; 10 mm optical path quartz cuvettes).

Decomposition of 1,2-Dioxetanes Induced by Fluoride Ions. 1,2-Dioxetanes **1** (4-(3-*tert*-butyldimethylsilyloxyphenyl)-4-methoxyspiro-[1,2-dioxetane-3,2′-adamantane]) and **2** (3,3-dimethyl-4-(3-*tert*-butyldimethylsilyloxyphenyl)-1,2-dioxetane) were prepared as described previously.[54,61] A stock solution of tetrabutylammonium fluoride in THF (TBAF, 1 mol L^{-1}) was used as the fluoride ion source. Stock solutions of the 1,2-dioxetanes **1** and **2** were prepared in pure solvents or Tol/DPM mixtures. Final concentrations were determined spectrophotometrically, as described elsewhere.[24,54]

A typical experimental procedure for chemiluminescence decay measurements is as follows: 30 μL of the stock solution of **1** or **2** was added to 3.0 mL of solvent in a quartz cuvet closed with a septum cap. The reaction was initiated by the addition of 3 μL of a solution of TBAF in THF/DMSO (1/1), followed by vigorous stirring for about 1 s. The whole procedure was carried out in a dark room. Final reagent concentrations are as follows: [**1**] = 90 μmol L^{-1}, [**2**] = 0.7 μmol L^{-1}, and [TBAF] = 2.5 mmol L^{-1}.

Peroxyoxalate System. Stock solutions were as follows: H$_2$O$_2$ (3.0 mol L^{-1}) in EtOAc, 9,10-diphenylanthracene (DPA, 10 mmol L^{-1}) in DPM, bis(2,4,6-trichlorophenyl)oxalate (TCPO, 12 mmol L^{-1}) in Tol, and imidazole (IMI-H, 24 mmol L^{-1}) in Tol. A typical experimental procedure for chemiluminescence decay measurements is as follows: solutions of H$_2$O$_2$ (2.5 μL), DPA (300 μL), IMI-H (63 μL), and adequate solvent (2.61 mL) were prepared in a quartz cuvet closed with a septum cap. The peroxyoxalate reaction was initiated by the addition of 25 μL of a TCPO stock solution, followed by vigorous stirring for about 1 s. Final reagent concentrations are as follows: [IMI-H] = 0.5 mmol L^{-1}, [H$_2$O$_2$] = 2.5 mmol L^{-1}, [DPA] = 1.0 mmol L^{-1}, and [TCPO] = 0.1 mmol L^{-1}.

Anhydrous hydrogen peroxide solution has been prepared in ethyl acetate; however, only a small amount of this solvent was added to the system (<0.1% v/v). Because of the limited solubility of some components in either Tol or DPM, the maximum concentration of DPM studied in this system is 90%.

Chemiluminescence Quantum Yields. Absolute singlet chemiexcitation quantum yields (Φ_{S_1}, in E mol^{-1}) were determined from the calibrated chemiluminescence quantum yields (Φ_{CL}, in E mol^{-1}) and fluorescence quantum yields of the emitting species (Φ_{FL}) according to eq 4, where Φ_{S_1} was determined from the area under the emission

$$\Phi_{S_1} = \frac{\Phi_{CL}}{\Phi_{FL}} \tag{4}$$

curves using luminol chemiluminescent oxidation as the secondary light emission standard.[9,62]

Fluorescence quantum yields (Φ_{FL}) of the cleavage products of **1** and **2**, i.e., formyl *m*-oxybenzoate anion and methyl *m*-oxybenzoate anion, respectively, were determined using quinine bisulfate (1.23 μmol L^{-1}) in 1 mol L^{-1} H$_2$SO$_4$ as the fluorescence standard (Φ_{FL} = 0.55).[63]

Data and Statistical Analysis. Data were analyzed using both the collisional and free-volume models for the dependence of Φ_{S_1} on the medium viscosity.[15,16,18−21] Detailed mathematical derivation of these models is provided in the Supporting Information. All values were expressed as mean ± standard deviation (SD) of at least three independent experiments. Statistical data analysis was achieved by one-way analysis of variance (ANOVA). The level of statistical significance was taken at $p < 0.05$. All analysis was carried out using origin 8.5 software (OriginLab, 2011).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, and figures giving mathematical derivation of the frictional and free-volume models, physicochemical parameters of solvents, and chemiluminescence and fluorescence data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*W.J.B.: tel, +55(11)3091.2371; e-mail wjbaader@iq.usp.br.

Present Address

†Biosystems and Biomaterials Division, Chemical Science Technology Laboratory, National Institute of Standards and Technology. Gaithersburg, MD, United States.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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