Linear free energy relationship analysis of solvent effects on singlet oxygen reactions

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Linear solvation energy relationship, LSER, and theoretical linear solvation energy relationship, TLSER, formalisms are applied to the analysis of solvent effects on singlet oxygen reactions. Treatments allow quantitative evaluation of solvent effects and are powerful tools for interpreting the mechanism of the process. Both formalisms are applied to several amino derivatives, where for all types of solvents there is a single pattern, implying a common reaction mechanism involving charge transfer intermediates. The relative contribution of the different descriptors depends upon the compound considered, but a common feature is a significant negative dependence on the ? parameter, which measures solvent acidity. Correlation equations obtained from analysis of singlet oxygen reactions with 1,3-dienes also exhibit a common dependence on the ?H parameter, that accounts for the cohesive energy of the solvent, and reflects the negative activation volume associated with concerted or partially