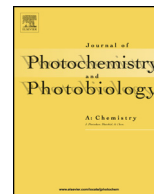




Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Peroxyoxalate chemiluminescence efficiency in polar medium is moderately enhanced by solvent viscosity



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ARTICLE INFO

Article history:

Received 11 January 2016

Received in revised form 28 January 2016

Accepted 2 February 2016

Available online 4 February 2016

Keywords:

Chemiluminescence

Peroxyoxalate

Solvent-cavity effect

Viscosity

Electron transfer

Chemically Initiated Electron Exchange

Luminescence

ABSTRACT

The peroxyoxalate reaction is one of the most efficient chemiluminescence transformations and the only system which is believed to occur by an intermolecular Chemically Initiated Electron Exchange Luminescence (CIEEL) mechanism with proven high efficiency. Although this reaction system is utilized in a variety of analytical applications, its exact reaction mechanism is still unknown, specifically with respect to the structure of the high-energy intermediate, the mechanism of its interaction with a chemiluminescence activator, as well as the reason for the extraordinarily high chemiexcitation efficiency. The solvent viscosity influence on the singlet quantum yields of the peroxyoxalate reaction is studied in this work, using the polar binary solvent mixture of ethyl acetate and dimethyl phthalate spanning a viscosity range of 0.42–14.4 cP. The viscosity increase of about forty times leads to a quantum yield increase of a factor of around five. Although the viscosity effect on the quantum yields is significant, it is considerably lower than that obtained before in less polar media. The quantum yield dependency on the viscosity can be described with both the collisional and the frictional model, with good correlation coefficients ($R^2 > 0.95$). However, the α values obtained from the frictional model would be more compatible with an intramolecular transformation than with the intermolecular interaction of a high-energy intermediate with an external activator. This apparent contradiction is thought to be due to stabilization of the charge-transfer complex between the high-energy intermediate and the activator by the polar medium, avoiding solvent cavity escape and increasing chemiexcitation efficiency. The high stability of the charge-transfer complex in the peroxyoxalate reaction might be due to the high planarity of the possible high-energy intermediate in this transformation, 1,2-dioxetanedione, the peroxidic carbon dioxide dimer.

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1. Introduction

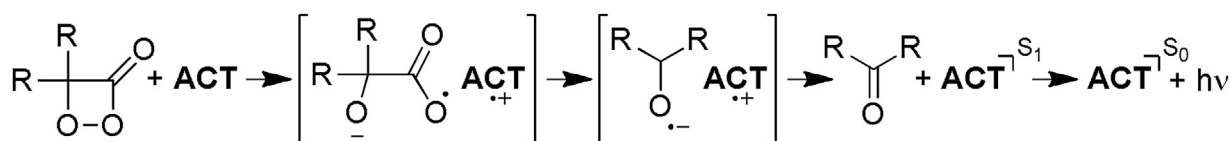
Chemical reactions that occur with light emission, transforming the chemical energy into electronic excitation energy, called chemiluminescence (CL) processes, are interesting study objects from the mechanistic point of view as they involve necessarily crossing between ground state and excited state potential energy surfaces [1–5]. Therefore, the mechanisms of chemiluminescent transformations are being studied by experimental [1,6,7], as well as theoretical approaches [8–17]. Additionally, CL transformations have found widespread analytical applications [18–23], indicating the need for an exact understanding of this kind of transformations.

Cyclic four-membered peroxides, like 1,2-dioxetanes and 1,2-dioxetanones, are important intermediates in several CL reactions and have also been postulated as key-intermediates in bioluminescence transformations [1,2,4,24]. The unimolecular decomposition of these high energy compounds leads to the preferential generation of triplet excited cleavage products which are non-emissive in oxygenated solutions [1,2,25–27]. However, the decomposition of 1,2-dioxetanones can be catalyzed by added compounds with low oxidation potential and high fluorescence quantum yield leading to preferential formation of singlet excited products. These catalysts are called activators (ACT), as they directly interact with the cyclic peroxide, increasing its rate of decomposition [2,28].

These observations have led to the formulation of the Chemically Initiated Electron Exchange Luminescence (CIEEL) mechanism, which involves a sequence of electron transfer, bond cleavage and electron back transfer steps (Scheme 1), leading to the ACT excited state formation, and has been utilized to

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Scheme 1. General CIEEL mechanism for 1,2-dioxetane decomposition.1.

rationalize several CL and bioluminescence transformations [2,29,30].

Notwithstanding, it has been shown recently that the quantum yields obtained in the catalyzed decomposition of 1,2-dioxetanes are much lower than the ones originally reported [31], although the involvement of an electron transfer from the peroxide to the ACT has been confirmed and it was suggested that the efficiency of these intermolecular CIEEL transformations might be determined by steric effects on the interaction between ACT and the peroxide [32].

