Why is the efficiency of the peroxyoxalate reaction so low in the presence of water?

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Abstract

The peroxyoxalate system, base catalyzed reaction of an activated oxalic ester with hydrogen peroxide in the presence of a chemiluminescence activator (ACT), is widely used in a great variety of analytical and bio-analytical application. The mechanism of this transformation has been intensively studied in anhydrous medium, however; only few mechanistic studies exist in aqueous conditions, which are important for the bio-analytical applications. Additionally, it is known that the peroxyoxalate reaction, highly efficient in anhydrous medium (with quantum yields of up to 50 %), possesses much lower efficiency in aqueous medium. In this work we report our preliminary results of a study on the chemiexcitation step of the peroxyoxalate reaction in organic solvents containing small amounts of water in order to understand why the chemiexcitation quantum yields of this transformation are drastically lowered in the presence of water. The overall rate constants proofed to be little affected by an increase in the water concentration, indicating the occurrence of preferential solvation by the organic solvent, avoiding undesired hydrolysis of the oxalic ester. The quantum yields showed to be more sensitive to the presence of water and in certain experimental conditions a maximum quantum yields is obtained for a molar fraction of 0.1 of water at constant ACT concentration. The variation of the ACT concentration allows the study of the chemiexcitation step and the determination of the chemiluminescence parameters of this transformation, which showed to be critically influenced by the presence of small amounts of water. In a preliminary conclusion it can be observed that the low chemiexcitation quantum yields obtained for the peroxyoxalate reaction in aqueous medium are not mainly due to concurrent oxalic ester hydrolysis but to the influence of water on the efficiency of the chemiexcitation step.

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