DFT Investigations for Mechanisms of the TCEP Degradation by Hydroxyl Radical

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Tris (2-chloroethyl) phosphate (TCEP) is one of the organophosphorus esters which are emerging environmental contaminants widely applied as annexing agents in a variety of industrial products and robust against conventional wastewater treatments [1]. However, it could be decomposed by hydroxyl radicals (OH·) which can be generated in UV/H_2O_2 or UV/TiO_2 photocatalytic systems. In our present attempts, two pathway mechanisms (see Figure 1), namely attack of OH· to one of the P-O bonds via Channel 1 or to one of the C-O bonds via Channel 2, were established by using the density functional theory (DFT) method. Based upon the typical geochemical conditions, the computational results indicate that the energy barrier via Channel 1 (ΔG= 24.8 kcal/mol) is significantly lower than that via Channel 2 (ΔG=54.7 kcal/mol), demonstrating that Channel 1 is more favourable. In the investigation of the mechanism to obtain product B in Figure 1, the energy barrier was calculated as 28.9 kcal/mol, which is in excellent agreement with the experimental observations of others that product A is preferentially to be detected over product B [2-4]. These are important for degradation insight of emerging contaminants.

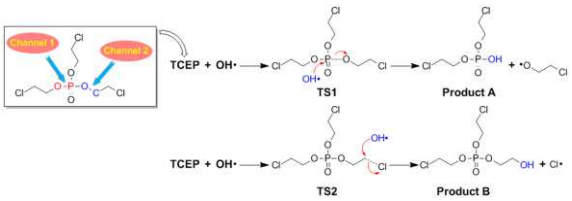

Figure 1: Possible pathways of TCEP degradation with OH·

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[1] HS Ou et al. ***Chem. Eng. J.*** 308 (**2017**) 386. [2] J Ye et al., ***Wat Res.*** 124 (**2017**) 29. [3] J Liu et al., ***Chemo.*** 190 (**2018**) 225. [4] X Xu et al., ***Chemo***. 185 (**2017**) 833.