

Chlorination of oxybenzone and prediction of transformation products using non-equilibrium “forced” molecular dynamics

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ABSTRACT

Oxybenzone (OxBZ) is a member of the benzophenone family of sunscreen filters. Despite its broad biotoxicity, OxBZ and its transformation products (TPs) have been detected in coastal seawater, wastewater, and drinking water supplies around the globe. Unfortunately, little is known about the fate of OxBZ during water treatment, especially when exposed to chlorine or ozone disinfection. In this report, a hybrid quantum/molecular mechanics (QM/MM) algorithm is described that simulates reactions between OxBZ and hypochlorous acid (HOCl) in an aqueous background. The algorithm uses non-equilibrium forced molecular dynamics (N_{eq} FMD) to force bi-molecular collisions between HOCl and OxBZ over a population of random reactant conformations and orientations. A semiempirical QM method (RM1) is used to control and manage reactant collisions and compute molecular orbital rearrangements leading to bond dissociation and formation, while explicit water is treated classically as a perturbation on the electronic wave function. The N_{eq} FMD method qualitatively emulated key aspects of aromatic ring activation and substituent directing effects (including an $-\text{OCH}_3$ π - σ^* hyperconjugation) associated with OxBZ pendent groups. When applied to the solvated HOCl–OxBZ system, a diversity of potential TPs was observed, several of which have been documented in prior experimental studies, including hydroxy radical ($\cdot\text{OH}$), chlorine radical ($\cdot\text{Cl}$), methyl radical ($\cdot\text{CH}_3$), formaldehyde ($\text{H}_2\text{C}=\text{O}$; or its di-radical precursor $\cdot\text{CH}_2\text{O}\cdot$), chloromethane (ClCH_3), mono-chloro-oxybenzone or its meta-stable Wheland intermediate, as well as open-ring and ring-scission products such as mono-chlorobenzene, para-chloromethoxyphenol (chloroguaiacol), and 4-methoxy-catechol. Halogen addition to the methoxy ring was preceded by homolytic cleavage of HOCl to form an $\cdot\text{OH}$ radical + a transitory “semi-bound” $\cdot\text{Cl}$ radical. The later underwent nascent covalent bonding to an ortho-carbon via π -resonance delocalization to form a meta-stable carbocation intermediate expected to devolve by hydrogen abstraction to the monochlorinated ortho-substituted OxBZ product observed in experimental studies. Chlorine electron density (which increased over the collision trajectory) delocalized inversely with the mean partial charge of the methoxy ring, as well as the total charge of the OxBZ molecule, consistent with an SEAr (arenium ion) mechanism. Kinetically induced conformational strain in OxBZ was accompanied by resonance fluctuations in conjugated π -bonds comprising the methoxy ring, as revealed by coupled interatomic oscillations in sp^2 aromatic carbon partial charges. Finally, an unusual ipso hydroxylation/di-radical mechanism not previously reported is described for the formation of formaldehyde in HOCl–OxBZ collisions. Results indicate that N_{eq} FMD simulations can complement and extend experimental approaches to predict reaction outcomes and assist in the elucidation of reaction mechanisms involved in disinfection by-product formation.

Keywords: Benzophenone; Chlorine; Disinfection; Disinfection by-product; Molecular dynamics; Molecular modeling; Oxybenzone; QM/MM; Reaction mechanism; Wastewater; Water reuse; Water treatment

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