

Viscosity Influence on the Singlet Quantum Yields of the Rubrene Catalyzed Diphenoyl Peroxide Decomposition.

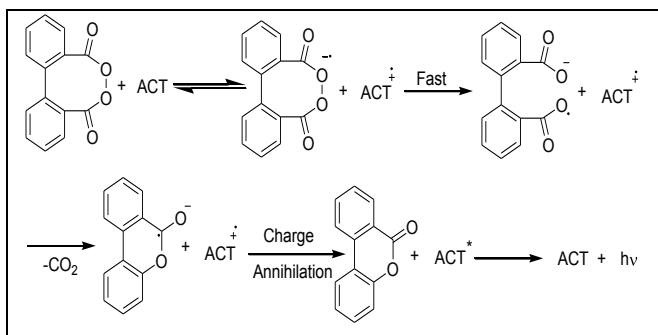
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Introdução

Chemiluminescence is the emission of light by a chemical reaction.¹ Chemiluminescent reactions usually involve cyclic organic peroxides as energy sources and the reactions are initiated by cleavage of the weak O-O bond and the resulting molecular reorganization liberates enough energy for excited state formation. The chemiluminescent decomposition of diphenoyl peroxide by rubrene as activator (ACT) is initiated by rate-limiting electron transfer from this activator to the antibonding σ^* orbital of the O-O bond in diphenoyl peroxide, followed by fast O-O bond cleavage, generating a radical anion from the peroxide and the rubrene radical cation. Decarboxylation takes place rapidly and ring closure of this species produces benzocoumarin radical anion, which is a powerful reducing agent and annihilation within the cage can produce the singlet excited state of rubrene which results in chemiluminescence emission (Scheme 1).



Scheme 1: Mechanism for the catalyzed decomposition of diphenoyl peroxide by an activator (ACT) like rubrene.²

Resultados e Discussão

In this work, we have studied the influence of solvent viscosity on the catalyzed decomposition of diphenoyl peroxide (DPP) and determined the singlet quantum yields (Φ_s) using a suitable solvent system like toluene / diphenyl ether (DPE). This system has a variation of the viscosity in the largest possible range without significant change in the polarity parameters of the solvent system (Table 1).

Table 1: Singlet quantum yields (Φ_s) for the rubrene catalyzed decomposition of diphenoyl peroxide (DPP).

% Solvent	η (cP) ^a	$\Phi_s / E \text{ mol}^{-1} \times 10^4$
A	0.5	1.06 ± 0.01
B	0.74	1.19 ± 0.02
C	1.1	1.27 ± 0.01
D	1.6	1.38 ± 0.06
E	2.17	2.26 ± 0.18

A=toluene; B=25%diphenyl ether; C=50%diphenyl ether; D=75%diphenyl ether; E=95%diphenyl ether. [DPP]=1.0 mmol L⁻¹; [rubrene] = 1.0 mmol L⁻¹; at 36.0 °C; mean values ± sd with triplicates. ^a measured by a Brookfield LVD VII Rheometer.

The singlet quantum yields (Φ_s) increased by a factor of ca. 1.3 from pure toluene ($\eta = 0.5$ cP) to 75% diphenyl ether ($\eta = 1.6$ cP). Interestingly, for 25 to 75 % of DPE, the singlet quantum yields are very similar, increasing only significantly in 95% of DPE ($\eta = 2.1$ cP) (Table 1). This fact might be due to preferential solvation of the radical ions in the chemiexcitation step of the diphenoyl peroxide system (Scheme 1).

Conclusões

The singlet quantum yields (Φ_s) for the rubrene catalyzed decomposition of diphenoyl peroxide increase only slightly with the solvent viscosity, a surprising fact for this intermolecular CIEEL system.

Agradecimentos

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¹ Baader, W. J., Stevani, C. V., & Bastos, E. L. In: *The Chemistry of Peroxides*; Rappoport, Z., Ed.; Wiley & Son., Chichester, 2006, Chapter 16, 1211.

² Koo, J.-Y. & Schuster, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 4496.