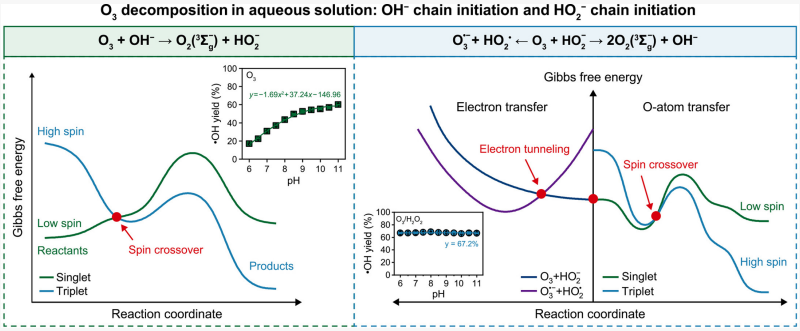
# Electron transfer drives hydroxyl radical formation in peroxone reactions

GA, UNITED STATES, June 1, 2026 /EINPresswire.com/ -- Ozone-based water treatment is widely used to remove pollutants, odors, color, and pathogens, yet one of its most important chemical engines has remained uncertain: how efficiently ozone reactions generate hydroxyl radicals (•OH), the highly reactive species that drive advanced oxidation. A new study revisits this long-standing question and finds that the peroxone process—ozone (O□) combined with hydrogen peroxide (H□O□)—produces an approximately 67% •OH yield, higher than the commonly assumed value of about 50%. By clarifying how radical chains begin, the work offers a more accurate chemical foundation for designing ozone-based systems for cleaner and safer water.



Dual pathways drive ozone decomposition in water.

Ozone (O□) oxidation has been used for decades in drinking water and wastewater treatment because O□ can directly oxidize contaminants and also decompose into •OH through chain reactions. Adding H□O□ accelerates this decomposition, making the peroxone process one of the major advanced oxidation process (AOP) based on O3. However, previous mechanism proposed that adduct formation was the rate-limiting step and suggested limited radical yield, leaving uncertainty over how O□ reactions actually begin in water. Because pollutant removal depends not only on ozone decay but also on radical generation efficiency, a clearer mechanism is needed. Based on these challenges, in-depth research is needed into the initiation pathways and •OH yield of ozone-based oxidation reactions.

The study, conducted by Yishi Wang, Wei Qiu, Yongbo Yu, and Jun Ma from the State Key Laboratory of Urban Water Resource and Environment, School of Environment, Harbin Institute of Technology, was accepted on May 16, 2026, and published in Environmental Science and Ecotechnology. The article combines radical-capture experiments, competition assays, and quantum-chemical calculations to revise the mechanism of how O□ and H□O□ initiate •OH-forming chain reactions in water.

The researchers first measured how pH and H□O□ concentration affected O□ decay and

pollutant degradation, using compounds such as atrazine (ATZ) and p-chlorobenzoic acid (pCBA) to track •OH-driven oxidation. They found that increasing pH and adding H□O□ both enhanced •OH exposure, but H□O□ was the more practical route under near-neutral water conditions. Complete-capture assays using tert-butanol (t-BuOH) and dimethyl sulfoxide (DMSO) showed that the O□/H□O□ system generated •OH at a stable yield of about 67%, while O□-only reactions showed pH-dependent yields. Competition experiments with multiple probe compounds further supported this value and helped resolve the disputed reaction rate between •OH and O□ as 1.1 × $10^{8}$ $M^{-1}$ $s^{-1}$. Theoretical calculations then revealed the chemical reason: O□ reacts with hydroxide ion (OH□) through oxygen-atom transfer (OAT), while O□ reacts with hydroperoxide ion (HO□□) through two nearly equal routes—electron transfer (ET) and oxygen atom transfer (OAT). This dual-pathway mechanism explains why peroxone chemistry produces more •OH than earlier models predicted.

The authors said the findings show that peroxone chemistry is not simply an ozone-decomposition shortcut, but a finely balanced radical-generating process driven by competing molecular pathways. They said the approximately 67% •OH yield provides a clearer benchmark for evaluating O□/H□O□ systems, while the identification of ET as a key initiation route helps explain why previous adduct-based models underestimated radical production. By connecting bench-scale radical measurements with Marcus electron-transfer theory, the study turns a debated reaction sequence into a more testable and design-ready mechanism.

These findings could improve how engineers design advanced oxidation processes (AOPs) for water purification. A more accurate •OH yield allows treatment systems to better estimate oxidant doses, reaction efficiency, and pollutant removal potential. The work also suggests that simply tracking O□ decay may not be enough; operators need to understand how much decay is converted into useful radical chemistry. By resolving the roles of OH□, HO□□, ET, and OAT, the study provides a mechanistic map for optimizing peroxone reactions under realistic water conditions. In the longer term, this knowledge may support more efficient degradation of persistent organic pollutants while reducing unnecessary chemical use in ozone-based treatment systems.

References

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