Direct Irradiation of Aromatic Methyl Thioether Compounds

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Dissolved organic compounds containing photolabile moieties are susceptible to photochemical transformations in aquatic systems. For example, compounds containing reduced sulfur are generally prone to photolytic reactivity. This study focuses on aromatic S-compounds having a methyl thiyl group. This group was proposed to be a precursor to the photoproduction of methane sulfonic acid, a crucial component of the sulfur biogeochemical cycle.[1] However, little is known about their photodegradation pathways that lead to methane sulfonic acid production. In this work, we selected two model aromatic methyl thioethers for in-depth mechanistic analysis and product identification. The first is thioanisole, a pollutant detected in the wastewater of an oil production site.[2] The second is 3-(methylthio)benzoic acid, like thioanisole in structure, but it has a meta-substituted carboxylic group. We observed that the aromatic methyl thioethers in this study undergo direct photolysis in the UVB region. The role of their triplet-excited states was significant in this process. The main products formed were the corresponding sulfoxides through an oxidation pathway. In addition, a cleavage pathway occurs, confirmed by the products identified, revealing the bond break between the aromatic ring and the sulfur methyl group. This work provides insight into the photochemistry of aromatic methyl thioethers and shows that the role of light can be crucial in elemental cycling, sulfur cycling in this case.

[1] Rachelle Ossola, Julie Tolu, Baptiste Clerc, Paul R. Erickson, Lenny Winkel, Kristopher McNeill, *Environmental Science & Technology*, **2019**, 3(22), 13191-13200.
[2] Oxana Botalova, Jan Schwarzbauer, *Water, Air, & Soil Pollution*, **2011**, 221, 77-98.