Contrarily, the induced decomposition of phenoxy-substituted 1,2-dioxetanes, thought to occur by an intramolecular version of the CIEEL mechanism, is highly efficient, reaching chemiexcitation quantum yields of up to 100% [33–37]. This transformation appears to occur by an entirely intramolecular chemiexcitation sequence, involving an initial electron transfer step [38], accompanied by stepwise O–O and C–C bond cleavage steps and finally an intramolecular electron back-transfer. Although, the efficiency of this transformation proved to be sensitive to solvent viscosity [39–44], this apparent solvent cavity effect was rationalized with the necessity of a specific conformation for efficient excited state formation in the electron back-transfer step [43].

Even so it appears that intermolecular CIEEL systems occur with low quantum yields, whereas intramolecular systems are highly efficient [45], the peroxyoxalate reaction (Scheme 2) has been shown by various research groups to have high emission quantum yields [46–48]. Additionally, several mechanistic studies on this transformation have indicated that the chemiexcitation step of this complex reaction should involve the intermolecular CIEEL mechanism (Scheme 1) [48–50], constituting therefore the only intermolecular CIEEL system with proven high quantum yields [1,45].

The solvent viscosity effect of this transformation has been studied before in a binary solvent system consisting of toluene and diphenylmethane, in comparison to the intramolecular induced 1,2-dioxetane decomposition [43]. However, the highly efficient peroxyoxalate system, with quantum yields reaching more than 50% in favorable experimental conditions [48], proved to be of low efficiency (less than 1%) in this low polarity solvent mixture.

Therefore, we studied here the solvent viscosity effect on the quantum yields of the peroxyoxalate reaction using a more polar binary solvent mixture of ethyl acetate and dimethyl phthalate, which have different viscosities but similar polarity parameters, where higher quantum yields are expected.

2. Materials and methods

2.1. Solvents

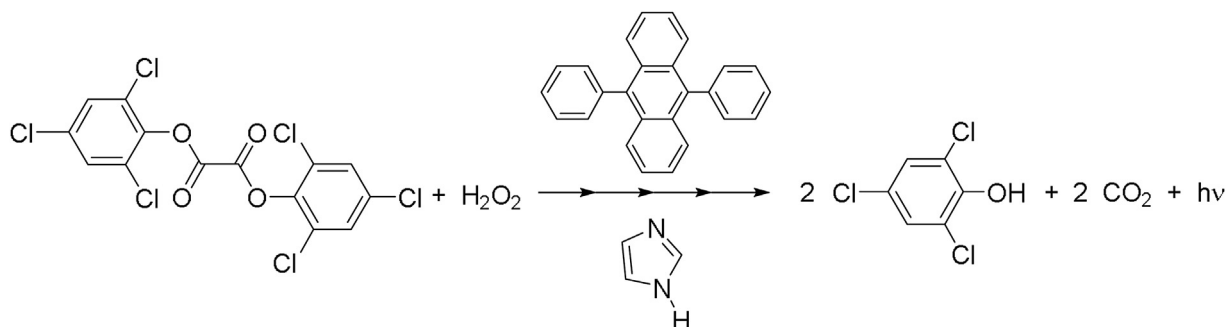
Ethyl acetate was treated overnight with anhydrous CaCl_2 , then stirred with solid sodium hydroxide (40 g/L) for 30 min at 0°C , filtered again and distilled. The distillate was left overnight over 4 Å molecular sieves, distilled over a 200 cm Vigreux column under inert atmosphere and stored over 4 Å molecular sieves. Methyl phthalate was treated overnight with sodium ethylenediamine-tetraacetate (EDTA) (50 g/L), filtered and treated overnight again with anhydrous MgSO_4 (40 g/L) and filtered again. The filtrate was allowed to stand overnight over 4 Å molecular sieves, filtered and stored over 4 Å molecular sieves under inert atmosphere. Viscosities of pure solvents and ethyl acetate/methyl phthalate mixtures were determined at $25.0 \pm 0.5^\circ\text{C}$ with a Brookfield LVD VII Rheometer (CP40 cone, 0.8° angle, 0.5 mL final volume, 3.4 cm radius).

2.2. Chemiluminescence emission measurements

Experiments were carried out at $25.0 \pm 0.5^\circ\text{C}$ with intense magnetic stirring to ensure complete mixing of the components in a Hitachi U-2000 spectrofluorimeter (photomultiplier tension, 750 V; band pass 2.5 nm; chemiluminescence mode; 10 mm optical path quartz cell).

2.3. Stock solutions

Stock solutions of anhydrous H_2O_2 ($\sim 1.0 \text{ mol L}^{-1}$) in ethyl acetate were prepared by treatment of a mixture of ethyl acetate and 60% aqueous H_2O_2 with MgSO_4 at 4°C overnight and its exact concentration determined iodometrically [51]. Stock solutions of



Scheme 2. Peroxyoxalate reaction with bis(2,4,6-trichlorophenyl) oxalate (TCPO), hydrogen peroxide and imidazole (IMI-H) as base catalyst in the presence of 9,10-diphenylanthracene (DPA) as CL activator.1.

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