Characterizing the Role of Carboxylic Acid Substituents in the Photocatalytic Degradation of Ibuprofen Structural Variants

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Contamination of natural waters by pharmaceuticals and personal care products (PPCPs) is a current and growing threat to both aquatic life and, through increased concentrations in drinking water and the upper levels of the food chain, to humans[1,2,3]. Ideally, wastewater treatment plants (WWTPs) would remove these chemicals as part of their purification process, but currently used methods are not entirely effective in removing the low concentration of PPCPs present in the water before it is discharged into the environment[2]. Ibuprofen (IBP), for example, which is consumed at a rate of 300 tons per year in the US,[4] primarily enters ecosystems through wastewater effluent,[5] where, due to its low rate of natural degradation and high fat solubility,[6] it accumulates. In aquatic organisms, multiple studies have found that prolonged exposure to high environmental IBP concentrations can damage cells and DNA, as well as cause problems with normal growth and reproduction[7].

Photocatalysis, with its use of a solid particle as the catalyst and light as an energy source for the catalytic pathway, provides an eco-friendly method by which IBP, and other PPCPs like it, might be degraded in WWTPs and thereby prevented from accumulating in ecosystems via wastewater. Since many PPCPs are very stable, strong oxidizers are required to break them apart, ideally into less harmful components like carbon dioxide, water, or ammonia[8]. However, much of the previous research in this area has focused on titanium dioxide (TiO_2), which, despite proving effective at degrading IBP, has also been found to degrade it into components that are just as toxic, if not more so, than the original structure[9]. Though TiO_2 continues to be studied for its use in the removal of other PPCPs, bismuth oxychloride (BiOCl) has recently become an active subject of research for its high photocatalytic activity and ability to oxidize organic compounds, including IBP, when irradiated with ultraviolet light[9]. This project worked to further elucidate the catalytic abilities of BiOCl by determining the structural patterns with which it yields the best reactions, helping to clarify BiOCl's potential uses in WWTPs and the PPCPs it is best able to degrade.

Specifically, this project focused on carboxylic acids, as the presence of a carboxylic acid group alpha to the central benzene ring has been shown to dramatically increase the rate at which degradation occurred. It was hypothesized that this increased rate occurred via direct hole oxidation, a mechanism in which an unstable electron radical is formed in the IBP variant through the loss of a CO2 group, which then quickly reacts with the surrounding IBP compound. To test this, two structural variants of IBP, specifically its F impurity and methyl ester, were irradiated with 254 nm light in order to determine the relative rates of their degradation via BiOCl, hypothesizing that an increased degradation rate would correlate with the relative ease of radical formation.

Initial work supported this hypothesis, as ibuprofen, which has the carboxylic acid alpha to the central benzene ring, yielded the highest degradation rate constant of 0.35 min^{-1}, while ibuprofen's F impurity, which distances the carboxylic acid from the central ring by an additional carbon, showed a much reduced degradation rate of 0.08 min^{-1}, despite identical conditions. Finally, ibuprofen's methyl ester, which contained no carboxylic acid group, and thus had the least ability to generate a radical via the proposed reaction, yielded the slowest degradation rate of the three molecules tested, at 0.03 min^{-1}.

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