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Kinetic study of the sulfapyridine photodegradation reaction in aqueous solution: Effects of ions and explicit solvation

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Sulfonamide antibiotics (SAs), encompassing drugs like sulfapyridine (SPY), have attracted significant attention due to their prevalence in both medical and agricultural applications.[1] However, this widespread usage has raised concerns regarding their potential ecological impact since these compounds reach aquatic environments by different pathways, including pharmaceutical manufacturing effluents, agricultural runoff, and wastewater treatment plant discharges.[1-2] This study contributes to the development of photodegradation methodologies for SAs by computationally exploring the effects of explicit solvation and interactions with selected ions (Ca^{2+}, Mg^{2+}, Zn^{2+}, Br^-, Cl^-, and NO_3^-) on the rate-determining step (RDS) of the triplet-sensitized photodegradation pathway involving SO_2 extrusion in aqueous solutions of SPY. Density Functional Theory (DFT) with dispersion corrections was employed to investigate the singlet ground state (S_0) and the lowest-lying triplet excited state (T_1) of SPY. Geometry optimizations and vibrational frequency calculations were performed at the PBE-D3(0)/cc-pVTZ level of theory in water using the polarizable continuum model (PCM).[3] Moreover, in order to achieve accurate reaction barrier heights, several exchange-correlation functionals were evaluated against reference data obtained by using the DLPNO-CCSD(T) method. Hence, CAM-QTP-02 and CAM-B3LYP-D3(BJ) emerged as the most reliable functionals, exhibiting mean absolute deviations (MADs) of 1.98 kcal.mol^{-1} and 1.42 kcal.mol^{-1}, respectively. Subsequently, Gibbs energies of activation (ΔG_{act}), Gibbs energies of reaction (ΔG_r), and rate constants (k) were determined using single-point calculations at the previously optimized geometries. The CAM-B3LYP-D3(BJ)/def2-QZVPP level of theory with the SMD solvation model and four explicit water molecules was employed for these calculations. The analysis revealed Pathway I (ΔG_{act} = 25.73 kcal/mol) as the RDS of SPY photodegradation. Furthermore, the influence of ions and explicit solvent interactions on Pathway I was investigated. Quasi-harmonic corrections to entropy and enthalpy contributions of vibrational modes were also included. Cations and nitride (NO_3^-) result in faster degradation rates (decrements in ΔG_{act}), while Cl^- and Br^- exhibited inhibitory effects (increased ΔG_{act} values). The inclusion of explicit solvent molecules also affected the barrier height significantly, particularly for cations, reinforcing the need for considering this approach in similar degradation investigations in aqueous solutions.

References

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