

Reaction of singlet molecular oxygen, $O_2(1\ ^1g)$, with the Cinchona tree alkaloids: Effect of absolute configuration on the total rate constant

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Detection of $O_2(1\ ^1g)$ emission, $\lambda_{max} = 1270$ nm, following laser excitation and steady-state methods were employed to measure the total reaction rate constant, k_T , and the reactive reaction rate constant, k_R , for the reaction between singlet oxygen and the Cinchona tree alkaloids, cinchonidine, cinchonine, quinine and quinidine in several solvents. In most solvents, the k_T values were close to 10^7 M⁻¹ s⁻¹, indicating that these compounds are good singlet oxygen quenchers. The reactive rate constants are smaller than 10^4 M⁻¹ s⁻¹, implying that quenching is essentially a physical process. The analysis of solvent effect on k_T by using LSER equations indicates that singlet oxygen deactivation by these drugs is accelerated by solvents with large π^* and β values, being inhibited by hydrogen bond donor (HBD) solvents. Correlations employing theoretical solvent parameters, TLSE, give similar results. These data support the formation of an exciplex with charge transfer character, resulting from