

Comment on “Mechanistic Understanding of Superoxide Radical-Mediated Degradation of Perfluorocarboxylic Acids”

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In their recent publication, Bai et al.¹ present a mechanistic exploration of the reactivity of a superoxide radical with perfluorocarboxylic acids (PFCAs). This is a valuable contribution that considers the role of solvation on superoxide reactivity and quantifies superoxide decay rates in the presence of PFCAs. However, PFCA degradation and defluorination data were not presented, and readers should be warned that superoxide by itself is not effective for PFOA degradation. This was demonstrated in our recent paper² (overlooked by Bai et al.), which showed no PFOA degradation under well-defined, highly favorable conditions with exaggerated superoxide concentrations that were stabilized to mitigate wasteful disproportionation. We produced superoxide by three methods: (1) xanthine oxidase with hypoxanthine in the presence of manganese oxide, which provides a mineral surface that stabilizes superoxide; (2) $\text{WO}_3/\text{ZrO}_2 + \text{H}_2\text{O}_2$, where superoxide is produced and stabilized on the catalyst surface; and (3) KO_2 dissolved with 18-crown-6 in the aprotic solvent dimethyl sulfoxide (DMSO), which stabilizes superoxide released by KO_2 . Superoxide presence and reactivity were confirmed in all three systems by EPR spectroscopy and by nitroblue tetrazolium and bisphenol A degradation as positive controls. PFOA was not degraded by any of these superoxide-producing systems, and no PFCA degradation byproducts or released fluoride were detected.

Bai et al. had previously developed a superoxide generation method by irradiating a pH 8-buffered solution of H_2O_2 and sodium formate with UV light for 30 s.³ In their latest publication,¹ they turned off the light, added a PFCA (C3–C8), and monitored superoxide decay as an indirect assessment of PFCA degradation. They performed DFT calculations to investigate the potential mechanism and also evaluated the thermodynamic feasibility of a superoxide radical's reaction pathway with $\text{C}_2\text{F}_5\text{CO}_2^-$. They concluded that superoxide would attack the α C atom ($\Delta G_R^\circ = -4.09 \text{ kcal mol}^{-1}$), leading to the cleavage of the C–F bond. However, fluoride release data (which is relatively easy to obtain) and degradation byproduct information are needed to prove this hypothesis. It is unclear why they did not follow common practice to monitor PFCAs and their degradation byproducts, usually with HPLC-MS/MS, and report fluoride release (which would demonstrate C–F bond cleavage) using ion chromatography.⁴ The authors used high PFCA concentrations, such as 50–150 μM PFOA (20.7–62.1 mg/L), which are readily detected by HPLC-MS/MS; PFOA can even be detected by HPLC-DAD (UV/vis detector).⁵ This shortcoming casts doubt on the claim of PFCA degradation.

Bai et al.'s system had multiple radicals present, including $\cdot\text{OH}$ ($E^\circ = +2.72 \text{ V}$), superoxide ($E^\circ = -0.33 \text{ V}$), and $\text{CO}_2^{\cdot-}$ ($E^\circ = -1.90 \text{ V}$).⁶ According to the authors, these are generated in the aqueous system when UV light homolytically splits H_2O_2 into hydroxyl radicals, which react with formate to produce $\text{CO}_2^{\cdot-}$. This radical then transfers an electron to dissolved oxygen to create superoxide ($\text{O}_2^{\cdot-}$) at millimolar concentrations. It is widely accepted that a hydroxyl radical (a stronger oxidant than superoxide) is by itself ineffective in degrading PFOA.^{7,8} However, it is unknown whether PFCA degradation may be mediated by interaction with multiple ROS and via multiple reaction pathways. The authors propose that UV/ H_2O_2 systems would be effective for degrading PFOA via $\text{HO}_2^{\cdot-}/\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$ -mediated reactions, although this system is known to be ineffective for PFOA degradation relative to UV_{254} photolysis alone,^{9,10} even under optimized conditions.¹¹ Previous research has also suggested that $\text{CO}_2^{\cdot-}$ may participate in PFOA degradation by donating an electron to PFOA, yielding $\text{C}_7\text{F}_{15}^\cdot$, CO_2 , and HCOOH (formic acid).¹² Therefore, if PFOA degradation is eventually demonstrated in this system, the authors should consider additional studies to rule out confounding effects from other reactive species (particularly $\text{CO}_2^{\cdot-}$) and reaction mechanisms.

Bai et al. also showed that the superoxide decay rate increased as the added PFOA concentration increased from 50 to 150 μM , with similar results for other PFCAs, and used this trend to conduct DFT analysis of superoxide-induced PFCA degradation. However, they did not provide experimental evidence of PFCA degradation, only superoxide decay, and this observation does not rule out the possibility that PFOA could simply accelerate superoxide decay via ancillary reaction pathways that do not involve degradation and defluorination. For example, PFOA introduces protons in the mixture, with $\text{p}K_a < 1$ for most PFCAs C3–C8.^{7,13} This influx of protons could accelerate superoxide disproportionation.^{14,15} Even though the system was buffered, the added H^+ could theoretically react preferentially with superoxide rather than with the conjugate base of the buffer and induce disproportionation.

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Overall, readers and practitioners should refrain from interpreting this study as an encouragement for superoxide-based technologies for PFCA treatment until the authors obtain and present significant PFCA degradation, transient byproducts formation, and defluorination data with associated mass balances. We posit that superoxide alone, even when stabilized to minimize disproportionation, cannot degrade PFOA. However, we cannot rule out the potential participation of superoxide in more complex systems, particularly with stabilizing catalytic surfaces and other factors that stretch bonds and make molecules more susceptible to attack by multiple reactive species.

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Notes

The authors declare no competing financial interest.

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