

Computational study of the mechanistic pathway of hydroxyl radical-initiated degradation of disperse red 73 dye

Olaide O. Wahab¹ · Lukman O. Olasunkanmi^{2,3} · Krishna K. Govender^{3,4} · Penny P. Govender³

¹ Department of Chemistry, Faculty of Natural and Applied Sciences, Nigerian Army University Biu, Biu, Borno state, Nigeria

² Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife 220005, Nigeria

³ Department of Chemical Sciences, University of Johannesburg, Doornfontein Campus, P. O. Box 17011, Johannesburg 2028, South Africa

⁴ Council for Scientific and Industrial Research, Centre for High Performance Computing, National Integrated Cyber Infrastructure, 15 Lower Hope Road, Rosebank, Cape Town 7700, South Africa.

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Abstract

The mechanisms of hydroxyl radical ($\cdot\text{OH}$) degradation of disperse red 73 (DR73) dye were investigated using density functional theory (DFT) calculations. Comparative feasibility of $\cdot\text{OH}$ attack at the azo ($\text{N}=\text{N}$) site or on a $>\text{C}-\text{N}$ group was examined based on their energies with a view to determine the more preferred pathway for DR73 degradation and predict its degradation products. Further decomposition of the cleavage products by $\cdot\text{OH}$ radical through processes such as deamination and loss of molecular nitrogen was also examined. The results showed that $\cdot\text{OH}$ radical attack on DR73 is more favourable via the azo ($\text{N}=\text{N}$) site. However, subsequent rupture of the $\text{N}=\text{N}$ bond was found to be kinetically and thermodynamically less favourable compared to the $\text{C}-\text{N}$ bond rupture arising from the attack of the radical on a ring carbon attached to the azo group. Introduction of water (as a solvent) was found to produce an accelerating and stabilising effects on the $\text{N}=\text{N}$ bond cleavage mechanism, but an inhibitory and destabilising effects on the $\text{C}-\text{N}$ counterpart. Deamination and nitrogen evolution reactions of the primary degradation products upon further $\cdot\text{OH}$ radical attack were found to be kinetically and thermodynamically feasible.